High-Efficiency Photon-Capturing Capability of Two-Dimensional SnS Nanosheets for Photoelectrochemical Cells

Xiaoguang Huang 1, Heechul Woo 2, Daseul Lee 3, Peinian Wu 1, Myungkwan Song 3 and Jin Woo Choi 3,*

Abstract: Cost-effective, abundant, and non-toxic SnS nanosheet semiconductors can be used as water-splitting cells. Herein, a photoanode based on high-purity and highly crystalline SnS nanosheets was fabricated. We used sodium thiosulfate (Na2S2O3·5H2O) and stannous chloride (SnCl2·H2O) as the tin and sulfur source materials, in place of SnCl4 and H2S gas, respectively, which have been used in previous studies. This gas-free fabrication process represents a new, environment-friendly fabrication method that can reduce the manufacturing cost of SnS nanosheets. The fabricated samples were characterized via X-ray diffraction, ultraviolet-visible spectroscopy, XPS, scanning electron microscopy, and Raman analyses. The XPS result indicated no Sn3+ or Sn4+ in the SnS nanosheet; the nanosheet was SnS. These results with XRD show that the SnS nanosheet has high phase purity and crystallinity. Its direct optical band gap is 1.31 eV, and its lattice parameters are similar to those of standard SnS. The SnS nanosheet-based photoanode exhibited a maximum saturation photocurrent of 6.86 mA cm−2 at 0.57 V versus Ag/AgCl, with high stability. The most effective photocurrent for the photocatalytic water-splitting cell is attained with an increase in the surface area and developed electrical conduction. This is attributed to thermal annealing, which eliminates nanoparticle imperfections. This study confirms that SnS nanosheets are excellent candidates for water-splitting applications.

Keywords: tin sulfide; photoelectrochemical cell; photoanode

1. Introduction

Human activities require sustainable energy and environmentally friendly resources; thus, converting solar energy into a storable and usable form is the most ideal approach [1]. This can be achieved by using a semiconductor that splits water into hydrogen and oxygen [2]. Notably, hydrogen produced via water-splitting has emerged as an environmentally friendly fuel for sustainable energy cycles [3]. The technique combines two system parts: solar energy collection and water electrolysis systems [4]. However, each challenge requires schemes to capture, convert, and store energy [5]. Certain precious metals (platinum) or oxides are considered to be ideal catalysts for this process, but their expensiveness and supply shortage restrict their large-scale production [6]. Meanwhile, SnS is known to have a tunable energy band gap, depending on the deposition conditions and preparation technique; thus, it can have a narrow band gap, which is crucial for utilizing solar energy [7]. In addition, SnS is inexpensive, abundant, and environmentally friendly, compared with PbS, GeS, etc. Moreover, SnS has a large absorption coefficient, normally over 104 cm−1, and its theoretical solar cell conversion efficiency reaches up to 25% [8]. Therefore, it is considered to be an ideal candidate for use in photon-capturing materials. Bulk materials typically exhibit low activity; thus, the nanostructure surface
area is required to realize high-efficiency solar energy conversion, which is achievable by high-efficiency photon-capturing capability, as well as by reducing minority carrier recombination [9]. Earth-abundant nanomaterials have an extremely significant potential based on their functional properties. Two-dimensional (2D) functional nanomaterials have garnered considerable attention in this regard [10]. Among these 2D nanostructures, graphene-like layered crystals (e.g., WSe$_2$, SnS, and MoS$_2$) have been recognized as promising candidates for cheap and lightweight catalytic materials for water-splitting [11,12]. Moreover, 2D semiconducting nanomaterials have tunable bandgaps (1.07–2.44 eV), which vary in terms of number of atomic layers [13,14]. Furthermore, these 2D nanosheets exhibit a more powerful sunlight-capturing capability than other semiconductors (GaAs and Si), accomplishing up to 10% incident solar radiation absorption for less than 1 nm of thickness [15]. In a pioneering study, exfoliated 2D sheets, functioning as photoelectrodes, were fabricated onto conductive substrates via a solution process. However, there were two inherent drawbacks with this approach: re-stacking and inevitable agglomeration through electrode fabrication. These limitations not only reduce the effective photon-capturing area but also hinder charge transfer, which could ensue considerable charge recombination [16]. Furthermore, it is difficult to establish a good ohmic contact between the fabricated 2D nanosheet film and the conductive substrate, thereby impeding charge carrier transport and inducing charge recombination [17].

To address the aforementioned limitations, vertically oriented 2D SnS nanosheet arrays having good electrical contact with a conductive substrate were fabricated via plasma enhanced chemical vapor deposition (PECVD) (Figure 1). This architecture exhibits effective photon-capturing and photocurrent harvesting owing to strong solar absorption, decreased extensive bare surface area and a few carrier transport distances for water splitting. To date, several techniques, such as vacuum evaporation [18], thermal evaporation [19], two-stage progress [20], PECVD, and pulsed electrodeposition, have been proposed to deposit SnS films. Although each approach has its merits and demerits, it remains challenging to optimize an easy, economical, and rapid technique for making controllable nanostructure materials. Among the above-mentioned techniques, the PECVD approach not only meets the fabrication demand of a simple, rapid, large-scale, equally distributed, inexpensive, and well-adherent process but also can be used to deposit thin films with controllable features because of the controllability of PECVD. In this work, we used harmless sodium thiosulfate (Na$_2$S$_2$O$_7$·5H$_2$O) as the tin source materials and stannous chloride (SnCl$_2$·2H$_2$O) as the sulfur source materials in the replacement of SnCl$_4$ and H$_2$S gas, which were used in previous studies, not only because H$_2$S gas is toxic and environmentally detrimental, but also because SnCl$_4$ gas is expensive. The solid source could broaden the application of this approach, especially for deposited films with scarce gas sources. This could be used to prepare more complex films through a simple process.

![Figure 1. Architecture of a vertically aligned 2D SnS nanosheet-based photoanode used in this work.](image-url)
2. Materials and Methods

The SnS films were fabricated on fluorine-doped SnO$_2$ (FTO)-coated glass slides via the PECVD method. The FTO substrate was ultrasonically cleaned in acetone three times, followed by ultrasonic cleaning three times in absolute alcohol. The substrates were then cleaned using argon plasma before the thin-film deposition process. Notably, SnCl$_2$·2H$_2$O/SnCl$_4$·5H$_2$O was used as the tin solid source material, and Na$_2$S$_2$O$_5$·5H$_2$O was used as the sulfur solid source material. These two sources were independently loaded into two quartz crucibles, which allowed for sufficient evaporation. To achieve 2D SnS nanosheet thin films in the fabrication process, there are certain controllable preformation conditions: t (the annealing time), $T_1$ (the FTO substrate temperature), $T_2$ (the source evaporation temperature), $T_3$ (the annealing temperature in vacuum), and P (the discharge power). The fabrication parameters set for the deposition of SnS films in this study are as follows:

- Sample 1 (S1): SnCl$_4$·5H$_2$O as the tin source, $t = 1$ h, $T_1 = 300 \, ^\circ C$, $T_2 = 600 \, ^\circ C$, $T_3 = 350 \, ^\circ C$, and P = 150 W;
- Sample 2 (S2): SnCl$_2$·2H$_2$O as the tin source, $t = 1$ h, $T_1 = 400 \, ^\circ C$, $T_2 = 600 \, ^\circ C$, $T_3 = 450 \, ^\circ C$, and P = 150 W;
- Sample 3 (S3): SnCl$_2$·2H$_2$O as the tin source, $t = 1$ h, $T_1 = 300 \, ^\circ C$, $T_2 = 600 \, ^\circ C$, $T_3 = 350 \, ^\circ C$, and P = 150 W.

The PEC cell for solar water-splitting was successfully developed. The working electrode was FTO glass, whereas the SnS nanosheet was deposited, while the counter electrode was Pt, and the reference electrode was 3.5 M KCl Ag/AgCl. The electrolyte was an aqueous solution, and the solution was saturated with N$_2$. A ~100 mW cm$^{-2}$ photolamp was used as a visible-light source, operated with a UV-cut-off filter, and the filter provided visible light over 420 nm. A ~100 mW cm$^{-2}$ incident light intensity was employed for detection using a power meter (FZ-A).

3. Results and Discussion

The phase purity of the SnS nanosheets was determined using powder X-ray diffraction (XRD) data. Figure 2a displays the SnS nanosheet XRD patterns. All diffraction peaks were prominent, indicating that all crystallized SnS nanosheets were well prepared, regardless of the synthesis method. The SnS nanosheets with different compositions were obtained. The SnS nanosheet XRD was performed using an X-ray diffractometer (D8 Advance, Rigaku Europe SE, Neu-Isenburg, Germany; the source was Cu Kα X-ray). The absorption spectra were characterized by running a UV-vis-near infrared spectrophotometer (Lambda 750 S). The morphology of the SnS nanosheets was measured via FESEM (Zeiss Ultra Plus, Oberkochen, Germany) run at 200 kV. A CHI 660E electrochemical workstation (Chenhua, Shanghai, China) was used to record the electrochemical measurements. A 350 W xenon lamp was used as a visible-light source, operated with a UV-cut-off filter, and the filter provided visible light over 420 nm. A ~100 mW cm$^{-2}$ incident light intensity was employed for detection using a power meter (FZ-A).
have implied that the deposition method, temperature, thickness, density, deposition rate, etc., intensely decided the favored orientation of films.

![Figure 2](image_url)

**Figure 2.** (a) XRD patterns of the SnS nanosheet samples; (b) $\alpha h v^2$ versus $hv$: direct band gap.

The sample lattice parameters of the SnS nanosheets are presented in Table 1. The S3 lattice parameters are most similar to the corresponding standard JCPDS data; specifically, the $a/c$ ratio (1.086) was approximately equal to 1.085, i.e., the standard SnS. This might be due to the film density, and this might be dependent on the crystallite size. When the sheets become small and uniform, the lattice dimensions are distinct from those of the chemically identical materials. When SnCl$_2$·2H$_2$O is the tin source, compared with SnCl$_4$·5H$_2$O in the same condition, the SnS lattice parameters may increase slightly.

**Table 1.** SnS nanosheet sample lattice parameters.

| Samples | Lattice Parameters (nm) | a/c Ratio | Preferred Orientation | Band Gap (eV) |
|---------|-------------------------|-----------|-----------------------|--------------|
|         | $a$ | $b$ | $c$ | $a/c$ |               |             |
| S1      | 0.4331 | 1.1314 | 0.4018 | 1.078 | (120) | 1.68 |
| S2      | 0.4344 | 1.1315 | 0.4015 | 1.082 | (040) | 1.41 |
| S3      | 0.4334 | 1.1241 | 0.3991 | 1.086 | (040) | 1.31 |

With the promise of converting sunlight into photocurrent, the material should obtain energy to perform work after the absorption of sunlight. We determined the band gap of SnS nanosheets by means of ultraviolet-visible (UV-vis) absorption measurements. The plot of the UV-vis absorption spectrum for all samples is shown in Figure 2b. All the samples have a direct band gap. For water splitting, a 1.24 eV gap is required. The direct band gaps of S1, S2, and S3 nanosheets are 1.68, 1.41, and 1.31 eV, respectively, all of which can capture photon energy from the solar spectrum, which also meets the requirements for water-splitting. All direct band gap values fit well with reported values. This suggested that all the SnS nanosheets were in the pure crystal phase. The maximum theoretical photocurrent densities ($J_{ph, max}$) [21] for the S1, S2, and S3 nanosheets were 25.1, 32.0, and
34.0 mA cm\(^{-2}\), respectively; they could be calculated from Equation (1) using the band gap value

\[ I_{\text{ph}, \text{max}} = e \int_{\text{band gap in eV}}^{\infty} \Phi \text{d}E, \]  

(1)

Here, \( e \) is electron charge, \( \Phi \) is photon flux.

Apparently, the S3 nanosheets showed the highest maximum theoretical photocurrent density among the three samples; thus, S3 nanosheets should be able to convert sunlight into photocurrent. Therefore, the following photochemical cell application proceeded, with a 1.31 eV band-gap S3 nanosheet film.

Figure 3, which depicts the X-ray photoelectron spectroscopy (XPS) results, reveals that the S3 nanosheet comprises the Sn and S elements. Meanwhile, no impurities were detected. The peaks at binding energies of 162.6 and 161.6 eV in Figure 3c correspond to the S 2p\(^{3/2}\) and S 2p\(^{1/2}\) of the S3 nanosheet, respectively, which were same as the S\(^{2-}\) binding energies. To confirm the Sn valence state in the S3 nanosheet, the peak XPS spectra for Sn\(^0\), Sn\(^{2+}\), and Sn\(^{4+}\) were analyzed and are presented in Figure 3b. These results indicated no Sn\(^0\) or Sn\(^{4+}\) in the S3 nanosheet; the nanosheet was pure SnS.

![Figure 3. (a) XPS survey spectra; (b) Sn 4d XPS spectra; (c) S 2p XPS spectra.](image)

To determine the morphology of the SnS nanosheet, the S1, S2, and S3 surface images were analyzed and are displayed in Figure 4a–c, respectively. The cross-sectional field-emission scanning electron microscopy (FESEM) images of S3 is shown in Figure 4d. The S1 film exhibits a rough topology, and the rough surface of S2 becomes slightly uniform because the substrate temperature increases to 400 °C, which may be due to the rearrangement of the nanosheet while being deposited. It is undesirably uniform in the S1 and S2 films; these imperfections in the grain boundary can inhibit electrical conduction. A better uniform surface was generated in the S3 film with SnCl\(_2\)·2H\(_2\)O as the tin source. The thickness of the nanosheet is observed to be 100 nm in the S3 cross-sectional FESEM image. Combining the observed crystallization phenomenon of the S3 nanosheet with the S3 direct band gap, S3 should evince good behavior during electrolysis.

The linear sweep voltammogram (LSV) spectrum of the photoelectrochemical (PEC) cell was chopped using visible light at a speed of 50 mV s\(^{-1}\), operated in 0.5 M NaSO\(_4\). The spectrum is shown in Figure 5. The onset potential of the S1 nanosheet was detected at −6.5 V versus the Ag/AgCl electrode. Because the majority of carriers accumulate on the electrolyte side, the n-type semiconductor was found to have a cathodic photocurrent. Meanwhile, another part is the depletion part, whereby the band of the other part begins to align and then returns to the applied potential. Photocurrent values of 6.86 mA cm\(^{-2}\) at 0.57 V versus Ag/AgCl were obtained for the S3 nanosheet, which exceeded that reported in previous studies on SnS nanosheets. [22,23] The stronger photocurrent is caused not only by the enhanced percolation path on the nanosheet structure, but also by the narrower optical band gap. It was evident that a quickly decaying point resembling a spike pattern occurred in the photocurrent during the chopped illumination. This implies that the kinetics reaction is rather sluggish at the photoanode surface. This occurs because of the immense surface area contrast with the extraction properties, leading to fast electron generation in the photoanode.
Figure 4. (a) S1; (b) S2; (c) S3; (d) S3 surface morphology cross-sectional field-emission scanning electron microscopy (FESEM) image.

Figure 5. Voltammogram run in 0.5 M Na$_2$SO$_4$, chopped light for the S3 nanosheet photoanode at 50 mV s$^{-1}$.

The responsibility of the film could be obtained by using chopped visible light with switching from the “OFF” state to the “ON” state. Chopped light was executed under 0.05 V implied sample versus Ag/AgCl for the stability measurement. The results are illustrated in Figure 6. The photocurrent takes 0.5 s to respond and decay, indicating that it is a rapid response current. The 5.68 mA cm$^{-2}$ photocurrent density was only reduced by 1% after 40 min. It is noteworthy that the SnS nanosheet photocurrent densities exhibited good behaviors after 2400 s of irradiation on stability (1% decrease) (Figure 6).
To evaluate the durability of the S3 nanosheet films, the PEC cells were set up for a durability measurement under 1-sun illumination (Figure 7). We studied the durability via Raman spectroscopy by detecting the different chemical changes due to the corrosion on the S3 nanosheet films before and after stability test. SnS is eight atoms in each cell, and it has an orthorhombic structure. This structure contains the 24 vibrational modes at the middle of the Brillouin zone [24].

\[ \Gamma = 4A_g + 2B_{1g} + 4B_{2g} + 2B_{3g} + 2A_u + 4B_{1u} + 2B_{2u} + 4B_{3u} \]  

(2)

There are 21 optical phonons in SnS. Raman active modes are 12 (4A_g, 2B_{1g}, 4B_{2g}, and 2B_{3g}), infrared active modes are 7 (3B_{1u}, 1B_2u, and 3B_{3u}), and inactive modes are 2 (2A_u). Raman results showed an A_g mode assigned at 188 and 216 cm⁻¹, B_{2g} mode assigned
at 171 cm\(^{-1}\) and \(B_{3g}\) mode assigned at 162 cm\(^{-1}\). No other obvious peak appeared. The Raman spectra show that no significant change occurred. If there were different chemical changes, SnS would become SnS\(_2\) (yellow), S (yellow), Sn (white), or SnO\(_2\) (white). We did not see this color change. Raman did not find another significant peak. Combining these two points, no significant change can be seen. This suggests that the S3 nanosheet film has strong anti-corrosion characteristics, even after 40 min of illumination. This durability study reveals that the S3 nanosheet photoanode is a potential candidate for stable water-splitting devices.

4. Conclusions

Freestanding and clean SnS nanosheets were artificially fabricated by means of a scalable strategy representing new nanosheet semiconductors for application in water-splitting cells. We optimized an SnS nanostructure device for better quality using an SnS nanosheet with a direct optical band gap of 1.31 eV and lattice parameters similar to those of standard SnS. The fabricated photoanode could achieve a photocurrent of 6.86 mA cm\(^{-2}\) at 0.57 V versus Ag/AgCl, which was significantly larger than that of the SnS nanosheet in our previous work. A 5.68 mA cm\(^{-2}\) photocurrent density was achieved, which was reduced by only 1% after 40 min. Moreover, the device exhibited high stability. The Raman spectra showed no significant change before and after the durability measurement. This work not only proves that SnS nanosheets are excellent candidates for water-splitting applications but also reveals novel approaches to operate the properties of nanostructured materials to produce several creative applications.

Author Contributions: Data curation, P.W.; investigation, H.W. and M.S.; resources, X.H., M.S. and J.W.C.; writing—original draft, X.H., H.W., P.W., M.S. and J.W.C.; writing—review and editing, D.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Fundamental Research Funds for the Central Universities, grant number WUT: 2016 IVA 087; and the Fundamental Research Program of the Korea Institute of Materials Science (KIMS), grant number PNK 7350.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Yang, L.J.; Zeng, L.L.; Liu, H.; Deng, Y.Q.; Zhou, Z.Q.; Yu, J.Y.; Liu, H.; Zhou, W.J. Hierarchical microsphere of MoNi porous nanosheets as electrocatalyst and cocatalyst for hydrogen evolution reaction. *Appl. Catal. B Environ.* 2019, 249, 98–105. [CrossRef]

2. Bai, Y.J.; Zhang, Q.F.; Xu, N.; Deng, K.M.; Kan, E.J. The Janus structures of group-III chalcogenide monolayers as promising photocatalysts for water splitting. *Appl. Surf. Sci.* 2019, 478, 522–531. [CrossRef]

3. Xu, Y.S.; He, X.; Zhong, H.; Singh, J.; Zhang, L.J.; Wang, R.H. Solid salt confinement effect: An effective strategy to fabricate high crystalline polymer carbon nitride for enhanced photocatalytic hydrogen evolution. *Appl. Catal. B Environ.* 2019, 246, 349–355. [CrossRef]

4. Wang, Q.; Fan, Y.; Wang, K.K.; Shen, H.M.; Li, G.J.; Fu, H.Y.; She, Y.B. Hierarchical tubular structures composed of CoPx and carbon nanotubes: Highly effective electrocatalyst for oxygen reduction. *Carbon* 2018, 130, 241–249. [CrossRef]

5. Huang, X.; Woo, H.; Wu, P.; Wang, Q.; Tan, G.; Choi, J.W. Low-cost processed antimony sulfide nanocrystal photoanodes with increased efficiency and stability. *J. Alloy. Compd.* 2019, 777, 866–871. [CrossRef]

6. Manathanath, M.; Xie, M.C.; Arunkumar, C.; Wang, Z.G.; Zhao, J.Z.; Sujatha, S. Synthesis, photophysical, electrochemical and photoluminescent oxygen sensing studies of trans-Pt(II)-porphyrins. *Dyes Pigments* 2019, 165, 117–127. [CrossRef]

7. Shiga, Y.; Umezawa, N.; Srinivasan, N.; Koyasu, S.; Sakai, E.; Miyauchi, M. A metal sulfide photocatalyst composed of ubiquitous elements for solar hydrogen production. *Chem. Commun.* 2016, 52, 7470–7473. [CrossRef] [PubMed]

8. Patel, M.; Chavda, A.; Mukhopadhyay, I.; Kim, J.; Ray, A. Nanostructured SnS with inherent anisotropic optical properties for high photoactivity. *Nanoscale* 2016, 8, 2293–2303. [CrossRef] [PubMed]

9. Huang, X.G.; Woo, H.; Wu, P.N.; Hong, H.J.; Jung, W.G.; Kim, B.J.; Vanel, J.C.; Choi, J.W. Simple eco-friendly synthesis of the surfactant free SnS nanocrystal toward the photoelectrochemical cell application. *Sci. Rep.* 2017, 7, 1–9. [CrossRef] [PubMed]

10. Li, Y.; Zhu, W.; Fu, X.; Zhang, Y.; Wei, Z.; Ma, Y.; Yue, T.; Sun, J.; Wang, J. Two-Dimensional Zeolitic Imidazolate Framework-L-Derived Iron–Cobalt Oxide Nanoparticle-Composed Nanosheet Array for Water Oxidation. *Inorg. Chem.* 2019, 58, 6231–6237. [CrossRef]
11. Jia, X.D.; Bai, J.; Ma, Z.F.; Jiang, X.U. BSA-exfoliated WSe\textsubscript{2} nanosheets as a photoregulated carrier for synergistic photodynamic/photothermal therapy. *J. Mat. Chem. B* 2017, 5, 269–278. [CrossRef] [PubMed]

12. Kou, Z.Y.; Wang, X.; Yuan, R.S.; Chen, H.B.; Zhi, Q.M.; Gao, L.; Wang, B.; Guo, Z.J.; Xue, X.F.; Cao, W.; et al. A promising gene delivery system developed from PEGylated MoS\textsubscript{2} nanosheets for gene therapy. *Nanoscale Res. Lett.* 2014, 9, 587. [CrossRef]

13. Andoshe, D.M.; Jeon, J.-M.; Kim, S.Y.; Jang, H.W. Two-dimensional transition metal dichalcogenide nanomaterials for solar water splitting. *Electron. Mater. Lett.* 2015, 11, 323–335. [CrossRef]

14. Shi, Y.M.; Li, H.N.; Li, L.J. Recent advances in controlled synthesis of two-dimensional transition metal dichalcogenides via vapour deposition techniques. *Chem. Soc. Rev.* 2015, 44, 2744–2756. [CrossRef]

15. Liu, G.B.; Li, Z.H.; Hasan, T.; Chen, X.S.; Zheng, W.; Feng, W.; Jia, D.C.; Zhou, Y.; Hu, P.A. Vertically aligned two-dimensional SnS\textsubscript{2} nanosheets with a strong photon capturing capability for efficient photoelectrochemical water splitting. *J. Mater. Chem. A* 2017, 5, 1989–1995. [CrossRef]

16. Cheng, L.L.; Liu, M.H.; Wang, M.X.; Wang, S.C.; Wang, G.D.; Zhou, Q.Y.; Chen, Z.Q. Preparation of SnS films using solid sources deposited by the PECVD method with controllable film characters. *J. Alloy. Compd.* 2012, 545, 122–129. [CrossRef]

17. Yu, X.Y.; Prevot, M.S.; Guijarro, N.; Sivula, K. Self-assembled 2D WSe\textsubscript{2} thin films for photoelectrochemical hydrogen production. *Nat. Commun.* 2015, 6, 7596. [CrossRef] [PubMed]

18. Gedi, S.; Reddy, V.R.M.; Kang, J.-Y.; Jeon, C.W. Impact of high temperature and short period annealing on SnS films deposited by E-beam evaporation. *Appl. Surf. Sci.* 2017, 402, 463–468. [CrossRef]

19. Coskun, H.; Isikgor, F.H.; Chen, Z.H.; Imran, M.; Li, B.C.; Xu, Q.H.; Ouyang, J. Thermally evaporated two-dimensional SnS as an efficient and stable electron collection interlayer for inverted planar perovskite solar cells. *J. Mater. Chem. A* 2019, 7, 4759–4765. [CrossRef]

20. Jiang, F.; Shen, H.L.; Gao, C.; Liu, B.; Lin, L.; Shen, Z. Preparation and properties of SnS film grown by two-stage process. *Appl. Surf. Sci.* 2011, 257, 4901–4905. [CrossRef]

21. Dotan, H.; Sivula, K.; Grätzel, M.; Rothschild, A.; Warren, S.C. Probing the photoelectrochemical properties of hematite (α-Fe\textsubscript{2}O\textsubscript{3}) electrodes using hydrogen peroxide as a hole scavenger. *Energy Environ. Sci.* 2011, 4, 958–964. [CrossRef]

22. Liu, Q.; Liu, S.; Wu, A.; Huang, H.; Zhou, L. SnS\textsubscript{2} and SnS/SnS\textsubscript{2} heterojunction nanosheets prepared by in-situ one-step sulfurization and visible light-assisted electrochemical water splitting properties. *J. Alloy. Compd.* 2020, 834, 155174. [CrossRef]

23. Gao, W.; Wu, C.; Cao, M.; Huang, J.; Wang, L.; Shen, Y. Thickness tunable SnS nanosheets for photoelectrochemical watersplitting. *J. Alloy. Compd.* 2016, 688, 668–674. [CrossRef]

24. Sohilaa, S.; Rajalakshmi, M.; Ghoshc, C.; Arora, A.K.; Muthamizhchelvan, C. Optical and Raman scattering studies on SnS nanoparticles. *J. Alloy. Compd.* 2011, 509, 5843–5847. [CrossRef]