One-step Hydrothermal Synthesis of Sn-doped Sb$_2$Se$_3$ for Solar Hydrogen Production

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Abstract

Antimony selenide (Sb$_2$Se$_3$) has recently been intensively investigated and has achieved significant advancement in photoelectrochemical (PEC) water splitting. In this work, a facile one-step hydrothermal method for the preparation of Sn-doped Sb$_2$Se$_3$ photocathodes with improved PEC performance was investigated. We present an in-depth study of the performance enhancement in Sn-doped Sb$_2$Se$_3$ photocathodes using capacitance-voltage (CV), drive level capacitance profiling (DLCP), and electrochemical impedance spectroscopy (EIS) techniques. The incorporation of Sn$^{2+}$ into the Sb$_2$Se$_3$ results in increased carrier density, reduced surface defects, and improved charge separation, thereby leading to improved PEC performance. With a thin Sb$_2$Se$_3$ absorber layer (270 nm thickness), the Sn-doped Sb$_2$Se$_3$ photocathode exhibits an improved photocurrent density of 17.1 mA cm$^{-2}$ at 0 V versus RHE ($V_{RHE}$) compared to that of the undoped Sb$_2$Se$_3$ photocathode (14.4 mA cm$^{-2}$). This work not only highlights the positive influence of Sn doping on Sb$_2$Se$_3$ photocathodes but also showcases a one-step method to synthesize doped Sb$_2$Se$_3$ with improved optoelectronic properties.

Keywords: hydrothermal synthesis, Sb$_2$Se$_3$ photocathode, tin doping, surface passivation, carrier density
1. Introduction

Photoelectrochemical (PEC) water splitting has been considered as a promising approach for producing renewable hydrogen from water and sunlight. To realize scalable hydrogen production with this approach, it is crucial to develop simple methods for the preparation of cost-effective semiconducting materials. Sb$_2$Se$_3$ has recently gained significant attention as a candidate for PEC water splitting and solar cells, benefiting from its excellent optoelectronic and electro(chemical) properties, such as high absorption coefficient ($\alpha > 10^5$ cm$^{-1}$ in the near-infrared and visible region), suitable band gap (1.1–1.3 eV), good carrier mobility ($\sim$10 cm$^2$ V$^{-1}$ s$^{-1}$), low cost, and photo-corrosion resistance. For PEC water splitting, the photocurrent density ($J_{\text{ph}}$) of Sb$_2$Se$_3$ photocathodes has been extensively improved from 2 mA cm$^{-2}$ to 35.7 mA cm$^{-2}$ at 0 V versus a reversible hydrogen electrode (V$_{\text{RHE}}$), nearly approaching the maximum theoretical value of 40.9 mA cm$^{-2}$. However, the photovoltage of Sb$_2$Se$_3$ photocathodes is still far behind the theoretical maximum value, attributed to a rich defect chemistry stemming from the two nonequivalent Sb and three nonequivalent Se atomic sites. The free carrier density of undoped Sb$_2$Se$_3$ determined from experimental data is only $10^{13}$ cm$^{-3}$, considerably below the optimal doping density ($10^{16}$ cm$^{-3}$). These inherent properties pose a substantial challenge towards further improvement of the photovoltage.

Doping is an effective strategy for modifying physical and electronic properties by generating benign defects, improving conductivity, regulating crystallization, and suppressing surface or grain boundary defects. Various types of dopants including Na, Fe, K, Te, S, Bi, and Cu have been extensively explored to improve the solar cell and PEC performance of Sb$_2$Se$_3$ photocathodes. For example, Te doping in Sb$_2$Se$_3$ solar cells, prepared through spin-coating, has been shown to effectively suppress deep-level defects by regulating the atomic ratio of Se/Sb. The Ding group successfully mitigated surface defects and enhanced conductivity in Sb$_2$Se$_3$ through KOH etching treatment, resulting in a notable increase in the power conversion efficiency (PCE) of Sb$_2$Se$_3$ solar cells from 4.8% to 7.16%. Theoretical modeling has suggested that Sn, acting as an extrinsic substitution (Sn$_{\text{Sb}}$), could improve the p-type conductivity of Sb$_2$Se$_3$. Recently, Liang et al. prepared Sn-doped Sb$_2$Se$_3$ solar cells by sputtering a Sn-doped Sb$_2$Se$_3$ target, suggesting enhanced p-type conductivity. In addition, Hobos et. al. confirmed that Sn as a dopant enhances the p-type conductivity of Sb$_2$Se$_3$ using the Hall effect and hot-probe measurements.
Various methods have been proposed for the fabrication of Sb$_2$Se$_3$, such as close-spaced sublimation,$^{3,21}$ thermal evaporation,$^{22}$ spin coating,$^{23}$, electrodeposition,$^{24}$ magnetron sputtering,$^{25}$ and chemical bath deposition.$^{26}$ In particular, the hydrothermal method offers precise control over nucleation and growth of inorganic thin films, which is regarded as a convenient and cost-effective strategy for fabricating thin films with low energy consumption. Currently, the most efficient Sb$_2$Se$_3$ solar cells have been achieved in superstrate configuration using a chemical bath deposition approach. With selenourea as an additive, the Sb$_2$Se$_3$ planar solar cells delivered a benchmark PCE of 10.57%.$^{26}$ In 2021, Chen et al. developed a hydrothermal approach for superstrate Sb$_2$Se$_3$ solar cells, reaching a PCE of 7.9%.$^{27}$ However, there has been relatively little attention on the hydrothermal synthesis of substrate-based Sb$_2$Se$_3$ solar cells and Sb$_2$Se$_3$ photocathodes for PEC water splitting, possibly because of challenges in nucleation on the substrate. Given the benchmark achievement in Sb$_2$Se$_3$ solar cells using a solution-processed strategy, developing a hydrothermal method for synthesizing substrate-based Sb$_2$Se$_3$ photocathodes becomes imperative.

Here, we propose a novel hydrothermal method for the synthesis of high-quality, compact, and phase-pure Sb$_2$Se$_3$ films in substrate configuration. By introducing Sn$^{2+}$ cations into the precursor solution, surface defects of Sb$_2$Se$_3$ films are significantly suppressed, reducing from $2.67 \times 10^{12}$ cm$^{-2}$ (undoped Sb$_2$Se$_3$) to $8.64 \times 10^{11}$ cm$^{-2}$ (Sn-doped Sb$_2$Se$_3$). Meanwhile, the carrier density is increased in the Sn-doped Sb$_2$Se$_3$ film. These advantages of Sn doping result in greatly enhanced PEC performance with a notable improvement in the fill factor (FF). Importantly, the reproducibility of Sb$_2$Se$_3$ photocathodes is also slightly enhanced upon adding Sn$^{2+}$ as a dopant.

2. Results and Discussion

2.1. Preparation of Sb$_2$Se$_3$ Films

The undoped and Sn-doped Sb$_2$Se$_3$ films supported on Mo-coated glass substrates were prepared using a simple hydrothermal method. This process involved fine-tuning precursor ratios between tin sulfate (SnSO$_4$) and potassium antimony tartrate trihydrate (K$_2$Sb$_2$(C$_4$H$_2$O$_6$)$_2$·3H$_2$O). The solution preparation process used for the hydrothermal synthesis of Sb$_2$Se$_3$ films is depicted in Figure S1 (Supporting information) and described in the experimental section. The potassium antimony tartrate trihydrate and selenourea precursors were dissolved in Milli-Q water (18.2 MΩ·cm) serving as Sb and Se sources, respectively. To prevent the formation of elemental selenium (Se$^0$), sodium sulfite (Na$_2$SO$_3$) was added into the
aqueous solution to scavenge traces of oxygen. After the addition of sodium sulfite, a white precipitate was formed, primarily attributed to the increase in the solution’s pH from 4.13 to 6.89. To improve reproducibility and achieve high-quality Sb$_2$Se$_3$ films, the white precipitation was removed from the solution by filtering. Powder X-ray diffraction (PXRD) was used to characterize the crystallographic identity of the white powders. The observed diffraction peaks were well indexed to Sb$_2$O$_3$ (Figure S2). The Sb$_2$Se$_3$ films were obtained by placing Mo-coated glass substrates in the solution, followed by holding the reaction at 165 °C for different durations, as illustrated in Figure S3. The resulting film thicknesses for reaction times of 3 hours, 4 hours, and 5 hours are shown in Figure S4 and are denoted as Sb$_2$Se$_3$-3h, Sb$_2$Se$_3$-Control, and Sb$_2$Se$_3$-5h, respectively. By adjusting the reaction duration, the thickness of the Sb$_2$Se$_3$ films was controlled, ranging from 200 nm to 400 nm. In this study, the optimal condition of 165 °C for 4 hours was selected for further analysis (see details below). To further elucidate the impact of sodium sulfite, a Sb$_2$Se$_3$ film was prepared without its addition. Figure S5 exhibits the scanning electron microscopy (SEM) and X-ray diffraction (XRD) of this film. This film exhibits a nanowire structure that is unable to fully cover the Mo substrate, leading to a dark current during measurements. Furthermore, the XRD pattern indicates the formation of a secondary phase, Se$^0$.

2.2. PEC Performance of Sb$_2$Se$_3$ Photocathodes
Figure 1. (a) Schematic illustration of the device configuration (Glass/Mo/Sb$_2$Se$_3$/TiO$_2$/Pt). (b) The corresponding cross-sectional SEM image of the Sb$_2$Se$_3$ photocathode. (c) LSV plots of Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) photocathodes under intermittent simulated light illumination (AM 1.5 G, 100 mW cm$^{-2}$), recorded with a scan rate of 10 mV s$^{-1}$ in 1 M H$_2$SO$_4$ solution (pH = 0). (d) IPCE and integrated photocurrent density of both photocathodes at 0 V$_{RHE}$ under 10% white light illumination.

A 30 nm TiO$_2$ layer was deposited on Sb$_2$Se$_3$ films using atomic layer deposition (ALD). Although a TiO$_2$ overlayer is often used for protecting unstable light absorber materials in PEC water splitting, the Sb$_2$Se$_3$ is resistant to photocorrosion and we use it here to construct a p-n junction, which promotes photogenerated electron-hole pair separation. Subsequently, 2 nm Pt, acting as a hydrogen evolution catalyst, was deposited by sputtering. The device configuration of the Sb$_2$Se$_3$ photocathode is shown in Figure 1a,b. The presence of TiO$_2$ and Pt was confirmed by EDS measurement, as seen in Figure S6. The PEC performance of Sb$_2$Se$_3$ photocathodes prepared at different reaction durations (3-5 hours) was compared (Figure 1c and Figure S7). The Sb$_2$Se$_3$-Control photocathode exhibits a $J_\text{ph}$ of 14.4 mA cm$^{-2}$ at 0 V$_{RHE}$, which is higher than that of the Sb$_2$Se$_3$-3h and Sb$_2$Se$_3$-5h photocathodes. For Sn-doped Sb$_2$Se$_3$ films, the molar ratios of Sn$^{2+}$/Sb$^{3+}$ prepared in the precursor solution were 0.5%, 1%, and 1.5%, respectively. Hereinafter, we refer to these films as Sb$_2$Se$_3$-Sn (0.5), Sb$_2$Se$_3$-Sn (1.0), and Sb$_2$Se$_3$-Sn (1.5). Figure 1c displays the PEC performance of undoped and Sn-doped Sb$_2$Se$_3$ photocathodes evaluated in a 1 M H$_2$SO$_4$ (pH = 0) electrolyte by the linear sweep voltammetry (LSV) method under intermittent light illumination (AM 1.5 G, 100 mW cm$^{-2}$). An improvement in PEC performance in the Sb$_2$Se$_3$-Sn (0.5) photocathode, compared to the undoped Sb$_2$Se$_3$ photocathode, was observed. The champion device of the Sb$_2$Se$_3$-Sn (0.5) photocathode exhibits a $J_\text{ph}$ of 17.1 mA cm$^{-2}$ at 0 V$_{RHE}$, which is higher than that of the Sb$_2$Se$_3$-Control photocathode. Furthermore, the Sb$_2$Se$_3$-Sn (0.5) photocathode also achieved a superior fill factor (FF) of 28.7%, in contrast to the 21.5% FF obtained by the Sb$_2$Se$_3$-Control. However, further increasing Sn doping concentrations, $J_\text{ph}$ gradually decreased to 13.5 mA cm$^{-2}$ and 12 mA cm$^{-2}$ at 0 V$_{RHE}$ for the Sb$_2$Se$_3$-Sn (1.0) and Sb$_2$Se$_3$-Sn (1.5) photocathodes, respectively (Figure S8).

To gain insight into the PEC performance enhancement in the Sb$_2$Se$_3$-Sn (0.5) photocathode, incident photon-to-current conversion efficiency (IPCE) measurements were performed at 0 V$_{RHE}$ in 1 M H$_2$SO$_4$ electrolyte under 10% white light illumination, as seen in Figure 1d. Both
photocathodes show the same photo-response onset (1050 nm), indicating the unchanged band gap with the Sn$^{2+}$ doping treatment. The Sb$_2$Se$_3$-Sn (0.5) photocathode exhibits improved photoconversion efficiency across a broad wavelength range from 400 to 800 nm and reaches 80% of IPCE at 400 nm. In contrast, the IPCE value of the Sb$_2$Se$_3$-Control photocathode is below 67% in the whole wavelength range. The IPCE values of both Sb$_2$Se$_3$ photocathodes gradually decrease as the wavelength increases. Moreover, the IPCE values of both Sb$_2$Se$_3$ photocathodes at longer wavelengths (over 850 nm) are identical. This finding potentially implies reduced recombination near the Sb$_2$Se$_3$/TiO$_2$ junction of the Sn-doped Sb$_2$Se$_3$ photocathode, as indicated by the higher IPCE in the blue region. Furthermore, the consistent IPCE in the longer wavelength region is likely attributed to the thin Sb$_2$Se$_3$ films, which are unable to fully absorb all incident radiation (around 270 nm thickness, Figure S4). To fully absorb the photons at higher wavelengths, $\lambda > 800$ nm, an 800 nm thick Sb$_2$Se$_3$ thin film is required. Integrating the IPCE values with the AM 1.5 G spectrum yields a current density of 18.4 mA cm$^{-2}$ and 20.6 mA cm$^{-2}$ for the Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) photocathodes, respectively. Both values are slightly higher than the $J_{ph}$ obtained from the LSV measurements (Figure 1c) tested under 100% illumination of simulated solar light. The slight discrepancy in the integrated current is due to the light intensity dependence of the photocurrent. The $J_{ph}$ of the Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) photocathodes at 0 V$_{RHE}$ under different light intensities are depicted in Figure S9. Both Sb$_2$Se$_3$ photocathodes exhibit increased recombination and therefore more losses at higher light intensity, which explains the higher integrated photocurrent obtained from IPCE measurement under 10% white light illumination. IPCE measurement was also carried out at 0.15 V$_{RHE}$. A considerable enhancement of the IPCE values in the wavelength range of 400–1050 nm was observed in the Sb$_2$Se$_3$-Sn (0.5) photocathode (Figure S10). The IPCE value for the Sb$_2$Se$_3$-Sn (0.5) photocathode reaches 65% at the 400 nm excitation wavelength, which is twice as high as that of the Sb$_2$Se$_3$-Control photocathode. This improvement indicates the increased light harvesting efficiency near the front surface of the Sb$_2$Se$_3$ absorber.
Figure 2. Statistical distribution based on more than ten devices for each condition: (a) photocurrent at 0 V$_{\text{RHE}}$, (b) photocurrent at 0.15 V$_{\text{RHE}}$, (c) open-circuit voltage, and (d) FF of Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) photocathodes.

Figure 2 shows the statistical distribution of $J_{\text{ph}}$ at 0 V$_{\text{RHE}}$, $J_{\text{ph}}$ at 0.15 V$_{\text{RHE}}$, $V_{\text{OC}}$, and FF for both Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) photocathodes. It is evident that the $J_{\text{ph}}$ of Sb$_2$Se$_3$-Sn (0.5) is notably higher than that of Sb$_2$Se$_3$-Control photocathodes. The $V_{\text{OC}}$ slightly increases from 300.2 ± 22.4 (Sb$_2$Se$_3$-Control) to 322.2 ± 17.6 mV for the Sb$_2$Se$_3$-Sn (0.5) photocathodes. In addition, the FF values display a rise from 21.7 ± 2.4% (Sb$_2$Se$_3$-Control) to 27.9 ± 1.9% (Sb$_2$Se$_3$-Sn (0.5)). It is unequivocal from these observations that the Sb$_2$Se$_3$-Sn (0.5) photocathodes outperform their Sb$_2$Se$_3$-Control counterparts. Furthermore, we performed the PEC stability test for the Sb$_2$Se$_3$-Sn (0.5) photocathode at a constant potential of 0.1 V$_{\text{RHE}}$ under illumination (Figure S11). The $J_{\text{ph}}$ of the Sb$_2$Se$_3$-Sn (0.5) photocathode steadily declined to 10.9 mA cm$^{-2}$ after 1.7 hours of illumination, which is approximately 77% of its initial value of 14.1 mA cm$^{-2}$, which we attribute to the detachment of the Pt catalyst. After re-depositing the Pt multiple times, the $J_{\text{ph}}$ recovers its initial value and then gradually decreases again. As it is not the main focus of this work, we did not attempt to further improve the stability of the devices, which likely lose performance due to an unoptimized TiO$_2$/co-catalyst interface.
The $J_{ph}$ of a photocathode is governed by Equation (1): $J_{abs}$ is the light absorption rate expressed as the current density, $\eta_{sep}$ is the charge separation efficiency of the photogenerated carriers, and $\eta_{inj}$ is the charge injection efficiency at the interface between the electrode and the electrolyte for water reduction.\(^{30}\)

$$J_{ph} = J_{abs} \times \eta_{sep} \times \eta_{inj}$$

Initially, the influence of $\eta_{inj}$ can be disregarded, given the identical deposition of Pt cocatalyst on both Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) photocathodes.\(^{23}\) Thus, $J_{abs}$ and $\eta_{sep}$ emerge as the primary determinants of PEC performance. Direct measurement of $J_{abs}$ for undoped and Sn-doped Sb$_2$Se$_3$ is challenging due to the opaque Mo substrate. Therefore, we combined ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) and thickness data of Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) photocathodes to deduce the value of $J_{abs}$. The UV-Vis DRS spectrum of Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) photocathodes with the structure of Mo/Sb$_2$Se$_3$/TiO$_2$ exhibits similar results, as seen in Figure S12. Based on the reflectance and identical thickness for Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) photocathodes (Figure S6), we can reasonably assume that their light absorption is roughly equal. The aforementioned analysis strongly suggests that the improvement in the PEC performance for the Sb$_2$Se$_3$-Sn (0.5) photocathode mainly originates from an increase in $\eta_{sep}$.

### 2.3. Characterization of Sb$_2$Se$_3$

To elucidate the origin of the enhanced $\eta_{sep}$ observed in Sb$_2$Se$_3$-Sn (0.5) photocathode, scanning electron microscopy (SEM) and X-ray diffraction (XRD) were first utilized to explore the morphology and orientation of undoped and Sn-doped Sb$_2$Se$_3$ films. Figure S13 displays the top-view and cross-sectional SEM images of undoped and Sn-doped Sb$_2$Se$_3$ films, clearly revealing the formation of compact, pinhole-free layers. From the cross-sectional SEM images, all Sb$_2$Se$_3$ films are stacked layer by layer, parallel to the Mo substrate. Observations from the high magnification top-view SEM images (Figure S14) show small particles aggregating on the surfaces of the Sb$_2$Se$_3$-Sn (1.0) and Sb$_2$Se$_3$-Sn (1.5) films, which could be related to the noticeable decrease in PEC performance. To evaluate this assumption, the surface composition was examined using Raman spectra (see below).

As shown in Figure S15a, the crystal structures of undoped and Sn-doped Sb$_2$Se$_3$ films were examined by XRD. The observed diffraction peaks of all as-prepared Sb$_2$Se$_3$ films well matched with the standard PDF card (JCPDS 15-0861) of orthorhombic Sb$_2$Se$_3$, confirming the absence of secondary phase formation even at higher Sn$^{2+}$ doping concentrations. Notably, the (020)
peak shifts to a higher angle in the Sb$_2$Se$_3$-Sn (1.5) film, implying the incorporation of Sn$^{2+}$ into the Sb$_2$Se$_3$ crystal lattice (Figure S15b). The evolution of crystal orientation in the Sb$_2$Se$_3$ films was evaluated by the texture coefficient (TC) according to the following Equation.$^{31}$

$$TC_{(hkl)} = \frac{I_{(hkl)}}{I_{0(hkl)}} / \left(\sum_{i=1}^{n} \frac{I_{(hkl)}}{I_{0(hkl)}}\right)^{\frac{1}{n}}$$

Where $I_{(hkl)}$ and $I_{0(hkl)}$ are the measured diffraction peak intensity and the corresponding peak intensity of the standard XRD pattern of Sb$_2$Se$_3$, respectively. The calculated TC values demonstrate that the as-prepared Sb$_2$Se$_3$ films are dominated by the (020) plane, and this effect becomes more prominent with increasing Sn doping concentrations (Figure S16). On the other hand, the intensity of the [hk1]-oriented planes shows a slight decrease. Previously reported hole mobilities of Sb$_2$Se$_3$ are 0.69, 1.17, and 2.59 cm$^2$ V$^{-1}$ s$^{-1}$ in the [010], [100], and [001] directions, respectively.$^{32}$ Therefore, we inferred that the crystal orientation evolution in the Sb$_2$Se$_3$-Sn (0.5) photocathode is not responsible for the PEC performance enhancement, primarily because of the lowest hole mobility in the [020] direction.
Figure 3. (a) Raman spectra of undoped and Sn-doped Sb$_2$Se$_3$ films. Sb 3d XPS spectra of Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) films (b) before and (c) after sputter etching. (d) ToF-SIMS sputter depth profile of the Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) films.

Figure 3a displays the Raman spectra of undoped and Sn-doped Sb$_2$Se$_3$ films. All Sb$_2$Se$_3$ films show three typical peaks at 152 cm$^{-1}$, 189 cm$^{-1}$, and 210 cm$^{-1}$, which are assigned to the orthorhombic Sb$_2$Se$_3$ phase.$^{33,34}$ With a further increase in Sn doping concentrations, additional vibration modes at 118 cm$^{-1}$, 253 cm$^{-1}$, 373 cm$^{-1}$, and 450 cm$^{-1}$ for Sb$_2$Se$_3$-Sn (1.0) and Sb$_2$Se$_3$-Sn (1.5) films are observed, suggesting the formation of Sb$_2$O$_3$.$^{12,27}$ Considering these findings along with the SEM images (Figure S14), the presence of small particles on the surface of the Sb$_2$Se$_3$ films is assigned to Sb$_2$O$_3$. Based on these observations, we infer that the decreased PEC performance of the Sb$_2$Se$_3$-Sn (1.0) and Sb$_2$Se$_3$-Sn (1.5) photocathodes is attributed not only to the presence of Sb$_2$O$_3$, serving as recombination centers, but also to the increased intensity of the [020]-dominated crystal plane, reducing charge separation.$^{35}$

X-ray photoelectron spectroscopy (XPS) characterization was carried out to characterize the chemical compositions of the undoped and Sn-doped Sb$_2$Se$_3$ films. Figure 3b and S17a show the Sb oxidation states on the surface of Sb$_2$Se$_3$ films. The typical XPS peaks at 529.1 eV and 538.5 eV confirm the formation of Sb$_2$Se$_3$, while peaks at 528.1 eV and 537.5 eV indicate the presence of Sb$^0$ in undoped and Sn-doped Sb$_2$Se$_3$ films. It should be noted that no Sb$_2$O$_3$ was detected in the Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) films. In contrast, additional peaks located at 529.8 and 539.2 eV in the Sb$_2$Se$_3$-Sn (1.0) and Sb$_2$Se$_3$-Sn (1.5) films were attributed to Sb$_{5/2}$ and Sb$_{3.2}$ of Sb$_2$O$_3$, which also agrees with the Raman results. The absence of Sb$_2$O$_3$ in the Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) films suggests that the hydrothermal method significantly suppresses Sb$_2$O$_3$ formation, unlike physical deposition methods, where Sb$_2$O$_3$ commonly forms on the surface of Sb$_2$Se$_3$.$^{5,36,37}$ After the removal of surface impurities by sputtering, only two peaks remained in undoped and Sn-doped Sb$_2$Se$_3$ films, indicating the phase purity in the bulk of the Sb$_2$Se$_3$ films (Figure 3c and 17b). The binding energies at 54.0 eV and 54.8 eV are ascribed to Se 3d$_{5/2}$ and Se 3d$_{3/2}$ of Sb$_2$Se$_3$, as shown in Figure S18. The presence of Sn was observed in the Sb$_2$Se$_3$-Sn (1.5) film, as seen in Figure S17c,d. The binding energies of Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$ are found to be 485.6 eV and 494.0 eV, which is consistent with a chemical state of Sn$^{2+}$ in the Sb$_2$Se$_3$-Sn (1.5) film. However, XPS is not sensitive enough to detect the presence of the Sn element in the Sb$_2$Se$_3$-Sn (0.5) film due to its low concentration. To gain insight into the distribution of the Sn element, time-of-flight secondary ion mass spectrometry
(ToF-SIMS) was conducted on Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) films. The ToF-SIMS results in Figure 3d indicate that no Sn was detected in the Sb$_2$Se$_3$-Control film. In contrast, the signal of Sn gradually declines and then becomes uniformly distributed with probing depth in the Sb$_2$Se$_3$-Sn (0.5) films, suggesting the accumulation of Sn near the surface of Sb$_2$Se$_3$. Figure S19 reveals that Sb and Se are uniformly distributed in both undoped and Sn-doped Sb$_2$Se$_3$ films.

2.4. Carrier Density and OCP Measurements

We further performed capacitance-voltage (CV) and drive-level capacitance profiling (DLCP) measurements to characterize the carrier density in the Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) devices.$^{38}$ The measurements were performed utilizing the device structure of Mo/Sb$_2$Se$_3$/TiO$_2$/Al employing a two-electrode system under dark conditions (Figure S20).

From the Mott-Schottky plots ((C$^{-2}$/V, Figure 4a) and S21), the flat band voltage ($V_{FB}$) can be extracted by linear fitting and extrapolation to the intercept with the x-axis. The $V_{FB}$ values of the Sb$_2$Se$_3$-Control devices are in the range of 0.30 to 0.42 V, whereas the $V_{FB}$ of the Sb$_2$Se$_3$-Sn (0.5) devices remains in a narrow range of 0.34 to 0.38 V. This spread of $V_{FB}$ values agrees well with the $V_{onset}$ results observed in Figure 2c, where the $V_{onset}$ of the Sb$_2$Se$_3$-Control photocathode is distributed over a larger range, while the $V_{onset}$ of the Sb$_2$Se$_3$-Sn (0.5) photocathode has less variation. The minimal discrepancy between $V_{onset}$ and $V_{FB}$ in the Sb$_2$Se$_3$-Sn (0.5) is indicative of reduced surface defects with the Sn$^{2+}$ treatment (see below). In general, the carrier density of CV profiling ($N_{CV}$) includes the response of free carriers, bulk defects, and surface defects, while the carrier density obtained from DLCP profiling measurements ($N_{DLCP}$) is insensitive to surface defects.$^{39}$ As seen in Figure 4b, U-shaped profiles of $N_{CV}$ and $N_{DLCP}$ were observed in both Sb$_2$Se$_3$ devices, which arises from the punch-through effect due to the relatively thin nature of the Sb$_2$Se$_3$ films (around 270 nm thickness, see Supplementary Note 1 for further details).$^{40}$ We therefore assigned the carrier density based on the lowest point of the DLCP profiles. As mentioned above, an increase in the p-type conductivity of Sb$_2$Se$_3$ with Sn doping treatment has been reported elsewhere.$^{20}$ This phenomenon was also found in our Sb$_2$Se$_3$ samples. The carrier density of the Sb$_2$Se$_3$-Sn (0.5) sample is $3.77 \times 10^{16}$ cm$^{-3}$, which is almost twice as high as that of the Sb$_2$Se$_3$-Control sample ($2.12 \times 10^{16}$ cm$^{-3}$). Considering the higher doping density of the ALD TiO$_2$ ($2.6 \times 10^{20}$ cm$^{-3}$),$^{41}$ the depletion layer is predominantly located within the Sb$_2$Se$_3$ layer near the Sb$_2$Se$_3$/TiO$_2$ junction. The surface defect density was calculated by subtracting $N_{DLCP}$ from $N_{CV}$ at 0 V and multiplying this value by the depletion layer width ($W_d$).$^{22,42}$ The corresponding surface defect density for Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-
Sn (0.5) devices were calculated to be $2.67 \times 10^{12} \text{ cm}^{-2}$ and $8.64 \times 10^{11} \text{ cm}^{-2}$, respectively. The obtained parameters are summarized in Table S1. We assume that the suppressed formation of surface defects could be attributed to the accumulation of Sn near the surface of the Sb$_2$Se$_3$-Sn (0.5) photocathode. The increased carrier density and reduced surface defects play a crucial role in the PEC performance enhancement of the Sb$_2$Se$_3$-Sn (0.5) photocathode through reduced interface recombination and better charge collection. Compared to the Sb$_2$Se$_3$-Control photocathode with a $W_d$ of 102 nm, the calculated $W_d$ of the Sb$_2$Se$_3$-Sn (0.5) photocathode drops to 76 nm due to the increased carrier density.

Figure 4. (a) Mott–Schottky plots, (b) CV and DLCP profiles, (c) OCP versus time under off/on cycles of light illumination, and (d) $R_{\text{rec}}$ of Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) photocathodes obtained from EIS. (a and b in 2-electrode mode and c and d in 3-electrode mode).

To assess the thermodynamic driving force for charge separation, we performed an open circuit potential (OCP) test.$^{43,44}$ The OCP measurement was conducted in a black box under H$_2$ purging (details in the experimental section). The changes in OCP between dark (OCP$_{\text{dark}}$) and
illuminated conditions (OCP\textsubscript{light}) for undoped and Sn-doped Sb\textsubscript{2}Se\textsubscript{3} photocathodes are illustrated in Figure 4c. It is noteworthy that the Fermi levels of both photocathodes equilibrate with the redox potential ($\text{E}_{\text{H}^+}\text{H}_2$, 0 V\textsubscript{RHE}) in the dark condition. Under illumination, the quasi-Fermi level of holes will shift to a more positive potential. The difference between OCP\textsubscript{dark} and OCP\textsubscript{light} is the photovoltage ($V_{\text{ph}}$). A larger $V_{\text{ph}}$ of 0.32 V\textsubscript{RHE} was observed for the Sb\textsubscript{2}Se\textsubscript{3}-Sn (0.5) photocathode, demonstrating improved charge separation and an earlier onset potential in the water splitting experiments. Another way to evaluate the quality of Sb\textsubscript{2}Se\textsubscript{3} is to study the photogenerated carrier lifetime as a function of OCP decay. Figure S22 displays the normalized transient OCP decay after stopping illumination (see Supplementary Note 2 for further details).

2.5. EIS Measurement
Electrochemical impedance spectroscopy (EIS) was conducted to further reveal the efficient charge separation kinetics within the Sb\textsubscript{2}Se\textsubscript{3} photocathodes. EIS measurements were recorded under 10% light illumination with an applied potential ranging from 0.4 to -0.2 V\textsubscript{RHE}. To ensure device stability, cyclic voltammetry measurements were recorded before and after the EIS tests, as shown in Figure S23. Figure S24 shows the Nyquist plots for Sb\textsubscript{2}Se\textsubscript{3}-Control and Sb\textsubscript{2}Se\textsubscript{3}-Sn (0.5) photocathodes, and an equivalent circuit was used to fit the Nyquist curves. Here, the parameter of charge recombination resistance ($R_{\text{rec}}$) represented by the semicircle in the Nyquist plots at the lowest frequencies is the prime concern. As seen from Figure S24, the semicircle diameter for the Sb\textsubscript{2}Se\textsubscript{3}-Sn (0.5) photocathode is larger than that of the Sb\textsubscript{2}Se\textsubscript{3}-Control photocathode, implying a higher charge separation efficiency in the former. The extracted $R_{\text{rec}}$ values for both Sb\textsubscript{2}Se\textsubscript{3} photocathodes from the EIS equivalent circuit fitting are presented in Figure 4d. The $R_{\text{rec}}$ of the Sb\textsubscript{2}Se\textsubscript{3}-Sn (0.5) photocathode shows a sharp and early rise compared to the Sb\textsubscript{2}Se\textsubscript{3}-Control photocathode. The $R_{\text{rec}}$ of the Sb\textsubscript{2}Se\textsubscript{3}-Sn (0.5) photocathode is approximately two times higher compared to the Sb\textsubscript{2}Se\textsubscript{3}-Control photocathode at potentials below 0.08 V\textsubscript{RHE}. This is indicative that the incorporation of Sn\textsuperscript{2+} into Sb\textsubscript{2}Se\textsubscript{3} suppresses charge recombination. This increased $R_{\text{rec}}$ value for Sn-doped Sb\textsubscript{2}Se\textsubscript{3} is in good agreement with the OCP enhancement, which promotes charge separation. Therefore, with the optimal concentration of Sn doping, the Sb\textsubscript{2}Se\textsubscript{3} films effectively increase $R_{\text{rec}}$ and therefore reduce recombination within the semiconductor, resulting in improved PEC performance.

3. Conclusion
In summary, we have developed a simple and effective hydrothermal method to synthesize high-quality Sb\textsubscript{2}Se\textsubscript{3} films, effectively reducing surface defects by incorporating Sn\textsuperscript{2+} as a
dopant. Moreover, the p-type conductivity is enhanced in Sn-doped Sb₂Se₃. OCP and EIS tests confirmed improved charge separation efficiency in the Sb₂Se₃-Sn (0.5) photocathode compared to the Sb₂Se₃-Control device. The photocurrent density increased from 14.4 mA cm⁻² (Sb₂Se₃-Control) to 17.1 mA cm⁻² (Sb₂Se₃-Sn (0.5)) at 0 V RHE, with FF rising from 21.5% to 28.7%. These findings underscore the potential of our approach to enhance Sb₂Se₃ photocathode performance in PEC applications. Future efforts should focus on optimizing film thickness and orientation, aiming for improved light absorption and enhanced charge separation efficiency, thus further enhancing PEC performance.

4. Experimental Section

4.1. Hydrothermal Deposition of Sb₂Se₃ Films

All Sb₂Se₃ films were deposited onto molybdenum (Mo)-coated glass substrates (Guluo, Luoyang). Before deposition, the Mo-coated glass was cleaned with acetone, soapy water, milli-Q water, and isopropanol in an ultrasonic bath for 10 min each. After cleaning, the Mo-coated glass substrates were dried under N₂ flow. The Sb₂Se₃ films were fabricated via a hydrothermal method, utilizing potassium antimony tartrate trihydrate (Sigma-Aldrich, ≥ 99%) and selenourea (Sigma-Aldrich, 98%) as the Sb and Se sources, respectively. First, 0.334 g (10 mM) of K₂Sb(C₄H₃O₅)₂·3H₂O and 0.126 g (20 mM) of Na₂SO₃ (Sigma-Aldrich, ≥ 98%) were sequentially added to a beaker containing 50 ml of milli-Q water (18.2 MΩ·cm). The solution was stirred at 400 rpm for 5 min after each addition. The addition of Na₂SO₃ caused an increase in the pH of the solution (from pH of 4.13 to pH of 6.89), leading to the formation of Sb₂O₃.

\[
K_2Sb_2(C_4H_2O_6)_2 \cdot 3H_2O \leftrightarrow Sb_2(C_4H_2O_6)_2^{2-} + 2K^+ + 3H_2O
\]  
(3)

\[
SO_3^{2-} + H_2O \leftrightarrow HSO_3^- + OH^-
\]  
(4)

\[
Sb_2(C_4H_2O_6)_2^{2-} + H_2O + 2OH^- \leftrightarrow Sb_2O_3 \downarrow + 2C_4H_4O_6^{2-}
\]  
(5)

Subsequently, 0.246 g (40 mM) of (NH₂)₂CSe was added to the above solution, leading to a decrease in pH to 6.61:

\[
Sb_2(C_4H_2O_6)_2^{2-} + n((NH_2)_2CSe) \leftrightarrow [Sb_2(C_4H_2O_6)_2^{2-}((NH_2)_2CSe)_n]
\]  
(6)

\[
(NH_2)_2CSe + OH^- \leftrightarrow HSe^- + (NH_2)_2CO
\]  
(7)
To remove the Sb$_2$O$_3$ precipitation, the as-prepared solution was allowed to precipitate for 4 hours and then filtered with filter paper. For the fabrication of Sn-doped Sb$_2$Se$_3$ films, various amounts of SnSO$_4$ (0.1 mM, 0.2 mM, and 0.3 mM) as a dopant were added to the filtered solution. The resulting solution was then transferred into a 100 ml Teflon-lined hydrothermal reactor. Mo-coated glass substrates, partially wrapped with Teflon tape and placed face down in a holder, were positioned in the Teflon tank. The reaction was held at 165 °C for 4 hours in an oven. Following the reaction, the autoclave was naturally cooled to room temperature. Then the Sb$_2$Se$_3$ films were successfully deposited on the Mo substrates.

\[
Sb_2(C_4H_2O_6)_2^{2-} + 3HSe^- + H^+ \leftrightarrow Sb_2Se_3 \downarrow + 2(C_4H_4O_6)^{2-}
\]  

The Sb$_2$Se$_3$ films were then rinsed with deionized water and dried with flowing N$_2$ in ambient air.

4.2. Deposition of TiO$_2$ Layer and Pt Catalyst

A 30 nm layer of TiO$_2$ was deposited onto the Sb$_2$Se$_3$ films using a thermal atomic layer deposition (ALD) system (PICOSUN, R200). The tetrakis(dimethylamino)titanium (TDMAT, Aldrich, 99.99%) and milli-Q H$_2$O were employed as the precursors for Ti and O sources, respectively. During deposition, the reaction chamber temperature was kept at 120 °C, while the temperature for the TDMAT was maintained at 85 °C. Pt was used as the hydrogen evolution reaction catalyst. Nominally 2 nm of Pt was sputtered onto the surface of the TiO$_2$ using a sputter coater (LEICA EM ACE600). The thickness of the deposited Pt was monitored by a gold-coated quartz microbalance.

4.3. PEC Performance and EIS Measurements

For PEC performance measurements, a three-electrode electrochemical cell with a potentiostat (BioLogic SP-300) was used. The light source consisting of AM 1.5 G filter was provided by a 150 W Xe-lamp to simulate AM 1.5 G sunlight. The light intensity was calibrated using a silicon diode from PV Measurement, Inc. (100 mW cm$^{-2}$). A Pt wire and an Ag/AgCl electrode (KOSLOW, saturated KCl, +0.197 V vs. normal hydrogen electrode) were used as the counter and reference electrodes, respectively. The electrolyte used for the measurements was 1 M H$_2$SO$_4$ (pH = 0) electrolyte. The J-V curves were recorded under intermittent or continuous light illumination with a scan rate of 10 mV s$^{-1}$. IPCE measurements were performed using a home-built system equipped with a halogen light source and a double monochromator. Before
the IPCE measurements, the light intensity was calibrated with a silicon photodiode. EIS measurement was scanned from 0.4 to -0.2 V with a small potential amplitude of 15 mV under 10% light illumination, applying an AC perturbation frequency ranging from 7 MHz to 0.2 Hz. The Nernst equation was applied to convert the potentials (vs. Ag/AgCl) into the reversible hydrogen electrode (RHE) scale.

\[ V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.059 \times pH + 0.197 \] (9)

### 4.4. OCP and Light Intensity Dependence of Photocurrent Measurements

For the OCP measurement in 1 M H₂SO₄, a potentiostat with two channels was used in a black box. One channel was used in a typical three-electrode system with a Ag/AgCl reference electrode, a Pt wire counter electrode, and the Sb₂Se₃ photocathode as the working electrode. The second channel was used in a 2-electrode configuration between the same counter electrode and an additional platinum wire that was placed just underneath the working electrode. Prior to the OCP measurement (using the first channel), an electrolysis was carried out using the second channel for 30 min, which ensured saturation of the electrolyte solution with H₂ in the vicinity of the Sb₂Se₃ photocathode surface (Figure 4c indeed shows that the potential of the Sb₂Se₃, calculated according to Equation 10, is 0 V_RHE in the dark). The light intensity dependence of the photocurrent measurement was performed at 0 V_RHE using a three-electrode system. For both measurements, an array of nine white light diodes was used (SP-12-W5, cool white Luxeon Rebel) controlled by a Keithley power source (PSW4323).

### 4.5. Material Characterization

A Zeiss Gemini 450 SEM was used to determine the morphology of the undoped and Sn-doped Sb₂Se₃ samples. The crystalline phase of the obtained Sb₂Se₃ films was detected by XRD (Rigaku Smartlab) with Cu Kα radiation (\( \lambda = 0.15406 \)). The white powder obtained from the solution precipitation was examined by PXRD. The reflectance spectra of the Sb₂Se₃/TiO₂ photocathodes were characterized using UV-Vis DRS recorded on a Shimadzu UV-3600 spectrometer. Raman spectra were measured on a Renishaw in Via Raman microscope with a 532 nm laser. XPS measurements were performed using a physical electronics Quantum 2000 X-ray photoelectron spectrometer featuring monochromatic Al Kα radiation, operated at 15 kV and 32.3 W. The energy scale of the instrument was calibrated by an Au reference sample. The analysis was conducted at a vacuum level of 1×10⁻⁶ Pa, employing an electron take-off angle of 45° and a pass energy of 23.5 eV. Instrument-specific sensitivity factors were applied for
Shirley background subtraction, and core-level spectra were plotted to deconvolute spectra with contributions from multiple elements as necessary. A GL 30 asymmetric line shape was assumed for the core level emissions, with a ΔE of 9.34 eV for the Sb 3d doublet and a ΔE of 0.86 eV for the Se 3d.

4.6. ToF-Sims measurements

Secondary ion mass spectrometry measurements were carried out using a ToF-SIMS 5 instrument from IONTOF GmbH, Germany. The instrument operated in depth profiling mode, performing simultaneous dual beam sputtering and analysis. Bi⁺ primary ions with current of 1.5 pA were employed for the elemental analysis in positive polarity of the undoped and Sn-doped Sb₂Se₃ samples. Sputtering was conducted with O₂ ions with energy of 1000 eV and sputtering current of 287 nA. The sputtering ion beam was rastered over a 500 µm × 500 µm area, with the primary beam overlaid in the center of the sputter area and rastered over 200 µm × 200 µm area. The sputter rate is around 1.3 nm/s.

4.7. CV and DLCP Measurements

To perform CV and DLCP measurements, 100 nm of TiO₂ and Al layers were deposited onto the Sb₂Se₃ surface, respectively. Standard CV and DLCP measurements were conducted using a potentiostat (Biologic SP-200) in a two-electrode configuration under dark condition at room temperature. For the standard CV measurements, a DC bias was scanned from -0.5 V to 1 V with an AC amplitude of 20 mV. The DLCP measurements were conducted with an AC amplitude ranging from 20 mV to 120 mV and a DC bias range of -0.2 V to 0.5 V. For each AC bias, an additional offset DC voltage was applied to maintain a constant maximum forward bias. An AC frequency of 10 kHz was applied to extract the carrier density in both CV and DLCP measurements. The carrier density from the CV measurement (N_{CV}) can be extracted by the following equation:

\[ N_{CV} = -\frac{2}{q\varepsilon\varepsilon_0 A^2} \left[ \frac{d(C^{-2})}{dV_{DC}} \right]^{-1} \]  \hspace{1cm} (10)

Here q represents the elementary charge, \( \varepsilon \) represents the dielectric constant of the Sb₂Se₃ (taken as 15.1), \( \varepsilon_0 \) is the permittivity of free space, and A is the measured area of the diode. In the DLCP measurements, the carrier density is derived from the nonlinear relationship between the change in charges (\( \delta Q \)) and the perturbation AC bias (\( \delta V \)):

\[ \frac{\delta Q}{\delta V} = C_0 + C_1 \delta V + C_2 (\delta V)^2 + \cdots \]  \hspace{1cm} (11)
The values of $C_0$ and $C_1$ can be obtained by fitting the capacitance versus perturbation AC bias plots with this function. The carrier density from the DLCP measurement ($N_{DLCP}$) can be calculated by:

$$N_{DLCP} \approx \frac{-C_0^3}{2q\varepsilon\varepsilon_0 A^2 C_1} \quad (12)$$

The profiling depth from the barrier junction $<\chi>$ for the CV (taking $C$ from equation (10)) and DLCP (taking $C_0$ from equation (12)) can be determined by:

$$<\chi> = \frac{\varepsilon\varepsilon_0 A}{C} \quad (13)$$

More details can be found in our previous paper.\textsuperscript{46}

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**Notes**

The authors declare no competing financial interests.

**Supporting Information**

Preparation of Sb$_2$Se$_3$ films; XRD pattern; SEM and EDS mapping images; Reflectance spectra; XPS measurements; PEC performance; ToF-SIMS measurements; OCP and EIS measurements; Device structure for CV and DLCP test; Additional discussions including OCP decay, CV, and DLCP.

**Acknowledgments**

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References


A novel and simple hydrothermal method was proposed for the fabrication of undoped and Sn-doped Sb$_2$Se$_3$ photocathodes. With the addition of Sn, the p-type conductivity was significantly enhanced, resulting in improved PEC performance. This hydrothermal method provides a new way for fabricating Sb$_2$Se$_3$ photocathodes in the field of PEC water splitting and substrate-based solar cells.
Supporting Information

One-step Hydrothermal Synthesis of Sn-doped Sb$_2$Se$_3$ for Solar Hydrogen Production

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Figure S1. Schematic illustration of the solution preparation process. SnSO₄ was added as a dopant after the filtration process.

Figure S2. XRD pattern of the Sb₂O₃ powders obtained from the solution precipitation. All peaks correspond to Sb₂O₃ except for the peak at 29 degrees, which corresponds to elemental selenium.

Figure S3. Schematic illustration of the Sb₂Se₃ thin film fabrication process. Mo-coated glass substrate held by a Teflon holder, facing down towards the solution.
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Figure S5. (a) The SEM image of the Sb$_2$Se$_3$ film that was prepared without the addition of Na$_2$SO$_3$. (b) XRD pattern of the corresponding Sb$_2$Se$_3$ film. All peaks correspond to Sb$_2$Se$_3$ except for the peak at 29 degrees, which corresponds to elemental selenium.
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Figure S8. (a) LSV plots of Sb\textsubscript{2}Se\textsubscript{3}-Sn (1.0) and Sb\textsubscript{2}Se\textsubscript{3}-Sn (1.5) photocathodes. (b) Photocurrent density at 0 V\textsubscript{RHE} of the best devices for undoped and Sn-doped Sb\textsubscript{2}Se\textsubscript{3}.
Figure S9. Dependence of photocurrent on white light intensity at 0 V\textsubscript{RHE} for Sb\textsubscript{2}Se\textsubscript{3}-Control and Sb\textsubscript{2}Se\textsubscript{3}-Sn (0.5) photocathodes.

Figure S10. IPCE and integrated photocurrent (dashed line) of Sb\textsubscript{2}Se\textsubscript{3}-Control and (b) Sb\textsubscript{2}Se\textsubscript{3}-Sn (0.5) photocathodes at 0.15 V\textsubscript{RHE} under 10% white light bias.
Figure S11. Stability tests of the Sb$_2$Se$_3$-Sn (0.5) photocathode under simulated solar light illumination (AM 1.5 G, 100 mW cm$^{-2}$) were recorded at 0.1 V$_{\text{RHE}}$ in 1 M H$_2$SO$_4$ solution (pH = 0).

Figure S12. Diffuse reflectance spectra of Sb$_2$Se$_3$-Control and (b) Sb$_2$Se$_3$-Sn (0.5) films with the structure of Mo/Sb$_2$Se$_3$/TiO$_2$. Three films for each were characterized.
Figure S13. Top-view and the corresponding cross-sectional SEM images of (a, b) Sb$_2$Se$_3$-Control, (c, d) Sb$_2$Se$_3$-Sn (0.5), (e, f) Sb$_2$Se$_3$-Sn (1.0), and (g, h) Sb$_2$Se$_3$-Sn (1.5) films.
Figure S14. High magnification top-view SEM images of (a) Sb$_2$Se$_3$-Control, (b) Sb$_2$Se$_3$-Sn (0.5), (c) Sb$_2$Se$_3$-Sn (1.0), and (d) Sb$_2$Se$_3$-Sn (1.5) films.

Figure S15. (a) XRD patterns of Sb$_2$Se$_3$-Control, Sb$_2$Se$_3$-Sn (0.5), Sb$_2$Se$_3$-Sn (1.0), and Sb$_2$Se$_3$-Sn (1.5) films. (b) Corresponding (020) peak with enlarged XRD patterns. Doping with the larger Sn$^{2+}$ ion may cause the creation of selenium vacancies that partly compensate the charge, resulting in an overall shrinking of the lattice parameter.
Figure S16. Texture coefficient of Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) films.

Figure S17. Sb 3d XPS spectra of Sb$_2$Se$_3$-Sn (1.0) and Sb$_2$Se$_3$-Sn (1.5) films (a) before and (b) after sputter etching. Sn 3d XPS spectra of Sb$_2$Se$_3$-Sn (1.5) film (c) before and (d) after sputter etching.
Figure S18. XPS spectra of Se 3d core level for Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) films.

Figure S19. ToF-SIMS sputter depth profile for Sb and Se in the (a) Sb$_2$Se$_3$-Control and (b) Sb$_2$Se$_3$-Sn (0.5) films.
Figure S20. The device structure for CV and DLCP measurements.

Figure S21. Mott-Schottky plots of (a) Sb$_2$Se$_3$-Control and (b) Sb$_2$Se$_3$-Sn (0.5) devices measured in 2-electrode mode. Three devices for each were measured.
Figure S22. Normalized OCP decay of Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) photocathodes.

Figure S23. Cyclic voltammetry measurements of Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) photocathodes under 10% light illumination were recorded with a scan rate of 50 mV s$^{-1}$ in 1 M H$_2$SO$_4$ solution (pH = 0) before and after EIS measurements.
Figure S24. (a) The equivalent circuit used for the Nyquist plots fitting. Nyquist plots of the (b) Sb$_2$Se$_3$-Control and (c) Sb$_2$Se$_3$-Sn (0.5) photocathodes.

Table S1. Summary of the parameters obtained from CV, DLCP, and OCP measurements of Sb$_2$Se$_3$-Control and Sb$_2$Se$_3$-Sn (0.5) photocathodes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carrier density (N$_{DLCP}$) [cm$^{-3}$]</th>
<th>Interface defects density [cm$^{-2}$]</th>
<th>$W_d$ [nm]</th>
<th>OCP [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb$_2$Se$_3$-Control</td>
<td>2.12 x 10$^{16}$</td>
<td>2.67 x 10$^{12}$</td>
<td>102</td>
<td>0.3</td>
</tr>
<tr>
<td>Sb$_2$Se$_3$-Sn (0.5)</td>
<td>3.77 x 10$^{16}$</td>
<td>8.64 x 10$^{11}$</td>
<td>76</td>
<td>0.32</td>
</tr>
</tbody>
</table>

**Supplementary Note 1:**

The formation of the right-hand branch of the U-shape was observed in the devices of Mo/Sb$_2$Se$_3$/TiO$_2$/Al and Mo/Sn-doped Sb$_2$Se$_3$/TiO$_2$/Al with increased reverse bias. This phenomenon is often interpreted as the result of non-uniform carrier density distribution within the absorber material. However, this conclusion would be hasty without considering the finite thickness (270 nm thickness) of the Sb$_2$Se$_3$ absorber in this case. The depletion region of the Sb$_2$Se$_3$/TiO$_2$ front junction extends toward the back contact with the increase of the applied reverse bias. At a certain applied potential, the depletion region from the Sb$_2$Se$_3$/TiO$_2$ front junction will reach the back contact, resulting in complete depletion of the Sb$_2$Se$_3$ absorber (the punch-through effect).  

This effect can be found in the Mott-Schottky plots (Figure 4a), in
which the linear region (representing the space charge region) begins to vanish at 0.1 V for the Sb$_2$Se$_3$-control and 0.03 V for the Sb$_2$Se$_3$-Sn (0.5) devices. Because of the large number of free carriers at the back contact with Mo metal (~$10^{23}$ cm$^{-3}$), there is no change of the depletion width on the p-side of the Sb$_2$Se$_3$/TiO$_2$ front junction with a further increase of reverse bias. While the depletion region may continue to expand on the n-side of the front junction (TiO$_2$/Al), the overall increase in depletion region width, such as a decrease of capacitance, is limited due to the higher carrier concentration in the atomic layer deposited TiO$_2$ (~2.6×$10^{20}$ cm$^{-3}$) and Al (~$10^{23}$ cm$^{-3}$). The manifestation of this punch-through effect in N$_{CV}$ is a sharp increase from $10^{16}$-$17$ cm$^{-3}$ to $10^{18}$-$19$ cm$^{-3}$ when the depletion width approaches the thickness of the Sb$_2$Se$_3$ absorber. This explanation can be confirmed by the shape of the carrier density profile, in which the depletion width didn’t significantly increase when the applied bias reached 0 V.

**Supplementary Note 2:**

Another way to evaluate the quality of Sb$_2$Se$_3$ is to study the photogenerated carrier lifetime as a function of OCP decay. Figure S20 displays the normalized transient OCP decay after stopping illumination. The slow decay of the Sb$_2$Se$_3$-Control on the order of 10s of seconds indicates the presence of trapped charge, likely at deep defects, that can serve as recombination centers for the photogenerated charges. A relatively fast decay is observed in the Sb$_2$Se$_3$-Sn (0.5) photocathode, indicating enhanced charge recombination when illumination is stopped.

Although it may seem counterintuitive at first sight why the better-performing device shows a faster OCP decay, several points can clarify this behavior. Firstly, the IPCE analysis reveals similar photon conversion at longer wavelengths within the bulk of both photocathodes, implying a similar trap density in the bulk of both Sb$_2$Se$_3$ photocathodes (see Figure 1d). However, in the short wavelength region, the Sb$_2$Se$_3$-Control photocathode exhibits lower IPCE conversion compared to the Sb$_2$Se$_3$-Sn (0.5) photocathode, indicating the primary difference between both devices lies in their interface between the absorber and TiO$_2$. This distinction is evident in the CV and DLCP measurements, which suggest a higher surface defect density observed in the Sb$_2$Se$_3$-Control device. Therefore, in the Sb$_2$Se$_3$-Control device, more charge carriers are trapped at the surface and are released at a slower rate, leading to decelerated OCP decay. The fast OCP decay observed in the Sb$_2$Se$_3$-Sn (0.5) device is probably also linked to the improved conductivity, facilitating rapid charge transport.
References

