Photocorrosion-Resistant Sb₂Se₃ Photocathodes with Earth Abundant MoS_x Hydrogen Evolution Catalyst

Rajiv Ramanujam Prabhakar¹, Wilman Septina¹, Sebastian Siol², Thomas Moehl¹, René Wick-Joliat¹, and S. David Tilley^{1*}

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Affiliations:

¹ University of Zurich, Zurich, Switzerland

² EMPA, Dübendorf, Switzerland

*Corresponding author: david.tilley@chem.uzh.ch

Abstract

The poor stability of high efficiency photoabsorber materials in aqueous media is one factor holding back the realization of photoelectrochemical (PEC) water splitting for large scale, practical solar fuels generation. Here, we demonstrate that highly efficient thin film Sb_2Se_3 —fabricated by a simple, low temperature selenization of electrodeposited Sb—is intrinsically stable towards photocorrosion in strongly acidic media (1 M H_2SO_4). Coupling with a photoelectrodeposited MoS_x hydrogen evolution catalyst gives high photocurrents (5 mA cm^{-2} at 0 V vs RHE) and high stability without protective layers. A low temperature sulfurization of the Sb_2Se_3 - MoS_x stack dramatically improved the onset potential, resulting in high photocurrent densities up to $\sim 16 \text{ mA cm}^{-2}$ at 0 V vs RHE. The simplicity with which these photocathodes are fabricated, combined with the high photocurrents and stability, make Sb_2Se_3 a strong candidate for scalable PEC cells.

1. Introduction

The direct conversion of solar energy into fuels is an elegant strategy to address the intermittency of solar energy, while sustainably maintaining our fuel-based economy.¹ One method to generate solar fuels is photoelectrochemical (PEC) water splitting.² Research in PEC water splitting has focused on improving both the efficiency and the stability of the semiconducting materials, which has a large impact on the cost of the resulting hydrogen.³ Although crystalline silicon sets the benchmark for solar conversion technology, it requires a large amount of energy and other resources for processing in order to make it highly efficient.⁴ Thus, researchers are searching for new materials that are more easily fabricated while retaining high efficiency. Sb_2Se_3 has been gaining importance in the photovoltaic community recently owing to its non-toxicity and Earth abundance along with promising solar cell efficiencies (6%).^{5,6} Although this material has been investigated for solar cell applications, there has thus far been only one report on Sb_2Se_3 as a PEC electrode for water splitting. Moon and coworkers showed H_2 evolution using Sb_2Se_3 nanoneedles, although the photocurrent densities obtained were much smaller than in solar cells ($\sim 2 \text{ mA cm}^{-2}$ at 0 V vs RHE), and rather poor stability was observed despite having a TiO_2 protection layer (<20 min).⁷ In addition to a highly efficient and stable photocathode, it is equally important to couple it with a low cost, non-toxic and Earth abundant catalyst. One such promising hydrogen evolution reaction (HER) catalyst is MoS_2 , with low overpotentials for water reduction. MoS_2 has been employed as an HER catalyst for both Cu_2O and GaInP_2 photocathodes, and provides comparable PEC performance as with a Pt catalyst.^{8,9} Since MoS_2 works efficiently only in strong acid (pH 0 or pH 1), protective TiO_2 overlayers were required to prevent corrosion of the photocathodes.¹⁰

In this work, we demonstrate that Sb_2Se_3 is resistant to photocorrosion without protective layers, and high photocurrent densities are obtained when coupled with an Earth abundant HER catalyst (MoS_x). By sulfurizing the Sb_2Se_3 - MoS_x stack, photocurrent densities as high as $\sim 16 \text{ mA cm}^{-2}$ were obtained at 0 V vs RHE in 1 M H_2SO_4 . We also show that the decrease in photocatalytic activity is due to the MoS_x catalyst, while the Sb_2Se_3 is inherently resistant to photocorrosion in the strongly acidic media. The simplicity with which these photocathodes are fabricated, combined with the high photocurrents and stability, make Sb_2Se_3 a strong candidate for scalable PEC cells.

2. Results and discussion

Sb_2Se_3 thin films used for this study were prepared by selenization of electrodeposited Sb thin films on Au-coated fluorine-doped tin oxide (FTO) substrates (the detailed procedure is provided in the methods section). The surface morphology of the Sb_2Se_3 thin films (Fig S1a) shows a grain size ranging from 300 to 600 nm with a largely void free surface. The X-Ray diffraction (XRD) pattern (Fig S1b) of these films was in good agreement with the orthorhombic phase of Sb_2Se_3 (JCPDS 15–0861) with no signs of secondary phases or impurities. Energy dispersive X-ray spectroscopy (EDX) spectra also show the presence of Sb and Se peaks (Fig S2a), and the Raman spectrum indicates a pure Sb_2Se_3 phase (Fig S2b).¹¹ In order to evaluate if Sb_2Se_3 could be employed as a photocathode for hydrogen evolution, the band positions of the Sb_2Se_3 were determined using Mott-Schottky (M-S) analysis. To circumvent frequency dispersion in the M-S plots, the space charge capacitance (C_{SC}) was determined by electrochemical impedance spectroscopy (EIS). As the rich redox chemistry of Sb and Se in water in the potential range between 0 and 500 mV vs standard hydrogen electrode (SHE) hinders the determination of C_{SC} ,

the measurement of C_{SC} was performed in dry acetonitrile. The plot of $1/C^2$ of the space charge capacitance reveals a p-type character of the Sb_2Se_3 and yields a flat band potential of 273 mV vs SHE for two separate samples, with a moderate doping density of $\sim 1e^{18} \text{ cm}^{-3}$ (Fig S3a). X-ray photoelectron spectroscopy (XPS) measurements show an energetic distance of the fermi level E_F to the valence band maximum of $E_{VBM} \sim 500 \text{ mV}$ (Fig S4), which is in good agreement with previously reported values for phase pure Sb_2Se_3 , and suggests a moderate p-type doping of the film.¹² With this information the conduction and valence band positions of Sb_2Se_3 in the SHE and vacuum scale were determined (Fig S3b). The conduction band of Sb_2Se_3 lies more negative than the water reduction potential and hence can be employed as a photocathode for hydrogen evolution.

Fig 1a illustrates the device architecture for the Sb_2Se_3 photocathode employing a photoelectrodeposited amorphous MoS_x catalyst for the hydrogen evolution reaction. The bare Sb_2Se_3 does not show any appreciable photocurrent during light chopping (Fig 1b). However, the Sb_2Se_3 photocathode with MoS_x catalyst shows a high photocurrent density ($\sim 5.2 \text{ mA cm}^{-2}$ at 0 V vs RHE) (Fig 1b). A Sb_2Se_3 -Pt photocathode was also fabricated as a bench mark system, which exhibited an earlier onset potential than the Sb_2Se_3 - MoS_x due to better catalytic activity of Pt over amorphous MoS_x (Fig S5).¹³ It is important to note that the amorphous MoS_x requires an activation to be in its catalytically active form (Fig S6).¹⁴ Large bubbles were generated from the Sb_2Se_3 - MoS_x photocathode upon illumination, and gas chromatography confirmed hydrogen evolution with $\sim 100 \%$ faradaic efficiency (Fig S7).

A recent theoretical study suggests that the ionization potential of Sb_2S_3 is higher than the selenide, which could lead to a valence band offset at the Sb_2S_3/Sb_2Se_3 interface.¹⁵ This offset can act as a hole-blocking layer, resulting in reduced interface recombination. Hence, a

sulfurization of the $\text{Sb}_2\text{Se}_3\text{-MoS}_x$ stack was performed at 250 °C in order to slightly sulfurize the surface (denoted as $\text{Sb}_2\text{Se}_3\text{-MoS}_x\text{-S}$). The current density vs potential plots for $\text{Sb}_2\text{Se}_3\text{-MoS}_x\text{-S}$ show a significant improvement in the photocurrent onset (~ 100 mV) and typical photocurrents of $\sim 14 \text{ mA cm}^{-2}$ were obtained at 0 V vs RHE with very low dark currents (Fig 1b, S8). Fig S9 shows the device statistics for four different $\text{Sb}_2\text{Se}_3\text{-MoS}_x\text{-S}$ photocathodes, which consistently show photocurrent densities higher than 13 mA cm^{-2} at 0 V vs RHE, and higher than 20 mA cm^{-2} at -0.16 V vs RHE. A thermal annealing control experiment in the absence of sulfur confirmed that sulfur was required for the improvement in performance (Fig S9). The incident photon to current efficiency (IPCE) spectrum of the $\text{Sb}_2\text{Se}_3\text{-MoS}_x\text{-S}$ sample revealed a similar onset as the non-sulfurized sample, indicating that the bandgap was unaffected by the sulfurization treatment (Fig 1c). The IPCE onset of ~ 1060 nm coincides with the bandgap of Sb_2Se_3 , indicating that all above bandgap radiation is able to be converted in these photocathodes, with greater than $\sim 40\%$ IPCE across the visible spectrum (400-700 nm) for the sulfurized sample. STEM-EDX elemental mapping revealed that the Mo/S was localized close to the surface without any sulfur penetration into the Sb_2Se_3 layer (Fig 2a).

To elucidate the reason for improvement in the PEC performance, the chemical composition was further investigated by XPS. Figure 2b and c shows the Sb 3d XPS spectra of $\text{Sb}_2\text{Se}_3\text{-MoS}_x$ before and after sulfurization. The key feature of these spectra is that the peaks corresponding to Sb_2O_3 decreased upon sulfurization treatment. This partial removal of Sb_2O_3 after the sulfurization could result in the improvement of the onset potential due to reduced interface recombination (e.g. due to trap elimination or better charge separation) and decreased contact resistance.¹⁶ Upon sulfurization, a conversion of Sb_2O_3 to Sb_2S_3 is likely, but the effects are difficult to quantify by XPS due to the similarities in core level emission between Sb_2S_3 and

Sb_3Se_3 , making the two components almost indistinguishable in the Sb3d spectra. Thus, further analysis was carried out in order to verify this hypothesis. There was not any significant change in the surface morphology (Fig S11a and b) after sulfurization of the $\text{Sb}_2\text{Se}_3\text{-MoS}_x$. Additionally, the XRD patterns and Raman spectrum were nearly identical for the sulfurized and non-sulfurized samples (Fig S11c and d). The $\text{Sb}_2\text{Se}_3\text{-MoS}_x\text{-S}$ also did not show any Raman peaks corresponding to crystalline MoS_2 , indicating that the crystallinity of the MoS_x catalyst did not change with sulfurization treatment.¹⁷ A prolonged sulfurization (2 h) produced a new Raman peak attributed to Sb_2S_3 (Fig S12a), which did not significantly affect the current density-potential characteristics in comparison to the shorter sulfurization time (Fig S12b). These data support our hypothesis of sulfurization of the Sb_2O_3 at the surface for the improvement of the photoelectrochemical performance.

Figure 3a shows the photocurrent stability of $\text{Sb}_2\text{Se}_3\text{-MoS}_x\text{-S}$ in 1 M H_2SO_4 at 0 V vs RHE, where the photocurrent density starts at $\sim 14 \text{ mA cm}^{-2}$ upon illumination and slowly decreased to $\sim 9.8 \text{ mA cm}^{-2}$ over a period of 2 h. Most of the photoactivity was recovered upon reapplication of the MoS_x catalyst, although the photocurrent again decreased gradually from $\sim 13 \text{ mA cm}^{-2}$ to $\sim 10 \text{ mA cm}^{-2}$ over another 2 h. Since the photocurrent was recovered after the reapplication of the catalyst, this would indicate loss of the MoS_x catalyst from the surface during operation.¹⁴ In order to verify this, XPS sputter depth profiles of the $\text{Sb}_2\text{Se}_3\text{-MoS}_x\text{-S}$ before and after operation were obtained. Despite the measurement uncertainties potentially introduced by preferential sputtering, qualitative comparisons between similar samples are possible. In this case the sample after operation shows a much faster decay of the relative atomic concentrations for Mo and S with increasing sputter depth as compared with the sample before operation (Fig 3b), indicating a loss of MoS_x catalyst from the surface during operation. Notably, an increase of oxygen is also

observed after measurement that is attributed to slight oxidation of the MoS_x layer, as an increase in Sb₂O₃ was not observed by XPS (Fig S13).

In order to further improve the stability of the Sb₂Se₃-MoS_x photocathode, a thicker MoS_x catalyst was loaded onto the Sb₂Se₃ photocathode [30 nm]. The thicker catalyst resulted in a significant improvement of the photocurrent stability in a 1 h time frame for both the sulfurized and non-sulfurized samples (Fig S14), and a stability up to 20 h was observed for the non-sulfurized sample (Fig 4a). For the higher performing sulfurized sample, high photocurrents were observed for hours, but the performance decayed to 1 mA cm⁻² after 10 h and then to nearly 0 mA cm⁻² after 20 h. In order to decouple whether the degradation at high current densities (>14 mA cm⁻²) was due to catalyst or the Sb₂Se₃, a MoS_x layer was deposited on a glassy carbon electrode using the same conditions as on the Sb₂Se₃ thin film. A potential corresponding to an initial current density of 14 mA cm⁻² was applied to the MoS_x electrode on glassy carbon in 1 M H₂SO₄ under 1 sun illumination, and the current density was monitored over time (Figure S15). The trend is similar to the photocathode experiment with the electrode completely degrading to 0 mA cm⁻² after 4 h. Fig 4b shows that at the surface of Sb₂Se₃-MoS_x after 20 h operation the relative oxygen content is significantly increased, while the relative sulfur content is significantly decreased. This observation indicates a conversion of MoS_x to MoO_x, which would deteriorate the catalytic performance for the HER reaction. This effect could be further accelerated when operating at higher current densities (>14 mA cm⁻²), hence resulting in faster degradation of the MoS_x catalyst in the high performing case. It has been shown that corrosion of MoS₂ can be induced by conversion of the MoS₂ into MoO_x, particularly at the edge sites.¹⁸ Since the edge sites are the main catalytically active sites in MoS_x, corrosion of these sites would result in the loss of catalytic activity.

To further evaluate the intrinsic stability of Sb_2Se_3 thin film, a photocorrosion stress test was carried out. Cyclic voltammetry of the bare Sb_2Se_3 thin film was performed in 1 M H_2SO_4 under 1 sun illumination for 285 cycles (10 mV/s, 4.75 h, Fig 5a). The bare Sb_2Se_3 thin film does not show significant photo corrosion currents during the CV cycling. After 285 cycles, MoS_x catalyst (~ 30 nm) was coated onto the Sb_2Se_3 thin film, and it exhibited similar PEC performance to a freshly prepared Sb_2Se_3 - MoS_x photocathode, with fairly good photocurrent stability for 10 h (Fig 5b and S16). The Sb_2Se_3 photocathode is therefore remarkably robust under the harsh conditions of the strongly acidic electrolyte and full sun irradiation. Sb_2Se_3 is therefore a strong candidate for practical PEC water splitting cells due to its intrinsic stability in strong acid, as well as high efficiency as a photoabsorber when produced with scalable and low-cost methods.

3. Conclusion

We demonstrated highly efficient Sb_2Se_3 photocathodes using Earth-abundant MoS_x as a catalyst for the first time. By employing a post-sulfurization strategy, photocurrent densities as high as $\sim 16 \text{ mA cm}^{-2}$ were obtained. The post-sulfurization does not convert the Sb_2Se_3 film to Sb_2S_3 or $\text{Sb}_2(\text{S,Se})_3$, but rather partially converts the Sb_2O_3 on the surface to Sb_2S_3 forming an effective hole blocking contact leading to an earlier photocurrent onset. The Sb_2Se_3 photocathodes also exhibited good photocurrent stability in strong acid (1 M H_2SO_4) for 20 h without any protection layers. We also showed that the Sb_2Se_3 thin film is robustly stable towards photocorrosion in strong acid, in contrast to other high efficiency photocathodes. The primary loss in the catalytic activity of the photocathodes at high current densities was due to changes in the MoS_x rather than degradation of the Sb_2Se_3 absorber.

4. Experimental section

Synthesis of Sb_2Se_3 thin films: FTO substrates used were FTO TEC 15 from Pilkington. 150 nm of Au was coated onto the FTO substrates using a Safematic CCU-010 sputter coater. Sb metal was electrodeposited onto the Au-coated FTO substrates following a literature procedure in a three-electrode configuration from a solution containing 15 mM $\text{K}_2(\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6)_2)$ and 50 mM tartaric acid at a pH of 1.3 (pH adjusted using conc. sulfuric acid, 95%) and a potential of -0.3 V vs Ag/AgCl.¹⁹ The thickness of the Sb metal was controlled by limiting the charge passed to 1.4 C cm^{-2} . The electrodeposited Sb metal was selenized in a one-zone furnace using selenium pellets (30 mg) as the selenium source in an Ar atmosphere at 350 °C. A ramping rate of $15 \text{ }^\circ\text{C min}^{-1}$ was used to reach 350 °C and the sample was maintained at this temperature for 40 min. Once the process was finished, the furnace was opened to cool down to room temperature within 60 min. Sulfurization of Sb_2Se_3 thin films was carried out in a two-zone furnace. Elemental sulfur powder (300 mg) was used as sulfur source to maintain a sulfur atmosphere in the tube for the entire sulfurization process. The Sb_2Se_3 was kept at 250 °C and the sulfur source was kept at 200 °C. The ramping rate to reach the required temperatures was $15 \text{ }^\circ\text{C min}^{-1}$ and these temperatures were maintained for a period of 40 min. Once the process was finished the furnace was opened to cool to room temperature within 60 min.

Photoelectrodeposition of MoS_x and Pt catalyst: MoS_x photoelectrodeposition was carried out using a 5 mM $(\text{NH}_4)_2[\text{MoS}_4]$ solution containing 0.5 M Na_2SO_4 in a 2-electrode setup under 1 sun illumination using a procedure described in the literature.²⁰ A constant current of $-50 \text{ } \mu\text{A cm}^{-2}$ was passed for 10 minutes for the thin MoS_x (~15nm). The thickness was estimated from the elemental mapping using STEM (Fig 2a). For thicker MoS_x (~30 nm), a constant current of $-120 \text{ } \mu\text{A cm}^{-2}$ was passed for 10 min. The thickness for the thicker MoS_x layer was estimated by

comparing the XPS sputter depth profiles. After the MoS_x deposition, the electrode was thoroughly washed with distilled water. Platinum catalyst was photoelectrodeposited from an aqueous solution of 1 mM H₂PtCl₆ containing 0.1 M Na₂SO₄, using a constant current of -0.03 mA cm⁻² for 10 min with constant irradiation from simulated 1 sun illumination.

Morphology and crystal structure characterization of Sb₂Se₃ thin films: The plan view and cross sectional scanning electron microscopy (SEM) images of Sb₂Se₃ thin films were obtained using a SEM - Zeiss Supra 50 VP that was equipped with an energy dispersive X-ray spectroscopy (EDX) detector (genesis). X-ray diffraction (Rigaku smartlab diffractometer) and Raman spectrum were obtained using a Renishaw System 2000 (excitation wavelength 532 nm and laser spot size ~2 μm).

Electrochemical and photoelectrochemical characterization of Sb₂Se₃ PEC:

The photoelectrochemical measurement of the photocathodes was evaluated in a three-electrode configuration using a BioLogic SP-200 potentiostat under irradiation from simulated AM 1.5 G illumination, calibrated using a silicon diode from PV Measurements, Inc. (100 mW cm⁻²). A 1 M H₂SO₄ (pH 0) solution was used as the electrolyte. The reference electrode was Hg/HgSO₄ (sat'd KCl), and a Pt wire was used as the counter electrode. Before measurement, the electrolyte was sparged with N₂ for at least 30 min to remove dissolved oxygen. The photocathode area was defined using epoxy (Loctite 9461) and the active area was determined by counting pixels using the image processing software gimp. The conversion between potentials vs. Hg/HgSO₄ and vs. RHE was performed using the equation:

$$E \text{ (vs. RHE)} = E \text{ (vs. Hg/HgSO}_4\text{)} + 0.059 \text{ V} \times \text{pH} + 0.634 \text{ V (E}_{\text{Hg/HgSO}_4}\text{)}$$

Incident photon-to-current efficiency (IPCE) was measured on a home-built IPCE system featuring a halogen light source with double monochromator and white light bias. The IPCE was

measured in a three-electrode configuration using Hg/HgSO₄ (sat'd KCl) reference electrode and Pt wire as the counter electrode at 0 V versus RHE at 5 nm wavelength intervals. The Faradaic efficiency was measured in a glass three-compartment cell using a Pt wire as counter electrode, Ag/AgCl reference electrode and 1 M H₂SO₄ (pH 0) electrolyte. The solution was stirred and sparged with Argon as carrier gas at a flow rate of 20 ml min⁻¹. The composition of the carrier gas was analyzed in a 450-GC Gas Chromatograph (Bruker Daltonics GmbH) every two minutes. For faradaic efficiency measurement 0 V vs RHE was applied for one hour under illumination by a white light LED. The light intensity was chosen to match the current density under one sun illumination in PEC measurements. The amount of hydrogen detected by the GC was determined by creating a calibration curve using several different galvanostatic current values applied to a freshly cleaned Pt working electrode in two electrode mode, and assuming 100 % faradaic efficiency for the HER on Pt.

Mott Schottky analysis and electrochemical impedance spectroscopy

The doping and the flat band potential were determined by electrochemical impedance analysis. Due to the rich chemistry of Sb and Se in water in the required potential region for Mott-Schottky (M-S) analysis, which complicates the interpretation, the M-S analysis was performed in dry acetonitrile solution with 0.2 M tetrabutylammoniumhexafluorophosphate as conduction salt. A leak free reference electrode (EDAQ; ET072) was used and calibrated against ferrocene in acetonitrile. The conversion of the electrochemical electrode potential to the absolute electrode potential was according to the IUPAC standard of $E_{(abs)} = E_{(SHE)} + 4.4 \text{ V}$.²¹ The impedance measurement was performed by applying a 15 mV sinusoidal potential perturbation onto the stepped bias potential (25 mV steps from -0.4 to 0.6 vs SHE). The frequency range for the potential perturbation was 200 kHz down to 0.2 Hz. 16 s was used as stabilization time at

each bias potential step. The Nyquist plots at the different bias potentials showed one semicircle and were therefore fitted with a simplified Randles circuit consisting of the series resistance (from cables, contacts and electrolyte), the charge transfer resistance (R_{ct}) and the space charge capacitance (C_{sc}). To account for the roughness of the semiconductor surface, a constant phase element (CPE) was used to model the space charge capacitance (with the exponent of the CPE not going below 0.85 during the fitting procedure).

After the fitting of the Nyquist plots, the CPE values were converted into the space charge

$$C_{sc} = \frac{(R_{ct} \times Q)^{\frac{1}{n}}}{R_{ct}} \quad (1)$$

capacitance:

with R_{ct} as the charge transfer resistance, Q as the charge from the CPE and n as the exponent of the CPE. By the fitting of the Nyquist plots the absolute values of the space charge capacitance are determined and therefore no frequency dispersion appears in the M-S analysis.

The space charge capacitance was used for the M-S analysis, relating $1/C_{sc}^2$ vs the applied potential to the flat band potential ($\propto$ x axis intercept) and doping ($\propto$ slope):

$$\frac{1}{C_{sc}^2} = \frac{2}{N_A \epsilon \epsilon_0 q} \left(E - E_{FB} - \frac{kT}{q} \right) \quad (2)$$

where q is the charge of an electron, ϵ is the relative dielectric constant of the materials ($\epsilon = 15$),²² ϵ_0 is the permittivity of free space, N_A acceptor density (for a p-type semiconductor), E is the potential applied, E_{FB} is the flat band potential, k is the Boltzmann constant and T is the temperature. As the surface of the absorber is not flat a roughness factor of 1.5 was assumed.

XPS

X-ray photoelectron spectroscopy (XPS) was conducted using a Physical Electronics (PHI) Quantum 2000 X-ray photoelectron spectrometer featuring monochromatic Al-K α radiation,

generated from an electron beam operated at 15 kV and 32.3 W. The energy scale of the instrument was calibrated using Au and Cu reference samples. The analysis was conducted at 1×10^{-6} Pa, with an electron take off angle of 45° and a pass energy of 23.50 eV. The measurements were performed without neutralizer. If not stated otherwise, the sputter depth profiles were obtained using Ar ions (1 kV potential) on an area of approximately 2x2 mm. Surface elemental concentrations were determined from the photoelectron spectra after Shirley background subtraction using the instrument specific sensitivity factors for calculation. As necessary, the core level spectra were fitted to deconvolute spectra with contributions from multiple elements. In particular fits of the Sb3d core level spectra were carried out for a semi-quantitative comparison of the different samples. A symmetric shape (GL 30) was assumed for the core level emissions with a separation of $\Delta E = 9.34$ eV for the Sb 3d doublet.

TEM and FIB sample preparation

A TEM lamella was prepared by the in-situ lift-out technique on a Zeiss NVision 40 FIB-SEM. The lamella was thinned using 30 kV Ga⁺ ions. For the 5-kV showering, to reduce the thickness and limit the damage of the layer, the lamella was tilted 10° into the beam. The FEI Talos F200X transmission electron microscope was operated at 200 kV and was equipped with a X-FEG emitter. The microscope can be operated in TEM as well as in STEM mode, and provides a point-to-point resolution of 0.12 nm for TEM and 0.16 nm for STEM imaging. For elemental analysis, it is equipped with a Super-X EDS (windowless, 4-detector configuration).

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Figures

Figure 1. **a** Schematic representation of $\text{Sb}_2\text{Se}_3\text{-MoS}_x$ photocathode. **b** Current density-potential characteristics of bare Sb_2Se_3 (light chopping), $\text{Sb}_2\text{Se}_3\text{-MoS}_x$ (non-sulfurized) and $\text{Sb}_2\text{Se}_3\text{-MoS}_x\text{-S}$ (sulfurized) photocathode in 1 M H_2SO_4 under simulated 1 sun illumination (100 mW cm^{-2}). **c** IPCE spectra of $\text{Sb}_2\text{Se}_3\text{-MoS}_x$ and $\text{Sb}_2\text{Se}_3\text{-MoS}_x\text{-S}$ photocathodes in 1 M H_2SO_4 at 0 V vs RHE.

Figure 2. **a** STEM HAADF image and EDX elemental mapping of $\text{Sb}_2\text{Se}_3\text{-MoS}_x\text{-S}$ (sulfurized). **b** XPS core level spectrum of Sb 3d for $\text{Sb}_2\text{Se}_3\text{-MoS}_x$ (non-sulfurized). **c** XPS core level spectrum of Sb 3d for $\text{Sb}_2\text{Se}_3\text{-MoS}_x\text{-S}$ (sulfurized).

Figure 3. **a** Current density vs time plots for Sb₂Se₃-MoS_x-S (~15 nm MoS_x thickness) in 1 M H₂SO₄ at 0 V vs RHE at 1 sun illumination (100 mW cm⁻²). **b** XPS depth profile of Sb₂Se₃-MoS_x-S before (as deposited) and after 2 h stability measurement (~15 nm MoS_x thickness). Shown are the relative atomic concentrations for Mo, S, Sb, Se and O.

Figure 4. **a** Current density vs time plots for Sb₂Se₃-MoS_x and Sb₂Se₃-MoS_x-S (~30 nm MoS_x thickness) in 1 M H₂SO₄ at 0 V vs RHE at 1 sun illumination (100 mW cm⁻²). **b** XPS depth profile of Sb₂Se₃-MoS_x before (as deposited) and after 20 h of stability measurement (~ 30 nm MoS_x thickness). Shown are the relative atomic concentrations of Mo, S, Sb, Se, and O.

Figure 5. **a** CV of a bare Sb₂Se₃ thin film (without MoS_x catalyst) in 1 M H₂SO₄ under 1 sun illumination (100 mW cm⁻²). The sweep rate was 10 mV s⁻¹ and the total experiment time was 4.75 h. **b** Current density vs potential plots of a Sb₂Se₃-MoS_x photocathode prepared after 285 CV cycles of bare Sb₂Se₃ in 1 M H₂SO₄ under 1 sun illumination.

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A highly efficient Sb_2Se_3 photocathode is resistant to photocorrosion in strongly acid media without protective overlayers.