Scalable Core–Shell MoS$_2$/Sb$_2$Se$_3$ Nanorod Array Photocathodes for Enhanced Photoelectrochemical Water Splitting

Liping Guo, Pravin S. Shinde, Yanxiao Ma, Lin Li, Shanlin Pan,* and Feng Yan*

Photoelectrochemical (PEC) hydrogen generation is a promising solar energy harvesting technique to address the concerns about the ongoing energy crisis. Antimony selenide (Sb$_2$Se$_3$) with van der Waals-bonded quasi-1D (Q1D) nanoribbons, for instance, (Sb$_4$Se$_6$)$_m$, has attracted considerable interest as a light absorber with Earth-abundant elements, suitable bandgap, and a desired sunlight absorption coefficient. By tuning its anisotropic growth behavior, it is possible to achieve Sb$_2$Se$_3$ films with nanostructured morphologies that can improve the light absorption and photogenerated charge carrier separation, eventually achieving Sb$_2$Se$_3$ absorber with Earth-abundant elements, suitable bandgap, and a desired sunlight harvesting technique to address the concerns about the ongoing energy crisis. Antimony selenide (Sb$_2$Se$_3$) with van der Waals-bonded quasi-1D (Q1D) nanoribbons, for instance, (Sb$_4$Se$_6$)$_m$, has attracted considerable interest as a light absorber with Earth-abundant elements, suitable bandgap, and a desired sunlight absorption coefficient. By tuning its anisotropic growth behavior, it is possible to achieve Sb$_2$Se$_3$ films with nanostructured morphologies that can improve the light absorption and photogenerated charge carrier separation, eventually boosting the PEC water-splitting performance. Herein, high-quality Sb$_2$Se$_3$ films with nanorod (NR) array surface morphologies are synthesized by a low-cost, high-yield, and scalable close-spaced sublimation technique. By sputtering a nonprecious and scalable crystalline molybdenum sulfide (MoS$_2$) film as a cocatalyst and a protective layer on Sb$_2$Se$_3$ NR arrays, the fabricated core–shell structured MoS$_2$/Sb$_2$Se$_3$ NR PEC devices can achieve a photocurrent density as high as $-10$ mA cm$^{-2}$ at $0$ V$_{RHE}$ in a buffered near-neutral solution (pH 6.5) under a standard simulated air mass 1.5 solar illumination. The scalable manufacturing of nanostructured MoS$_2$/Sb$_2$Se$_3$ NR array thin-film photocathodes for efficient PEC water splitting to generate solar fuel is demonstrated.

1. Introduction

Solar energy conversion technologies promise a renewable, sustainable, and affordable way of addressing the energy crisis due to depleting fossil fuel sources. The photovoltaic effect-based solar cell is one of the best examples of effective solar energy conversion and storage applications. For example, a considerable number of oxides such as Fe$_2$O$_3$, Cu$_2$O, TiO$_2$, and BiVO$_4$ and the chalcogenides such as Cu(In, Ga) S$_2$, Cu$_2$ZnSnS$_4$, CdTe, and SnS have been intensely investigated as PEC absorbers. Recently, the antimony selenide (Sb$_2$Se$_3$) chalcogenide has emerged as a promising light absorber material for photovoltaic devices whose power conversion efficiency (PCE) reaches as high as $\approx 9.2\%$. The high optical absorption coefficient ($>10^5$ cm$^{-1}$), ideal low bandgap ($\approx 1.2$ eV), low toxicity, high stability, and abundance in Earth make Sb$_2$Se$_3$ a promising candidate in PEC devices. Sb$_2$Se$_3$ is also popularly known as a quasi-1D (Q1D) material with an anisotropic orthorhombic structure, which can assist the transport of photoexcited carriers along the oriented (Sb$_4$Se$_6$)$_m$ ribbons. Nanostructured Sb$_2$Se$_3$ is reported to achieve a decent PEC hydrogen generation performance in the forms of nanoneedles, nanowires, and nanoribbons. These nanostructures could efficiently elevate the electrical and optical properties due to improved light absorption and charge carrier transportation. Furthermore, to realize the scalability of PEC applications, Sb$_2$Se$_3$ polycrystalline thin-film photocathodes have been investigated. The best stable PEC performance is reported in a benign neutral electrolyte (pH $\approx 6.5$) for cost-effective solar energy conversion and storage applications. For example, a considerable number of oxides such as Fe$_2$O$_3$, Cu$_2$O, TiO$_2$, and BiVO$_4$ and the chalcogenides such as Cu(In, Ga) S$_2$, Cu$_2$ZnSnS$_4$, CdTe, and SnS have been intensely investigated as PEC absorbers. Recently, the antimony selenide (Sb$_2$Se$_3$) chalcogenide has emerged as a promising light absorber material for photovoltaic devices whose power conversion efficiency (PCE) reaches as high as $\approx 9.2\%$. The high optical absorption coefficient ($>10^5$ cm$^{-1}$), ideal low bandgap ($\approx 1.2$ eV), low toxicity, high stability, and abundance in Earth make Sb$_2$Se$_3$ a promising candidate in PEC devices. Sb$_2$Se$_3$ is also popularly known as a quasi-1D (Q1D) material with an anisotropic orthorhombic structure, which can assist the transport of photoexcited carriers along the oriented (Sb$_4$Se$_6$)$_m$ ribbons. Nanostructured Sb$_2$Se$_3$ is reported to achieve a decent PEC hydrogen generation performance in the forms of nanoneedles, nanowires, and nanoribbons. These nanostructures could efficiently elevate the electrical and optical properties due to improved light absorption and charge carrier transportation. Furthermore, to realize the scalability of PEC applications, Sb$_2$Se$_3$ polycrystalline thin-film photocathodes have been investigated. The best stable PEC performance is reported in a benign neutral electrolyte (pH $\approx 6.5$)
for thermally evaporated Sb2Se3 film in a p–n junction substrate configuration by coupling with an n-type CdS/TiO2 followed by the use of expensive Pt coating as the cocatalyst on the surface that exhibits a photocurrent density of −6.6 mA cm−2 at 0 V versus reversible hydrogen electrode (V_RHE).[26] Recently, the solution-processed Sb2Se3 photocathodes achieved −11 mA cm−2 at 0 V versus reversible hydrogen electrode in the near-neutral electrolytes.[19] In a strongly acidic electrolyte (1 M H2SO4, pH ≈ 1), Sb2Se3 thin film prepared with the selenization of electrodeposited Sb and Pt cocatalyst further improves the photocurrent density to 16 mA cm−2 at 0 V_RHE.[27] By introducing a Cu-doped NiOx hole-selective layer as an effective bottom contact layer for a solution-processed Sb2Se3 photocathode, a record photocurrent density of 17.5 mA cm−2 at 0 V_RHE in acidic electrolytes is achieved.[28]

Although Sb2Se3 photocathodes were reported as intrinsically stable toward photocorrosion in acidic electrolytes (pH ≈ 1), to achieve high stability, anti-photo corrosion layers were widely applied.[27] Among all the stable performances reported so far, Sb2Se3 has been protected by precious metal cocatalysts such as Pt or RuOx and high bandgap oxides, e.g., TiO2, to avoid the inevitable photocorrosion.[1,29] Therefore, the use of inexpensive protective materials or catalysts is in high demand, to be suitable for scalable manufacturing. Few efforts have been directed toward using the nonprecious cocatalysts such as transition metal dichalcogenides (TMDs) to improve the PEC hydrogen generation further and avoid the photocorrosion of Sb2Se3.[26,30–32] Molybdenum sulfide (MoS2), one of the TMDs, is a typical 2D layered material and has promising properties for HER such as a suitable band alignment and good chemical as well as photocorrosion stability.[30,31,34] Recently, we have shown that the ≈30–40 nm crystalline MoS2 layer on the Cu2O photocathode solves the photocorrosion issue with dramatic improvement in photocurrent.[34] A solution-based approach of synthesizing amorphous/crystalline MoS2 has been used to protect several photocathodes, including Cu2O, Sb2Se3, and Sb2Se3.[27,34,35] However, the solution-processed MoSx catalyst faces various issues, including thickness uniformity, composition dependence of the synthetic procedure, and scalability.[2] In contrast, the physical vapor deposition (PVD) techniques such as sputtering offer a better way to synthesize stable, uniform, and large-area MoS2 thin films with great control.[36,37] However, minimal efforts have been made to synthesize the large-scale MoS2 heterostructures by PVD techniques and use them for photocatalysis applications.

Herein, we present an efficient polycrystalline Sb2Se3 thin-film photocathode with a nanostructured surface and MoS2 catalytic layer for PEC water splitting. This Sb2Se3 photocathode has been fabricated with a relatively unexplored close-spaced sublimation (CSS) method. CSS is a low-cost and high-yield method commonly used in solar cell fabrication, such as CdTe thin-film solar cells, as shown by our recent study.[38] The fast deposition rate of 1 μm min−1 can be achieved with CSS to fabricate numerous compound semiconductors. We have successfully fabricated high-quality Sb2Se3 thin films using the CSS technique for thin-film solar cell applications with PCE ≈7%.[17,39,40] Here, we tailor the CSS growth condition to grow Sb2Se3 nanorod (NR) arrays on top of the Sb2Se3 film simultaneously during deposition to increase light absorption and scattering. Using a scalable sputtered MoS2 catalyst to protect the CSS-grown Sb2Se3 NR arrays, a stable photocurrent density of −10 mA cm−2 at 0 V_RHE has been demonstrated in a near-neutral electrolyte (pH ≈ 6.5), which exhibits one of the highest PEC performances reported for the Sb2Se3 film-based photocathodes without using expensive Pt catalyst.

2. Results and Discussion

As shown in Figure 1a, the Sb2Se3 thin films were deposited using a CSS method, where the pure Sb2Se3 powder was sublimated at a high temperature in a short time and was deposited onto the fluorine-doped tin oxide (FTO) substrate. The CSS growth rate can reach ≈1 μm min−1, which is suitable for large-scale manufacturing.[17] The top-view surface and cross-sectional topographies of the as-grown Sb2Se3 film were examined using scanning electron microscopy (SEM) (Figure 1d,e). The Sb2Se3 film thickness is ≈1 μm, and the surface of the Sb2Se3 film is covered by the Sb2Se3 NR arrays (≈200 nm in diameter and ≈1000 nm), which is associated with the fast CSS growth rate of its orthorhombic structure. The CSS-deposited NR-structured Sb2Se3 film shows a texture behavior with preferred growth direction (confirmed in the X-ray diffraction [XRD] results later). The cross-sectional view of as-grown Sb2Se3 reveals uniform and dense films without any voids at the interface of Sb2Se3/FTO, indicating the better adhesiveness of noncubic Sb2Se3 on transparent conducting oxides (TCOs) than that of cubic chalcogenides (Figure 1g) such as CdTe (see Supporting Information).[41] Sb2Se3 was then introduced to a high-vacuum radio frequency (RF) sputtering system for MoS2 deposition (Figure 1b). Figure 1f shows that the Sb2Se3 film still preserves its NR structure after being coated with 30 nm MoS2. The corresponding cross-sectional SEM image (Figure 1g) shows that the MoS2 layer entirely covers the Sb2Se3 NRs and exhibits core–shell structures of MoS2/Sb2Se3 NRs. We anticipate an improved PEC performance with such core–shell MoS2/Sb2Se3 NR arrays on the Sb2Se3 films because of the increased surface area and NR structures enabling enhanced light absorption via light scattering and localization (Figure 1c).

To ascertain the coverage of the 30 nm-thick sputtered MoS2 on the Sb2Se3 film and the Sb2Se3 NR surfaces, we used the SEM equipped with energy-dispersive X-ray spectroscopy (EDS) to identify the core–shell structured MoS2/Sb2Se3 NR arrays in detail. As shown in Figure 2a, the CSS-deposited Sb2Se3 film has no visible physical defects in the bulk of the film, and the sputtered MoS2 coating is uniformly distributed on top of the Sb2Se3 film to have the completely covered core–shell NR structure. The morphology of the sputtered MoS2 film on the FTO substrate exhibits a granular structure (see Figure S1, Supporting Information). The magnified image of the NR arrays (Figure 2b) reveals the full coverage of MoS2 on the Sb2Se3 NR. The elemental SEM–EDS mapping of Sb, Se, Mo, and S shows that the Se content is weak on the surface, whereas the Sb exhibits a strong signal on the surface, but the Sb mapping is smaller than that of Mo and S. This elemental spatial distribution feature confirms that the MoS2/Sb2Se3 core–shell NR structure is formed with the help of sputtered MoS2. Moreover, the uniform
and full coverage of MoS$_2$ coating indicates well adhesion and proper heterojunction formation between the sputtered MoS$_2$ shell and Sb$_2$Se$_3$ NR array core. The rough surface of MoS$_2$ could also benefit HER due to the more facet and active sites.

To determine the coverage of the sputtered MoS$_2$ shell layer grown on the Sb$_2$Se$_3$ NR surface and the junction interface elemental distribution, transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) with attached EDS were used to characterize the MoS$_2$/Sb$_2$Se$_3$ core–shell NR and interface. As shown in Figure 3a,b, the sputtered MoS$_2$ was uniformly coated on the Sb$_2$Se$_3$ NR and formed a core–shell structure. Notably, the sputtered MoS$_2$ layer ($\approx$30 nm thickness) contains remarkable nanocrystalline particles ($\approx$10 nm). This morphology of the accumulated MoS$_2$ structure exists not only on the Sb$_2$Se$_3$ NR but also segregates among the valleys between the NRs and...
voltammetry (CV) measurements show that 30 nm-thick MoS2 for different thickness grown on the FTO substrate. The cyclic sputtered MoS2 turns from light to dark brown with increasing thickness. The bandgap of the MoS2 thin film changes from 2.56 eV for 20 nm to 1.67 eV for 50 nm. The optical image of the splitting reactions.

To elucidate the structural impacts on the PEC performance of the core–shell MoS2/Sb2Se3 NR array, the structure of the CSS-grown Sb2Se3 and 30 nm MoS2-coated Sb2Se3 was characterized using both XRD and Raman spectra. Figure 4c shows the XRD patterns of FTO, as-grown MoS2, pristine Sb2Se3, and MoS2/Sb2Se3. The pristine Sb2Se3 shows an orthorhombic structure with a space group of Pbnm (JCPDS 15-0861) with no secondary phase. The (120), (211), and (221) peaks are indexed, and the texture coefficient is calculated (see Figure S4, Supporting Information), which suggests that the CSS-deposited Sb2Se3 has a (221)-preferred orientation. This texture behavior indicates that the Sb2Se3 NR with overlay, Se, Sb, S, and Mo elements distribution.

To ascertain the role of sputtered MoS2 in inhibiting photocorrosion, we systematically characterized the optical and electrocatalytic performance of the pure MoS2 layer as a function of thickness. Figure 4a shows the optical bandgap extracted from the transmittance of the bare Sb2Se3/FTO and MoS2/FTO grown with various thicknesses. Sb2Se3 has a bandgap of ∼1.1 eV, whereas MoS2 gradually shows a bandgap decrease with increasing thickness. The bandgap of the MoS2 thin film changes from 2.56 eV for 20 nm to 1.67 eV for 50 nm. The optical image of the sputtered MoS2 turns from light to dark brown with increasing thickness (Figure S2, Supporting Information), which corresponds to the optical bandgap change. Figure 4b shows the electrocatalytic behavior of the sputtered MoS2 thin films of different thicknesses grown on the FTO substrate. The cyclic voltammetry (CV) measurements show that 30 nm-thick MoS2 is desired to provide the highest catalytic current density. Figure 4b is replotted in Supporting Information to calculate the Tafel slopes (Figure S3, Supporting Information). A 30 nm-thick MoS2 exhibits a lower overpotential compared with other thicknesses. HER activity can be expressed in terms of the lower Tafel slope from the polarization plots. The 30 nm-thick spin-coated MoS2 was enough to protect the cuprous oxide and help catalyze the water-splitting reactions.

The inset of Figure 4b shows the atomic force microscopy (AFM) surface morphology of the 30 nm-thick MoS2 with root mean square (RMS) roughness of ∼5 nm, and the MoS2 crystalline size is ∼100 nm.
To provide surface charge transport insights into the PEC device, we conducted the local electrostatic force microscopy (EFM) to determine its charge generation sites with high spatial resolution. Considering that the NR grew on the matrix of the Sb$_2$Se$_3$ film, as shown in Figure 5a, with the sputtered MoS$_2$ coating, we expected that the MoS$_2$/Sb$_2$Se$_3$ core–shell NR arrays distribute on top of Sb$_2$Se$_3$ films, as shown in Figure 5b. This unique hybrid nanostructure would help enhance the light absorption cross section and the populations of active sites for proton reduction reaction for solar water splitting. The NR structure would also shorten the electron transport distance to reduce protons at the MoS$_2$–electrolyte interface while enabling efficient hole transport to the conductive substrate. Figure 5c shows the AFM images revealing the surface topography of a bare Sb$_2$Se$_3$ NR with its bottom embedded in the Sb$_2$Se$_3$ film matrix. The charge generation map in the EFM images shows that the charging rate varies across the surface of the film, with a spatial resolution better than 100 nm (see Figure S7, Supporting Information, for EFM details). The NR structure itself presents a low charge accumulation slower than that of the surrounding regions. This could be due to the

Figure 4. a) Tauc plots of sputtered MoS$_2$ layer with different thicknesses on FTO, b) polarization curves for HER performance of MoS$_2$ grown on FTO substrate. The inset shows the AFM of the sputtered MoS$_2$ (thickness ≈30 nm) with a smooth surface; c) XRD patterns of FTO, MoS$_2$, Sb$_2$Se$_3$, and MoS$_2$-coated Sb$_2$Se$_3$; and d) Raman spectra of sputtered MoS$_2$, Sb$_2$Se$_3$, and MoS$_2$-coated Sb$_2$Se$_3$.

Figure 5. The schematic of a) Sb$_2$Se$_3$ NR/film and b) MoS$_2$/Sb$_2$Se$_3$ core–shell NR, showing the cross-sectional view of the core–shell NR structure, and c) the AFM topography (upper panels) and EFM (lower panels) images of the Sb$_2$Se$_3$ and MoS$_2$/Sb$_2$Se$_3$ NR (Area: 1.5 × 1.5 mm$^2$). d) The band diagram for the FTO, Sb$_2$Se$_3$, MoS$_2$ at different energy scales, vacuum, and the normal hydrogen electrode (NHE).
lower charge concentration at the top of the NRs. By applying the sputtered MoS2 layer, the AFM topography of the MoS2/Sb2Se3 core–shell NR shows a smooth surface and uniform coverage. The EFM image of the core–shell MoS2/Sb2Se3 NR shows a more uniform photogenerated charge distribution. It is believed that MoS2 is helpful for charge transfer due to its larger work function (≈5.1 eV) than that of Sb2Se3 (≈4.6 eV). As shown in Figure 5d, the band diagram for the MoS2/Sb2Se3 core–shell NR shows a more uniform photogenerated charge distribution. It is believed that MoS2 is helpful for charge transfer due to its larger work function (≈5.1 eV) than that of Sb2Se3 (≈4.6 eV). As shown in Figure 5d, the band diagram for the MoS2/Sb2Se3 core–shell NR shows a more uniform photogenerated charge distribution.

Figure 6 shows the PEC performance of the core–shell MoS2/Sb2Se3 NR-based electrodes illuminated under air mass (AM) 1.5 G simulated sunlight. As shown in Figure 6a, the pristine Sb2Se3 NR array electrodes show cathodic photocurrents under a linear voltammetry sweep from +0.5 to −0.2 V_RHE. Surprisingly, the CSS-deposited pristine Sb2Se3 film achieves a photocurrent of ≈4.2 mA cm⁻² at 0 V_RHE during the first scan, which is much higher than the reported Sb2Se3 films fabricated by other deposition techniques. For example, the thermally evaporated pristine Sb2Se3 films show ≈10 μA cm⁻², whereas the solution-processed Sb2Se3 nanostructure displays ≈100 μA cm⁻² at 0 V_RHE. In addition, the PEC performance of Sb2Se3 film with NR arrays is also higher than that of pure nanostructured Sb2Se3 photocathodes. For example, Sb2Se3 nanoneedles with TiO2 and Pt surface modification yields 2 mA cm⁻² at 0 V_RHE. Hence, CSS-deposited Sb2Se3 shows a significant photocurrent improvement for the pristine Sb2Se3 film with NR surface structure, which suggests that CSS is suitable for high-quality Sb2Se3 production. However, with increasing the number of scans, the photocurrent decreased sharply to ≈1 mA cm⁻² at 0 V_RHE (76% drop after the 3rd scan), which is also noticed for Sb2Se3 films prepared by other growth techniques. Nevertheless, the high PEC performance stems from the contribution of the Sb2Se3 NR structure surface, enabling efficient light absorption and short electron transport, although the film suffers from photocorrosion of the Sb2Se3 film surface. The photocorrosion is evidenced by the PEC product of the film, which is rich in Sb2O3, as shown in Figure S5, Supporting Information, X-ray photoelectron spectroscopy (XPS) data for Sb2O3 surface after PEC testing; the thickness of Sb2O3 is ≈2–3 nm.

To protect Sb2Se3 NRs from photocorrosion, a MoS2 layer is sputtered onto the NR structure to prevent light-driven electrochemical oxidation while enhancing the selective proton reduction. It is expected that the MoS2 can effectively protect the Sb2Se3 NR from direct contact with the 0.5 M Na2SO4 electrolyte. After 20 nm-thick MoS2 coating, a significant improvement in photocurrent up to −8.0 mA cm⁻² at 0 V_RHE was observed for the core–shell MoS2/Sb2Se3 NR arrays during the first scan (Figure 6b). The improved photocurrent originates partially from the core–shell MoS2/Sb2Se3 heterostructure formation to increase the light absorption range with a broad bandgap of MoS2 and enhance the photogenerated carrier separation. However, with an increasing number of linear sweep voltammetry (LSV) scans, this core–shell MoS2/Sb2Se3 still suffers from...
corrosion, which indicates that 20 nm-thick MoS2 is not sufficient to fully protect the Sb2Se3 NR arrays. The photocorrosion can stem from the grain boundary regimes between MoS2 and Sb2Se3 NRs as the Sb2Se3 NR size is on the order of micrometer scale. A remarkable photocurrent enhancement up to -10 mA cm\(^{-2}\) at 0 V\(_{RHE}\) is achieved with an increase in MoS2 thickness to 30 nm (Figure 6c), which is stable for several LSV scans. This is on par with excellent photocurrent reported for Sb2Se3 photocathodes fabricated using other deposition techniques and more complicated PEC device structures, e.g., -8.6 mA cm\(^{-2}\) at 0 V\(_{RHE}\) in Sb2Se3/CdS/TiO2/Pt structure at pH \(\approx 6.5\).\(^{[4]}\) However, with a further increase in the MoS2 thickness to 50 nm (Figure 6d), the dark current dominates the PEC performance due to the thicker MoS2 and may block the light absorption in Sb2Se3 (discussion later). This observation indicates that core–shell MoS2/Sb2Se3 NR arrays are of high efficiency in water splitting as a photocathode. Moreover, the sputtered MoS2 could be effective in protecting the Sb2Se3 NR and reduce the degradation for the Sb2Se3 NR array-based photocathodes.

To gain insights into the chemical states and stability during the photoactivity measurement, the core–shell structured MoS2/Sb2Se3 NR array film was characterized using the EDS as well as XPS before and after the PEC test. Figure 7a–c shows the SEM with EDS spectra for the Sb2Se3, MoS2/Sb2Se3 NR arrays before and after the PEC test, respectively. It is shown that the as-grown Sb2Se3 has a stoichiometric ratio between Sb and Se. With sputtered MoS2 coating, the chemical composition of MoS2 is close to 1:2, although it shows a slight overdose of S, which could be ascribed to the fact that S is easier to be sputtered due to its lighter weight. After the several scans of the PEC test (e.g., after the third scan), the pristine Sb2Se3 shows great degradation (Figure 6a), which could be due to the surface Sb2O3 that has dissolved (see Figure S5, Supporting Information, for XPS data), although there is no clear degradation mark in the optical image, as shown in the inset of Figure 7a. Remarkably, the MoS2/Sb2Se3 NR arrays are more stable (Figure 7b,c), and no discernible photocorrosion occurs on the MoS2 shell on the Sb2Se3 NR arrays, as shown in the inset of Figure 7c (see Figure S6, Supporting Information, for more optical images). The stoichiometric ratio between Mo and S is slightly increased, which is good for photoactivity because it is reported that the photogenerated electrons are easier to transfer to the catalytically active S sites.\(^{[34,35]}\) XPS spectra were further analyzed in detail to elucidate the structural variations of MoS2-modified photocathode before and after the PEC test (Figure 7d–h). The XPS survey shows that the MoS2 shell can effectively cover Sb2Se3 that led to the suppressed XPS intensity. When the XPS of MoS2/Sb2Se3 NR arrays are compared before and after PEC measurement, the key observation is that Sb3d\(5/2\), Se3d\(5/2\), and S2p\(3/2\) show no shift in binding energy, but the XPS intensity is significantly increased. The variation in peak intensity suggests that Sb2Se3/MoS2 interfacial diffusion occurs during the PEC test. This high-vacuum-sputtered MoS2 behaves differently with the amorphous MoS2 fabricated using the solution process due to the MoO\(_x\) surface oxides layer during solution process fabrication.\(^{[47]}\) It was reported that the sulfurization of MoS2–Sb2Se3 could lead to the partial conversion of surface Sb2O3 into Sb2S3 while keeping the Sb2Se3 unchanged.\(^{[47]}\) Thus, the interfacial diffusion between Sb2Se3 and MoS2 can contribute to the improved stability of the PEC performance. Here, the surface Sb2O3 on the CSS-deposited Sb2Se3 may also be sulfurized by MoS2 during PEC, and the interfacial resistivity due to the existence of Sb2O3 can be decreased to benefit photoexcited charge transfer.

Figure 8a shows the linear sweep voltammograms recorded under chopped light illumination for as-grown Sb2Se3 and 30 nm-coated MoS2/Sb2Se3 photocathodes. The current–voltage measurement suggests the occurrence of a recurring reduction peak at \(\approx 0\) V versus RHE for the pristine Sb2Se3 electrode. Such behavior is due to the photocorrosion of Sb2O3 that undergoes...
reductive decomposition. No reduction peak appears for the MoS2-protected Sb2Se3 sample. To realize the band alignment and protection of Sb2Se3 by MoS2, the cyclic voltammograms of pristine Sb2Se3 and core–shell structured 30 nm MoS2/Sb2Se3 were recorded at the scan rate of 10 mV s\(^{-1}\). When CV is swept toward a negative direction, the onset potential of Sb2Se3 improves at least by 300 mV after its decoration by MoS2. During reverse scan, pristine Sb2Se3 exhibits a prominent oxidation peak at 0.23 V, whereas a slight oxidation peak appears for MoS2/Sb2Se3 at 0.46 V (Figure 8b). This confirms that MoS2 protects Sb2Se3 from electrochemical corrosion. It is also remarkable to note that the MoS2/Sb2Se3 heterojunction exhibits a higher onset potential (low overpotential) than that of pristine Sb2Se3, meaning that the onset potential of Sb2Se3 is improved upon passivation of MoS2 layer. The improvement in onset potential (toward the anodic region) of the MoS2/Sb2Se3 heterojunction photocathode suggests a higher photovoltage. Thus, the indication of significant improvement in the onset potential of Sb2Se3 suggests a small conduction band offset while forming a junction with MoS2. In other words, MoS2 and Sb2Se3 form a favorable band alignment or reduced band-energy mismatch, which is essential for efficient water-splitting reactions. To further evaluate the enhancement in photocurrent performance and the increased onset potential, the electrochemical impedance spectroscopy (EIS) and Mott–Schottky (M–S) measurements are carried out to shed light on the charge transfer processes occurring at the electrolyte interface and obtain information about the nature and concentration of majority charge carriers in the Sb2Se3 photoelectrode before and after MoS2 coating. Figure 8c shows the Nyquist plots of Sb2Se3 and MoS2/Sb2Se3 electrodes obtained at ±0.0 V versus RHE (−0.6 V Ag/AgCl) in the dark and under front-side illumination. The Nyquist curves were fitted using an equivalent electrochemical circuit (see inset of the figure) that comprised series resistance (\(R_s\)) and two or more resistance and capacitance in parallel (RC) circuits. \(R_s\) constitutes the sum of all the serial resistances consisting of the electrolyte, contact, conducting support, and electrical connections. For fitting the Nyquist plot of MoS2/Sb2Se3, three RC circuits are used due to the additional interface of MoS2. The charge transfer resistance (\(R_{ct}\)) which inversely dictates the photocurrent response by controlling the charge transport across the interface of the electrode surface and electrolyte, is decreased for Sb2Se3 after MoS2 coating in both dark and light. A considerably lower \(R_{ct}\) value of 19.19 Ω is observed under illumination for the MoS2-protected Sb2Se3 electrode as against 1770.00 Ω for pristine Sb2Se3 (see Table 1 for all the electrochemical parameters obtained from the fitting). M–S plots of pristine Sb2Se3 and MoS2/Sb2Se3 electrodes measured at 1 kHz frequency in the dark. Electrolyte: 0.1 M phosphate-buffered 0.5 M Na2SO4 solution (pH 6.5); light source: simulated 1 sun (100 mW cm\(^{-2}\)).

Figure 8. a) LSVs of bare Sb2Se3 and 30 nm MoS2/Sb2Se3 photocathodes under intermittent AM 1.5 G simulated sunlight illumination. b) Cyclic voltammograms of pristine Sb2Se3 and MoS2/Sb2Se3 photocathodes at 10 mV s\(^{-1}\). c) Nyquist plots of Sb2Se3 and MoS2/Sb2Se3 electrodes recorded at 0 V versus RHE (−0.6 V vs Ag/AgCl) both in the dark and under the light. The equivalent electrochemical circuit is used to fit the Nyquist plots, as shown in the inset. The discrete symbols and the solid lines represent the experimental and fitted data, respectively. Table 1 shows the electrochemical parameters obtained from the fitting. d) M–S plots of pristine Sb2Se3 and MoS2/Sb2Se3 electrodes measured at 1 kHz frequency in the dark. Electrolyte: 0.1 M phosphate-buffered 0.5 M Na2SO4 solution (pH 6.5); light source: simulated 1 sun (100 mW cm\(^{-2}\)).
Table 1. Electrochemical parameters of photoelectrodes obtained from EIS study.

<table>
<thead>
<tr>
<th>Samples/parameters</th>
<th>Pristine Sb2Se3</th>
<th>MoS2/Sb2Se3 NR array</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dark</td>
<td>Light</td>
</tr>
<tr>
<td>( R_1 ) [Ω]</td>
<td>18.32</td>
<td>18.24</td>
</tr>
<tr>
<td>( R_t ) [Ω]</td>
<td>98.76</td>
<td>128.70</td>
</tr>
<tr>
<td>CPE ( [\mu F \text{cm}^{-2}] )</td>
<td>0.1435</td>
<td>0.2437</td>
</tr>
<tr>
<td>( R_0 ) [F cm^{-2}]</td>
<td>5765.00</td>
<td>1770.00</td>
</tr>
<tr>
<td>CPE1 ( [F \text{cm}^{-2}] )</td>
<td>28.7380</td>
<td>117.26</td>
</tr>
<tr>
<td>CPE2 ( [F \text{cm}^{-2}] )</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

CPE = constant phase element (meant for imperfect capacitance).

parameters). This implies that charge carrier resistance at the Sb2Se3-electrolyte interface is dramatically decreased. Thus, MoS2 coating not only protects the surface of the Sb2Se3 electrode from photocorrosion but also facilitates the charge transfer properties at Sb2Se3, thereby actively improving the photocurrent response. A similar role of MoS2 is reported for Cu2O photocathodes.[34] The conduction behavior of the core–shell structured MoS2/Sb2Se3 NR array was studied using the M–S plot (Figure 8d). The negative slopes of the M–S plots confirm the p-type semiconducting behavior of both as-grown Sb2Se3 and MoS2/Sb2Se3 NR array electrodes. The flat band potential (\( E_{fb} \)) measured in 0.5 M Na2SO4 electrolyte is 0.76 ± 0.005 V for both the samples. \( E_{fb} \) is identical for both the electrodes, which indicates that the MoS2 does not impact the conduction type of Sb2Se3, and also suggests that MoS2 decoration protects the Sb2Se3 photocathode and the band bending is unaffected by it. Here, the CSS-deposited pristine Sb2Se3 and MoS2/Sb2Se3 NR array electrodes have a higher \( E_{fb} \) value than that reported for the thermally evaporated Sb2Se3 film (e.g., 0.55 V).[36,48] The acceptor densities (see Supporting Information) estimated for pristine Sb2Se3 and MoS2/Sb2Se3 are \( \approx 2.0 \times 10^{16} \) and \( 5.6 \times 10^{16} \) cm\(^{-3} \), respectively. These values are one order of degree larger than that of the thermally evaporated Sb2Se3 film (e.g., \( 1.14 \times 10^{15} \) cm\(^{-3} \)).[36] The improved \( E_{fb} \) is associated with the enhanced heterojunction quality and increased doping density with the sputtered MoS2 layer. However, the measured carrier density is much lower than that of the reported carrier density \( (1 \times 10^{18} \) cm\(^{-3} \) ) in the electrodeposited Sb2Se3 film, which could be due to more dopants involved during electrodeposition.[30] This also indicates that the photocurrent improvement for the MoS2/Sb2Se3 NR arrays is attributed to the increased carrier concentration.

Figure 9 shows the incident photon to current conversion efficiency (IPCE) spectra of MoS2, Sb2Se3, and MoS2-coated Sb2Se3 grown on the FTO substrate under monochromatic illumination. The Sb2Se3 photocathodes with 1.1 eV bandgap can harvest solar spectrum as high as 1000 nm. An IPCE as high as 38% is observed at 800 nm for MoS2-coated Sb2Se3 in comparison with the 23% IPCE of a pristine Sb2Se3 sample (23%). The higher IPCE of MoS2-coated Sb2Se3 at 800 nm is in response to its photocurrent density of 9.5 mA cm\(^{-2} \) by integrating the IPCE spectra, which agrees with the photocurrent density from LSV measurements (Figure 6c). The IPCE and integrated current for MoS2 alone are very small, indicating little photoactivity from MoS2 alone to contribute to the enhanced IPCE of the Sb2Se3/MoS2 heterojunction, which allows a rapid charge separation at the Sb2Se3/MoS2 interface upon light absorption to dramatically improve the photoconversion efficiency. Figure 8, Supporting Information, shows the transient responses of pristine Sb2Se3 and MoS2-coated Sb2Se3 photocathodes measured with chopped and steady illumination at 1 sun and a buffered 0.5 M Na2SO4 electrolyte at a constant potential of 0.2 V versus RHE. The photocurrent of as-grown Sb2Se3 degrades fast in the first 5 min and gradually becomes stable, whereas the photocurrent of MoS2-coated Sb2Se3 shows rapid degradation in the first 10 min and gradually decreases until 1 h and stabilizes further. The MoS2-coated Sb2Se3 NR arrays show higher photocurrent and durability, suggesting that MoS2 can protect Sb2Se3 from photocorrosion. In the middle and end of the 2 h photostability measurement, the light was chopped “ON” and “OFF” to observe the photoactivity of the photocathodes. It is shown that the MoS2-coated Sb2Se3 NR arrays possess a smaller dark current than that of the as-grown Sb2Se3, indicating that MoS2 can effectively protect Sb2Se3.

3. Conclusions

In summary, we have demonstrated the scalable fabrication of sputter-deposited MoS2 as an HER catalyst on the CSS-deposited Sb2Se3 NR array to form the core–shell structured MoS2/Sb2Se3 NR array photocathodes. The PEC devices are suitable for water splitting with photocurrents as high as \(-10\) mA cm\(^{-2} \) at 0 VRHE in a near-neutral (pH 6.5) buffered solution under simulated AM 1.5 solar illumination. The improved photocurrent generated in this core–shell structured MoS2/Sb2Se3 NR arrays is associated with enhanced electronic carrier transport and light absorption by unique Q1D (Sb4Se6) ribbons in the Sb2Se3 NR on the surface of the Sb2Se3 film. The thin sputtered MoS2 layer on the Sb2Se3 NR arrays could effectively protect photocorrosion and further enhance carrier transport with the desired band

Figure 9. IPCE and integrated photocurrent density as a function of wavelength for MoS2, Sb2Se3, and MoS2-coated Sb2Se3 electrodes.
alignment. MoS₂ also catalyzes proton reduction to enhance the photocurrent response. This design of core–shell MoS₂/Sb₂Se₃ nanostructured photocathodes makes these types of low-dimensional antimony-based chalcogenides suitable for scale-up manufacturing for solar water-splitting applications.

4. Experimental Section

Deposition of Sb₂Se₃ Thin Films by CSS: The Sb₂Se₃ thin films (film thickness ≈1 μm) were deposited by a CSS system using high-purity Sb₂Se₃ powder (99.999%, Alfa Aesar) according to a previous report.[17] The transparent conducting FTO (TEC-15 NSG, US) was used as the substrate and was subsequently cleaned using detergent, acetone, isopropanol, and deionized water in the ultrasonic bath. Figure 1a shows the schematic process of the CSS deposition system, wherein the FTO substrate was held at the top of the AlN plate, and the appropriate amount of Sb₂Se₃ powder was placed at the bottom on the AlN plate. ALN plates with halogen lamps served as top and bottom heaters. The optimization condition for the growth of Sb₂Se₃ was as follows: the substrate temperature was held at 300 °C and Sb₂Se₃ powder temperature at 530 °C for 1 min with a chamber pressure of ≈10⁻² Torr.

Deposition of MoS₂ Thin Films by Sputtering: MoS₂ thin films with thicknesses ranging from 20 to 50 nm were deposited by an RF magnetron sputtering system (AJA International, USA) using a 2 in. MoS₂ target (99.9% Kurt J. Lesker, USA) at room temperature with a target power of 50 W. The base pressure was 3 × 10⁻⁵ Torr, and the working pressure was 3 × 10⁻³ Torr with an Ar flow of 20 sccm. The thickness was controlled by sputtering deposition time.

Materials Characterization: The Sb₂Se₃ thin films were estimated by using a standard three-electrode cell configuration, where a Pt wire was used as the counter electrode and a Ag/AgCl electrode as the reference electrode. The X-ray diffraction patterns of the Sb₂Se₃ and MoS₂ and MoS₂-coated Sb₂Se₃ films were characterized using the X-ray diffractometer (X’Pert MPD, Philips, USA). The morphology and the chemical compositions of the films were analyzed using the SEM technique on a JEOl-7000 SEM machine equipped with EDS. High-resolution transmission electron microscopy (HRTEM) was performed using an FEI Tecnai F-20 TEM with scanning transmission electron microscopy, HAADF detector, and EDS. The Raman experiments were evaluated on a JEOL-JSM-7400F (Tokyo, Japan) scanning electron microscope. The chemical compositions of the Sb₂Se₃ deposited thin films were analyzed using X-ray fluorescence spectroscopy (XRF) and energy-dispersive X-ray spectroscopy (EDS). The Raman experiments were evaluated on a JEOL-JSM-7400F (Tokyo, Japan) scanning electron microscope. The chemical compositions of the Sb₂Se₃ deposited thin films were analyzed using X-ray fluorescence spectroscopy (XRF) and energy-dispersive X-ray spectroscopy (EDS).

PEC Measurements: The PEC measurements were carried out using a standard three-electrode cell configuration, where a Pt wire was used as the counter electrode and a Ag/AgCl electrode as the reference electrode, in an electrochemical workstation (CH1760C, CH Instruments, USA). A near-neutral buffered 0.5 M Na₂SO₄ solution (pH ≈ 6.5) was used as the electrolyte. The sunlight was simulated using a commercial AM 1.5 G solar simulator (Newport Oriel, USA), which was calibrated to 1 sun (100 mW cm⁻²) by a spectroradiometer. The incident photon-to-current conversion efficiency (IPCE) plots were obtained in the wavelength range of 300–1100 nm in a two-electrode structure, i.e., superstrate solar cells with the architecture FTO/Sb₂Se₃/MoS₂/graphite electrode using a quantum efficiency measurement system (Enlitech). EIS and M–S measurements were carried out using the same CH1760c workstation, which was equipped with an electrochemical interface and impedance analyzer facility. The EIS plots were obtained in the alternating current (AC) frequency range of 0.01 Hz–100 kHz in the dark and light. The EIS data were fit with a suitable equivalent electrochemical circuit model. The M–S plots were recorded in the dark condition in the applied potential range from −0.6 to 0.1 V versus Ag/AgCl at 1 kHz frequency. The AC signal amplitude was 10 mV for both EIS and M–S measurements.

Supporting Information

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

Acknowledgements

L.G. and P.S.S. contributed equally to this work. L.P.G. and F.Y. acknowledge the support received from Alabama Water Institute at the University of Alabama, National Science Foundation (NSF) fund award 1844210, and the seed fund from the NSF-EPSCoR Track II award (OIA-1539035). P.S.S., M.Y., and S.P. acknowledge the support of National Science Foundation (NSF) under award nos. OIA-1539035 and CHE-1508192.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

close-spaced sublimation, MoS₂/Sb₂Se₃, core–shell, nanorods, photocathodes, photoelectrochemical

Received: October 6, 2019
Revised: October 22, 2019
Published online: