# Tailored Annealing and Surface Treatment of Bi<sub>2</sub>S<sub>3</sub> Thin Film to Enhance Optoelectronic Performance

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#### ABSTRACT

Metal sulfides with moderate band gaps are desired for efficient generation of electricity or fuels from sunlight via photovoltaic or photoelectrochemical energy conversion. Bi<sub>2</sub>S<sub>3</sub>, with a direct optical band gap of 1.3 eV, has been commonly synthesized by successive ion layer adsorption and reaction (SILAR) to produce quantum dots or nanocrystalline films. Annealing of the solution-deposited  $Bi_2S_3$ nanocrystals has been attempted at temperatures equal to or lower than 300 °C, which may not improve the crystallinity of Bi<sub>2</sub>S<sub>3</sub>. Here, we report a highly crystalline Bi<sub>2</sub>S<sub>3</sub> photoelectrode synthesized by hightemperature annealing of the solution-deposited nanocrystalline films in a sulfur vapor environment, which simultaneously improves the crystallinity and phase purity of Bi<sub>2</sub>S<sub>3</sub>. The S-annealed Bi<sub>2</sub>S<sub>3</sub> film exhibits greatly enhanced light absorption ( $\eta_{abs}$ ) and charge separation ( $\eta_{sep}$ ) efficiencies compared to the nanocrystalline film. Furthermore, photoelectrochemical measurements show that Bi<sub>2</sub>S<sub>3</sub> demonstrates significantly larger photocurrent by either pre-treating the material with aqueous Na<sub>2</sub>S solution or by directly measuring the material in an electrolyte containing Na<sub>2</sub>S. X-ray photoelectron spectroscopy analysis shows that the sulfide ions displace anionic surface impurities and passivate defect states of  $B_{12}S_3$ that form during the synthesis and the photoelectrochemical measurement. These results indicate that sulfur vapor annealing and sulfide surface treatment can improve the optoelectronic performance of  $Bi_2S_3$ for solar-electricity or solar-chemical energy conversion processes.

#### **EXECUTIVE SUMMARY**

In this work, we synthesized Bi<sub>2</sub>S<sub>3</sub> thin film photoelectrodes via a combination of solution deposition and sulfur vapor annealing. We identified four major advantages of the tailored annealing process from materials characterizations and photoelectrochemical measurements. Firstly, the sulfur vapor annealing improves crystallinity of the solution-deposited Bi<sub>2</sub>S<sub>3</sub> nanocrystals by increasing the crystallite size from 10 nm to 50 nm. Secondly, introducing sulfur vapor during high-temperature annealing prevents formation of Bi<sub>2</sub>O<sub>3</sub> bulk crystal impurities and leads to phase-pure Bi<sub>2</sub>S<sub>3</sub>. Thirdly, sulfur vapor annealing may fill in sulfur vacancies of the un-annealed film to sulfides. Lastly, sulfur vapor annealing may fill in sulfur vacancies of the un-annealed Bi<sub>2</sub>S<sub>3</sub> to significantly increase the photoexcited carrier lifetimes. The S-annealed Bi<sub>2</sub>S<sub>3</sub> exhibits significantly enhanced light absorption and charge separation efficiencies, which makes it promising for photovoltaic and photoelectrochemical energy conversion applications. We additionally attempted Na<sub>2</sub>S surface treatment and vacuum annealing of the S-annealed Bi<sub>2</sub>S<sub>3</sub> to further passivate the surface defects that form during the synthesis. The Na<sub>2</sub>S surface treatment may displace anionic surface impurities and passivate defect states of Bi<sub>2</sub>S<sub>3</sub>. However, the reason for the improved performance by vacuum annealing is still under investigation.

Moreover, we performed Density Functional Theory (DFT) calculations to elucidate the influence of defects and impurities on the electronic structure of  $Bi_2S_3$ . We discovered that sulfur vacancy in  $Bi_2S_3$ creates mid-gap charge trapping states that act as active electron-hole recombination sites, while sulfur interstitial results in shallow charge trapping states close to the valence band that cause much less recombination. We additionally found that  $Bi_2S_3$  is tolerant to low concentrations of oxygen substitution of sulfur, while oxygen interstitial creates shallow hole trapping states close to the valence band. Additionally, DFT density of states calculations show that hydrogen doping creates effective donor levels at the conduction band edge, which should increase electron conductivity without introducing recombination sites.

Overall, we have demonstrated several synthetic and processing methods to effectively improve the optoelectronic performance of  $Bi_2S_3$  thin films, in conjunction with DFT calculations to provide fundamental understanding of these improvements. These strategies could also be extended to synthesize and process many other sulfide materials to enhance their optoelectronic performance for photovoltaic and photoelectrochemical energy conversion applications. Future work should be focused on (1) experimentally investigating the influence of sulfur vacancies and hydrogen impurities on the optoelectronic properties and performance of  $Bi_2S_3$  and (2) fabricating  $Bi_2S_3$  into solid-state or liquidjunction photovoltaic devices and studying chemical properties and charge dynamics at the interfaces.

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#### **1. INTRODUCTION**

Energy harvested from sunlight is believed to a viable option to satisfy the increasing world energy demand.<sup>1</sup> Photovoltaics (PV) allow us to use semiconductors to harvest solar energy and simultaneously convert it to electric power. Conventional crystalline silicon-based solar cells have demonstrated up to 25% efficiency and high stability, but have rigid construction and high manufacturing cost due to the energyintensive production of silicon wafers. While the emerging thin-film photovoltaic technologies have the potential to decrease the cost/performance ratio of solar cells, many of the materials such as CdTe, copper indium gallium selenide (CIGS), and lead halide-based perovskite contain toxic or rare elements, which limit their sizable deployments. Photovoltaic devices including dve-sensitized solar cells (DSSCs) and polymer-based organic solar cells (OSCs) are considered as low-cost alternatives. However, liquid electrolyte-based DSSCs suffer from solvent leakage and instability of dyes, and polymer-based OSCs experience substantial degradation.<sup>2</sup> To overcome these disadvantages, semiconductor-sensitized metal oxide solid-state solar cells, which are based on the configuration of DSSCs but are composed of semiconductor light absorbers and organic hole transporting materials (HTMs), have been designed and investigated. With their small band gaps, metal sulfides such as Sb<sub>2</sub>S<sub>3</sub> (Eg  $\approx$  1.7 eV),<sup>2-7</sup> PbS (1.0 eV),<sup>8,9</sup> and  $Bi_2S_3$  (1.3 eV)<sup>10-16</sup> have been studied as the light absorber semiconductor materials to photosensitize metal oxides (TiO<sub>2</sub>, WO<sub>3</sub>, SnO<sub>2</sub>, ZnO) with large band gaps. Polymers such as P3HT,<sup>2-4, 6, 7</sup> PEDOT:PSS,<sup>2-</sup> <sup>4, 6</sup> and spiro-MeOTAD.<sup>17</sup> and inorganic p-type semiconductors such as CuSCN<sup>9</sup> have been commonly utilized as the HTMs. One of highest certified efficiencies for a single metal sulfide sensitized solar cell was reported to be 10.2%, which was achieved by a p-n junction PbS quantum dot sensitized ZnO solar cell with I<sub>2</sub> treatment.<sup>9</sup> Additionally, one of the highest power conversion efficiencies reported for Sb<sub>2</sub>S<sub>3</sub>based solar cells was around 5.7%, which was achieved by a Ti-doped Sb<sub>2</sub>S<sub>3</sub>-based ETA nanocrystalline-TiO<sub>2</sub> solar cell.<sup>5</sup> In contrast, Bi<sub>2</sub>S<sub>3</sub> has been mostly studied as sensitizer in photoelectrochemical applications.<sup>11, 14-16, 18</sup> There have not been many reports on Bi<sub>2</sub>S<sub>3</sub>-based solid state solar cells until recent

years. A study fabricated a Bi<sub>2</sub>S<sub>3</sub> nanowire core/AgS shell solar cell with spiro-MeOTAD HTM, which achieved an efficiency of 2.5%,<sup>17</sup> and another study synthesized a hybrid solar cell comprised of Bi<sub>2</sub>S<sub>3</sub> nanowires and P3HT, which achieved an efficiency of 3.3%.<sup>19</sup> These promising efficiencies motivated us to discover effective synthesis and processing methods and to study the fundamental materials properties. The knowledge gained will be essential to further improve the efficiencies of Bi<sub>2</sub>S<sub>3</sub>-based solar cells.

## 2. BACKGROUND

#### 2.1. Synthesis of Bi<sub>2</sub>S<sub>3</sub>

Many groups have synthesized Bi<sub>2</sub>S<sub>3</sub> as either powder or thin film using various techniques, such as hydrothermal synthesis,<sup>16, 18</sup> electrochemical deposition,<sup>20</sup> chemical bath deposition,<sup>21, 22</sup> vapor deposition,<sup>23</sup> and successive ionic layer adsorption and reaction (SILAR).<sup>12-15, 17</sup> Among these synthetic methods, SILAR is one of the most common method due to its facile processing, versatile application to different surfaces and nanostructures, and tunable coating thickness and packing density. However, Bi<sub>2</sub>S<sub>3</sub> synthesized by SILAR consists of nanocrystalline films or quantum dots. The solution-deposited film has poor electric contact at the semiconductor/substrate interface, which leads to high resistance at the heterojunction.<sup>16</sup> Additionally, the high concentration of grain boundaries may favor formation of defects, which could reduce the optoelectronic performance of the material. Several studies have reported annealing of the solution-deposited Bi<sub>2</sub>S<sub>3</sub> at relatively low temperatures ( $\leq$ 300 °C), as a post-synthesis method to improve the crystallinity.<sup>13, 14, 18</sup> However, this low-temperature annealing may not lead to highly crystalline Bi<sub>2</sub>S<sub>3</sub>. Therefore, it is necessary to find alternative annealing methods to improve crystallinity and phase purity of the solution-deposited Bi<sub>2</sub>S<sub>3</sub>.

#### 2.2. Photoelectrochemical Performance of Bi<sub>2</sub>S<sub>3</sub>

The Bi<sub>2</sub>S<sub>3</sub> quantum dots or nanocrystals have been utilized to sensitize mesoporous n-type metal oxide semiconductors (WO<sub>3</sub>, TiO<sub>2</sub> and SnO<sub>2</sub>) for photoelectrochemical applications. Several reports have studied the photoelectrochemical performances of the Bi<sub>2</sub>S<sub>3</sub>-sensitized metal oxide photoanodes in various aqueous electrolytes. It has been discovered that these photoanodes can generate significantly greater photocurrents in aqueous electrolytes containing Na<sub>2</sub>S than in electrolytes without Na<sub>2</sub>S but containing other hole scavengers such as Na<sub>2</sub>SO<sub>3</sub> and ethanol.<sup>14-16, 18</sup> One report has proposed possible explanations for the effect of Na<sub>2</sub>S by studying the band-edge tuning strategies of Bi<sub>2</sub>S<sub>3</sub> quantum dots sensitized TiO<sub>2</sub>, which is the most commonly used metal oxide scaffold. The study discovered that in the absence of Na<sub>2</sub>S, the conduction band of TiO<sub>2</sub>, which restricts electron injection from Bi<sub>2</sub>S<sub>3</sub> to TiO<sub>2</sub>. In contrast, in the presence of Na<sub>2</sub>S, the adsorbed HS<sup>-</sup> ions will change the surface dipole of the Bi<sub>2</sub>S<sub>3</sub> quantum dots, which shifts the conduction bands to more negative potentials. The negative shift leads to more negative photocurrent onset and also facilitates the electron injection to TiO<sub>2</sub> from the Bi<sub>2</sub>S<sub>3</sub> quantum dots are too large to act as sensitizers in the absence of Na<sub>2</sub>S.<sup>10</sup>

This influence of Na<sub>2</sub>S on the band alignment between  $Bi_2S_3$  and  $TiO_2$  is possible when the  $Bi_2S_3/TiO_2$  interface is exposed to the Na<sub>2</sub>S electrolyte, as in the case of  $TiO_2$  sensitized by  $Bi_2S_3$  quantum dots. This allows direct contact between the interface and the electrolyte, which causes the change in surface dipole of  $Bi_2S_3$  to simultaneously shift the conduction band energy at the  $Bi_2S_3/TiO_2$  interface. In the case of bulk  $Bi_2S_3$  on  $TiO_2$ , the change in surface dipole caused by Na<sub>2</sub>S might only influence the band energies of  $Bi_2S_3$  at the  $Bi_2S_3$ /electrolyte interface without changing the band alignment at  $Bi_2S_3/TiO_2$  interface. This should only result in more negative photocurrent onset but not photocurrent magnitudes when the bulk  $Bi_2S_3/TiO_2$  photoanode is measured in Na<sub>2</sub>S electrolyte compared to other aqueous

electrolytes. However, there has been no report on the influence of  $Na_2S$  on bulk  $Bi_2S_3$ . Thus, the photoelectrochemical performance of  $Bi_2S_3$  in the presence of  $Na_2S$  needs more in-depth study.

#### 2.3. Bi<sub>2</sub>S<sub>3</sub>-based Solid-state Photovoltaics

Despite the fact that there have been studies on  $Bi_2S_3$  quantum dot sensitized solar cells based on polysulfide electrolytes,  $Bi_2S_3$  has never been utilized in solid-state photovoltaic application due to the reported unfavorable band energy alignment at the  $Bi_2S_3/TiO_2$  interface in the absence of sulfide ions. One study has synthesized nanocrystalline  $Bi_2S_3$  onto mesoporous  $TiO_2$  by annealing bismuth xanthate at 160 °C and has measured the band energies at the interface using X-ray photoelectron spectroscopy. The study has shown that the conduction band potential of  $Bi_2S_3$  is more positive than that of  $TiO_2$ , which is consistent with the study discussed previously.<sup>24</sup> These studies have indicated that  $Bi_2S_3$  nanocrystals or quantum dots cannot efficiently sensitize  $TiO_2$  in a solid-state solar cell configuration. However, this does not limit the application of  $Bi_2S_3$  to a solid-state solar cell due to two reasons. Firstly, other n-type metal oxide semiconductors (WO<sub>3</sub>, SnO<sub>2</sub>) which have more positive conduction band potentials can be utilized in place of  $TiO_2$ .<sup>11, 12, 15, 16</sup> This would enable favorable electron transfer from  $Bi_2S_3$  to the metal oxides. Second, all the studies on  $Bi_2S_3$ -based solar cells have only focused on the applications of nanocrystals or quantum dots. Thus, knowledge gaps exit in the electronic properties of highly crystalline or bulk  $Bi_2S_3$ .

#### 3. EXPERIMENTAL AND THEORETICAL METHODS

#### 3.1. Synthesis of Bi<sub>2</sub>S<sub>3</sub> Thin Films

 $Bi_2S_3$  thin films were synthesized by a combination of solution deposition and sulfur vapor annealing. First,  $Bi_2S_3$  thin films were deposited onto fluorine-doped tin oxide (FTO) substrates (2.5 × 1.5 cm, 2.2 mm thick, TEC 7, Hartford Glass) by spin-coating a bismuth nitrate solution as a  $Bi^{3+}$  source and reacting with a sodium sulfide solution to form  $Bi_2S_3$ . The bismuth precursor was prepared by dissolving 0.485 g of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (98%, Sigma Aldrich) in 10 mL acetic acid (≥99.7%, Sigma Aldrich). The sodium sulfide solution was prepared by dissolving 0.033 g of Na<sub>2</sub>S (anhydrous, Sigma Aldrich) in 35 mL methanol. Each layer of Bi<sub>2</sub>S<sub>3</sub> was first spin-coated onto FTO using 150 µL of the Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O solution at a spin speed of 2000 rpm for 40 s, then immersed in the Na<sub>2</sub>S solution for 2 min, thoroughly washed with methanol, and completely dried under compressed air.<sup>15</sup> After 5, 10 or 15 layers of Bi<sub>2</sub>S<sub>3</sub> were coated, the samples were annealed in sulfur vapor with argon as a carrier gas. Control experiments were performed by annealing the solution-deposited  $Bi_2S_3$  in argon only. The annealing in sulfur vapor or argon was performed in a tube furnace (Lindberg/Blue M 1100 °C, Thermo Fisher Scientific) equipped with a 1-inch diameter quartz tube (Quartz Scientific). For annealing in sulfur vapor, sulfur powder (2.5 g, 99.5%, Sigma Aldrich) was placed outside the hot zone and sublimed at ~110 °C. Argon (99.995% purity, 80 sccm flow rate) was used to convey the sulfur vapor to the downstream substrate. The substrates coated with solutiondeposited Bi<sub>2</sub>S<sub>3</sub> films were placed inside the hot zone at 400 °C, 445 °C and 470 °C, respectively. For annealing in pure argon, the substrates coated with solution-deposited Bi<sub>2</sub>S<sub>3</sub> films were annealed at 445 °C with argon flowing at 100 sccm. For all annealing conditions, the annealing pressure was set at one atmosphere with an annealing time of  $\sim 60$  min.

#### 3.2. Materials Characterizations

The morphologies, crystal structures, and chemical compositions of the  $Bi_2S_3$  thin films were characterized by scanning electron microscopy (SEM, JEOL 7000F, 10 kV), transmission electron microscopy (TEM, JEOL 2010F, 200 kV), parallel beam X-ray diffraction (XRD, PANalytical Empyrean, Cu-Ka, 45 kV, 40 mA), and X-ray photoelectron spectroscopy (XPS, PHI 5600, Al-Ka, 13.5 kV, 300 W). The average crystallite size was calculated from the Scherrer equation (Equation 1):

$$\tau = \frac{0.94\lambda}{\beta\cos\theta_B},$$

where  $\lambda$  is the X-ray wavelength,  $\beta$  is the measured width of the peak at half-maximum intensity in radians, and  $\theta_B$  is the Bragg angle.

The wavelength-dependent optical absorption properties of the samples were obtained using illumination from a Xe lamp (Model 66902, Newport). Two spectrometers (USB 2000+ and Flame-NIR, Ocean Optics) were used to measure the incident, transmitted and reflected light at UV-visible and near-infrared regions, respectively. Bi<sub>2</sub>S<sub>3</sub> thin films were prepared on quartz slides (1 mm thick, Ted Pella) for the optical measurements to minimize diffuse scattering by FTO substrates. For both the transmission and reflection measurements, light was incident at a 45° angle to the back-side (quartz) surface of the sample. For the transmission measurements, the spectrometers were aligned with the incident light to capture the transmitted light (*T*). For the reflection measurements, the spectrometers were placed at a 90° angle to the incident light to capture the reflected light (*R*). The absorption efficiency was calculated by Equation 2:

 $A(\lambda) = 100 \% - T(\lambda) - R(\lambda).$ 

The absorption coefficient ( $\alpha$ ) was then calculated by Equation 3:

$$\alpha = \frac{1}{z} \ln \left[ \frac{100 \% - R (\lambda)}{T (\lambda)} \right],$$

where z is the film thickness measured from cross-section SEM images.

#### **3.3.** Photoelectrochemical Measurements

The PEC measurements were performed in a three-electrode configuration, using a potentiostat (Model SP-200, BioLogic) under back-side broadband illumination from a Xe lamp. Linear sweep voltammograms (LSVs, i.e. *J-V* curves) were measured at a scan rate of 10 mV/s. LSVs in aqueous electrolytes were measured in a three-electrode configuration with the Bi<sub>2</sub>S<sub>3</sub> photoanode as the working electrode, a Pt wire (0.5 mm diameter) as the counter electrode, and a saturated calomel (SCE) reference electrode. The aqueous electrolytes used were 0.3 M Na<sub>2</sub>S electrolyte (pH  $\approx$  13) and 0.3 M Na<sub>2</sub>SO<sub>3</sub>

electrolyte (pH  $\approx$  10). Potentials (in volts) in aqueous electrolytes are reported versus RHE using Equation 4:

$$V_{\rm RHE} = V_{\rm SCE} + 0.244 + [0.059 \times \text{pH}].$$

The incident light intensity from the Xe lamp at each wavelength was measured by a spectrometer. The integrated power of the Xe lamp output at wavelengths shorter than 950 nm (1.3 eV) was 81.7 mW/cm<sup>2</sup>, as compared to 71.0 mW/cm<sup>2</sup> for the standard AM 1.5G spectrum (Figure A1a). The incident photon-to-current efficiencies (IPCE), also known as external quantum efficiency (EQE), were measured at 0.6  $V_{RHE}$  using a Xe lamp equipped with a monochromator (Cornerstone 130 1/8 m, Newport). The spectral irradiance of monochromatic light at each wavelength was measured by a spectrometer. The IPCE was calculated using Equation 5:

IPCE 
$$(\lambda) = \frac{J_{\rm ph} \times 1240}{P_{\rm mono} \times \lambda} \times 100\%$$
,

where  $J_{ph}$  is the measured photocurrent density in mA/cm<sup>2</sup>,  $P_{mono}$  is the intensity of the incident monochromatic light in mW/cm<sup>2</sup>, and  $\lambda$  is the wavelength of the monochromatic light in nm. The absorbed photon-to-current efficiency (APCE), also known as internal quantum efficiency (IQE) was then calculated by Equation 6:

APCE 
$$(\lambda) = \frac{\text{IPCE } (\lambda)}{A (\lambda)} \times 100\%$$

The product of light absorption efficiency ( $\eta_{abs}$ ) and charge separation efficiency ( $\eta_{sep}$ ) was calculated at each potential by Equation 7:

$$\eta_{\text{sep}}(V) \times \eta_{\text{abs}}(V) = \frac{J_{\text{max}}}{J_{\text{ph}}(V) \times \eta_{\text{trans}}(V)}$$

where  $J_{\text{max}}$  is the maximum photocurrent of the photoelectrode under the Xe lamp illumination in mA/cm<sup>2</sup>,  $J_{\text{ph}}$  is the measured photocurrent in mA/cm<sup>2</sup> at different potentials,  $\eta_{\text{trans}}$  is the charge transfer efficiency

at the semiconductor/electrolyte interface. The maximum photocurrent  $(J_{max})$  for Bi<sub>2</sub>S<sub>3</sub> photoanodes is 43.5 mA/cm<sup>2</sup>, which was obtained by integrating the Xe lamp spectrum at wavelengths shorter than 950 nm (1.31 eV). The surface charge transfer efficiency is assumed to 100% for PEC measurements in a Na<sub>2</sub>S electrolyte due to the fast kinetics of sulfide oxidation.

# 3.4. Density Functional Theory Calculations

DFT calculations were implemented in the Vienna *ab initio* simulation package (VASP) code.<sup>25, 26</sup> We used the generalized gradient approximation (GGA) exchange and correlation functionals as parameterized by Perdew, Burke, and Ernzerhof (the PBE functional).<sup>27, 28</sup> The electron–ion interactions were treated within the framework of the standard frozen-core projector augmented-wave (PAW) method with valence configurations of  $6s^26p^35d^{10}$  for Bi and  $3s^23p^4$  for S.<sup>29, 30</sup> An energy cut-off of 400 eV was used in the plane-wave basis-set expansion. Gaussian smearing with width of 0.2 eV was used for ionic relaxation and the tetrahedron method with Blöchl corrections was used for density of states (DOS) calculations. The Grimme D3 correction method was used to account for dispersion interactions between layers of Bi<sub>2</sub>S<sub>3</sub>.<sup>31</sup> For calculations of the pristine Bi<sub>2</sub>S<sub>3</sub> bulk unit cell (1 × 1 × 1), a 6 × 2 × 2 Monkhorst–Pack *k*-point sampling was used for ionic relaxation. Spin-polarized DFT calculations were performed for Bi<sub>2</sub>S<sub>3</sub> bulk supercell (3 × 1 × 1). A 2 × 2 × 2 *k*-point sampling was used for ionic relaxation and a higher 8 × 8 × 8 *k*-point sampling was used for density of states calculations. Electronic band structure calculations were performed with 50 *k*-points for each high symmetry direction in the reciprocal space of the crystal. Defect formation energies were calculated by Equation 8:

$$\Delta E_{\text{defective}} = E_{\text{defective}} - E_{\text{stoichiometric}} + \sum n_{\text{defect}} \mu_{\text{defect}},$$

where  $E_{\text{defective}}$  and  $E_{\text{stoichiometric}}$  are the ground-state energies of Bi<sub>2</sub>S<sub>3</sub> with and without defect, respectively and  $n_{\text{defect}}$  is the number of atoms removed (added) from (to) the system to form the defect.  $n_{\text{defect}} = 1$  if an atom is removed from the system, whereas  $n_{\text{defect}} = -1$  if an atom is added to the system.

#### 4. RESULTS AND DISCUSSION

#### 4.1. Sulfur Vapor Annealing

The XRD pattern (Figure 1a) of the un-annealed Bi<sub>2</sub>S<sub>3</sub> shows peaks indexed to FTO only, which suggests that the film is either amorphous or nanocrystalline. The crystallite size of the un-annealed Bi<sub>2</sub>S<sub>3</sub> nanocrystals is measured to be ~10 nm by TEM (Figure 1b). The Bi<sub>2</sub>S<sub>3</sub> film annealed in pure argon at 445 °C contains a large amount of tetragonal Bi<sub>2</sub>O<sub>3</sub> (ICDD PDF 04-007-1443), which is likely due to oxidation of the film by oxygen and water vapor adsorbed on the tube wall in the annealing environment. In contrast, pure orthorhombic Bi<sub>2</sub>S<sub>3</sub> (ICDD PDF 04-014-6675) can be consistently synthesized by annealing the solution-deposited Bi<sub>2</sub>S<sub>3</sub> thin film in sulfur vapor. The average crystallite size of the S-annealed Bi<sub>2</sub>S<sub>3</sub> film at 445 °C was calculated from the (112) reflection plane as ~50 nm, which is similar to the average diameter of the nanoparticles measured by SEM (Figure 1c). This indicates that sulfur vapor annealing significantly improves the crystallinity and phase purity of the solution-deposited Bi<sub>2</sub>S<sub>3</sub> thin film.



**Figure 1.** (a) XRD patterns of  $Bi_2S_3$  thin films without annealing and with Ar and sulfur vapor annealing at 445 °C. (b) TEM images of un-annealed  $Bi_2S_3$  nanocrystals. (c) and (d) Top-view and cross-section SEM images of 10 layers of un-annealed and S-annealed  $Bi_2S_3$  thin films.

The surface chemical composition of the  $Bi_2S_3$  films was characterized by XPS. The XPS spectra were calibrated based on a binding energy of 284.8 eV for adventitious carbon. It was reported that the binding energies of Bi  $4f_{7/2}$  are 158.9 eV for  $Bi_2S_3$  and 159.3 eV for  $Bi_2O_3$ .<sup>32</sup> As shown in Figure 2a, both  $Bi_2S_3$  (158.6 eV binding energy) and a large amount of  $Bi_2O_3$  (159.4 eV binding energy) are present on the surface of the un-annealed  $Bi_2S_3$ , which suggests that the film was oxidized in the solution deposition by air and/or solvents. Additionally, low intensity S 2s peaks exist at binding energies of about 232.6 eV

(Figure 2b), which indicates that a small amount of  $S^{2-}$  (225.8 eV binding energy) was also oxidized to SO<sub>x</sub> species. The oxidation is further confirmed by the O 1s (Figure A2). According to Figure A2, an O 1s peak is observed at lower binding energy of 530.4 eV than the adventitious oxygen (531.9 eV) for the un-annealed Bi<sub>2</sub>S<sub>3</sub> film, which is due to the presence of Bi<sub>2</sub>O<sub>3</sub> on the surface. Another O 1s peak is observed at higher biding energy of 533.1 eV than the adventitious oxygen, which is then assigned to oxygen in SO<sub>x</sub> species. However, a large amount of Bi<sub>2</sub>O<sub>3</sub> and SO<sub>x</sub> species are present on the surface of the Ar-annealed  $Bi_2S_3$  film, while the amount of  $S^{2-}$  species significantly decrease, which suggests that surface was completely oxidized. In contrast, the surface of the S-annealed Bi<sub>2</sub>S<sub>3</sub> thin film mainly contains  $Bi_2S_3$  with a small amount of  $Bi_2O_3$ , which further confirms the purity of the film. This also suggests that sulfur vapor annealing converts the surface oxide formed in the solution deposition process to sulfide, and suppresses oxidation of the material at high temperatures. Additionally, a greater amount of elemental sulfur species was observed on the surface of the S-annealed Bi<sub>2</sub>S<sub>3</sub> film (S 2s, 228.3 eV binding energy, Figure 2b) as compared to the un-annealed  $Bi_2S_3$ . This is likely attributed to incorporation of interstitial sulfur into the Bi<sub>2</sub>S<sub>3</sub> crystal lattice and/or residual sulfur that remains on the surface of the film during the cooling-down process.



**Figure 2.** X-ray Photoelectron Spectra of  $Bi_2S_3$  thin films without annealing and with Ar and sulfur vapor annealing at 445 °C. (a) Bi 4f and S 2p XPS spectra and (b) S 2s XPS spectra.

The influence of defects on the electronic structures was then analyzed by calculating the density of states of pristine  $Bi_2S_3$  as well as  $Bi_2S_3$  containing sulfur vacancy  $(S_v)$ , sulfur interstitial  $(S_i)$ , oxygen substitution of sulfur  $(O_S)$ , and oxygen interstitial  $(O_i)$  along with their formation energies (Figure 3). The fundamental band gap of pristine  $Bi_2S_3$  was found to be 1.25 eV indirect band gap (Figure 3a and Figure A3). The defect states related to  $S_v$  are filled electronic states found deep in the band gap, at 0.63 eV above the VBM. This finding is consistent with previous reports that  $S_v$  creates deep hole trapping states that allow electron-hole recombination.<sup>33-36</sup> These defect states are "deep" in a sense that the energy required to remove a hole from the trapping states to the valence band is much larger than the characteristic thermal

energy at room temperature, 0.026 eV. Thus, the photoexcited holes trapped in the defect states will likely recombine with the electrons that occupy these states, which results in reduced photoexcited carrier lifetime. Additionally, Bi<sub>2</sub>S<sub>3</sub> containing two S<sub>v</sub> possesses a higher DOS of mid-gap charge trapping states, which further shows that  $S_v$  in Bi<sub>2</sub>S<sub>3</sub> can act as recombination sites. In contrast,  $S_i$  creates shallow hole trapping sites that are 0.12 eV above the VBM, which would cause much less recombination than  $S_v$  due to the lower energy required to remove the trapped holes to the valence band. On the other hand,  $Os-Bi_2S_3$ exhibits similar electronic structure to pristine  $Bi_2S_3$ . Oxygen has the same number of valence electrons as sulfur, so we expect similar chemical properties and behavior for oxygen-substituted  $Bi_2S_3$ .  $O_i$ - $Bi_2S_3$ has a similar DOS to S<sub>i</sub>-Bi<sub>2</sub>S<sub>3</sub>, resulting in shallow electronic states 0.12 eV above the VBM. Based on the XRD and XPS results, the un-annealed  $Bi_2S_3$  likely contains more oxygen impurities in the form of Os and O<sub>i</sub>, the formation of which are thermodynamically favorable due to the negative formation energies, -0.93 and -0.57 eV, respectively. S-annealed Bi<sub>2</sub>S<sub>3</sub> likely contains more S<sub>i</sub> due to the low formation energy of this defect in a S-rich environment,<sup>35</sup> which is consistent with the elemental sulfur species observed on the surface of the film. Moreover, previous reports have shown that sulfur vacancies are abundant defects in solution-processed Bi<sub>2</sub>S<sub>3</sub>.<sup>33-36</sup> Additionally, we postulate that the sulfur vapor may fill sulfur vacancies of the un-annealed Bi<sub>2</sub>S<sub>3</sub> during the annealing by diffusing into the Bi<sub>2</sub>S<sub>3</sub> crystals. Therefore, it is expected that while both un-annealed and S-annealed Bi<sub>2</sub>S<sub>3</sub> films may possess shallow hole trapping states due to the presence of oxygen defects and sulfur interstitial, respectively, the un-annealed  $Bi_2S_3$  may contain a higher concentration of mid-gap  $S_v$  charge trapping states that can act as active recombination sites, which will significantly decrease its photoexcited carrier concentrations and lifetimes. Moreover, the electrons occupying the defect states of  $S_v$ ,  $S_i$  and  $O_i$  are found to be localized at the defect sites (Figure 3), which can also limit the photoexcited electron mobility of the material.

The n-type conductivity of Bi<sub>2</sub>S<sub>3</sub> has been attributed to the presence of S<sub>v</sub> and S<sub>i</sub> donor defects.<sup>35</sup> However, for defect states to become effective donor levels, the energetic barrier between the defects states and the CBM should be equal to or smaller than the characteristic thermal energy at room temperature (0.026 eV). Therefore,  $S_v$  and  $S_i$  defect states cannot act as effective donor levels due to the large energetic barrier between the defect states and the CBM, suggesting that these defects cannot be responsible for the n-type conductivity of Bi<sub>2</sub>S<sub>3</sub>. We additionally calculated the density of states of Bi<sub>2</sub>S<sub>3</sub> containing hydrogen substitution of sulfur  $(H_s)$  and hydrogen interstitial and the corresponding formation energies. As shown in Figure 3b, DOS of  $H_S$  and  $H_i - Bi_2S_3$  show Fermi levels within the conduction band of Bi<sub>2</sub>S<sub>3</sub>, which suggests that these hydrogen impurities can create effective donor levels in Bi<sub>2</sub>S<sub>3</sub> without introducing mid-gap charge trapping states. Moreover, the formation energy of H<sub>i</sub> is negative and the formation energy of H<sub>S</sub> is lower than those of S<sub>v</sub> and S<sub>i</sub>, which indicate that the incorporation of hydrogen is energetically favorable. In fact, hydrogen impurities have previously been to found to determine the ntype conductivity of BiVO<sub>4</sub>.<sup>37</sup> Hydrogen can be incorporated in to Bi<sub>2</sub>S<sub>3</sub> during the solution deposition process via decomposition of metal-organic precursors and/or from water vapor in the annealing environment.



**Figure 3.** (a) DFT-calculated density of states (DOS) of pristine  $Bi_2S_3$ ,  $Bi_2S_3$  with sulfur vacancies ( $S_v$ ), sulfur interstitials ( $S_i$ ), oxygen substituting sulfur ( $O_s$ ), and oxygen interstitial ( $O_i$ ). Also shown with each DOS plot are the formation energies of the defects in eV. (b) Charge localization at  $S_v$ ,  $S_i$  and  $O_i$  defect sites. Purple and orange spheres correspond to Bi and S atoms, respectively. Yellow indicates electron density at the defect states.

The photoexcited carrier lifetimes of the un-annealed and S-annealed  $Bi_2S_3$  films were analyzed by time-resolved terahertz spectroscopy. As shown in Figure 4a, the photoexcited charges decay after 0.7 ps. The short lifetime indicates that the un-annealed  $Bi_2S_3$  film contains a large concentration of active recombination sites, which can be associated with the presence of a large concentration of mid-gap  $S_v$ defect states in the un-annealed film. In contrast, the S-annealed  $Bi_2S_3$  exhibits significantly improved lifetimes with bi-exponential decays of 3 ps and 23 ps. The shorter decay of 3 ps is likely due to charge recombination on the surface of the film, while the longer decay of 23 ps may be attributed to the recombination in the bulk crystal, which does not possess as much defects states as the surface of the film. This also suggests that sulfur vapor annealing leads to reduction of the active recombination sites by filling in sulfur vacancies.

The light absorption efficiency of the Bi<sub>2</sub>S<sub>3</sub> thin film significantly increases after sulfur vapor annealing (Figure 4b), with an overall absorption of 60.8 % of above-gap photons for the S-annealed film as compared to 39.6 % for the un-annealed. From the measured optical absorption spectra, the indirect band gaps can be determined from the  $(\alpha h v)^{1/2}$  vs hv Tauc plot (Figure 4c). The S-annealed Bi<sub>2</sub>S<sub>3</sub> was thus determined to possess an indirect band gap of ~1.24 eV, which corresponds well to the theoretically predicted fundamental band gap. However, the un-annealed Bi<sub>2</sub>S<sub>3</sub> appears to have a larger band gap of ~1.37 eV, which may be due to quantum confinement caused by nanoscale grain size. The S-annealed Bi<sub>2</sub>S<sub>3</sub> has higher absorption at longer wavelengths due to the increased crystallite size. The sub-bandgap absorption of the un-annealed Bi<sub>2</sub>S<sub>3</sub> is lower than 10%, which suggests that the diffuse scattering by quartz substrate is negligible. Moderate sub-bandgap absorption is observed for the S-annealed Bi<sub>2</sub>S<sub>3</sub>, which is attributed to electronic transitions from the defects states to the conduction band, as will be discussed later along with IPCE.



**Figure 4.** (a) Photoexcited carrier lifetimes, (b) Optical absorption efficiencies, and (c) Tauc plots to determine the indirect band gaps of 10 layers of un-annealed and S-annealed Bi<sub>2</sub>S<sub>3</sub> thin films.

The PEC performance of the 10 layers of Bi<sub>2</sub>S<sub>3</sub> thin film photoanodes with and without sulfur vapor annealing at 445 °C was evaluated by measuring the potential-dependent charge separation efficiencies ( $\eta_{sep}$ ) and wavelength-dependent photon-to-current efficiencies (Figure 5). The film thickness and annealing temperature were optimized for maximum photocurrent under white light illumination (Figure A4 a and b). IPCE and APCE were measured at 0.6 V<sub>RHE</sub>, which is the onset potential for sulfide oxidation in the dark, as can be seen from the dark J-V curves. IPCE shows photon-to-current conversion up to 1100 nm for the S-annealed Bi<sub>2</sub>S<sub>3</sub> film and 1050 nm for the un-annealed Bi<sub>2</sub>S<sub>3</sub>, with the IPCE of the S-annealed higher than that of the un-annealed at all wavelengths (Figure 5a). The enhanced IPCE with sulfur vapor annealing is due to simultaneous improvements in both light absorption efficiencies and photoexcited carrier lifetimes. The IPCE at 1000-1100 nm (1.24-1.13 eV) is low, and increases more sharply for wavelengths shorter than 950 nm (1.31 eV). The band gaps of both un-annealed and S-annealed  $Bi_2S_3$  films were then estimated to be between 1.24 eV and 1.31 eV. The sub-bandgap IPCE for the unannealed  $Bi_2S_3$  is likely attributed to the electronic transition from the O<sub>i</sub> defect states to the CBM (1.10 eV) due to the expected abundance of  $O_i$  in the un-annealed film. As for the S-annealed Bi<sub>2</sub>S<sub>3</sub>, the IPCE at 1000–1100 nm is likely due to transition from the  $S_i$  defect states to the CBM (0.93 eV) due to the large amount of S<sub>i</sub> expected in the film. Additionally, the products of  $\eta_{abs}$  and  $\eta_{sep}$  at 0.6 V vs. RHE are calculated from the J-V curves to be 16.3% for the S-annealed Bi<sub>2</sub>S<sub>3</sub> and 4.0% for the un-annealed (Figure 5b). Moreover, the APCE of S-annealed Bi<sub>2</sub>S<sub>3</sub> is higher than that of un-annealed at all wavelengths (Figure 5c). This indicates that the S-annealed  $Bi_2S_3$  has significantly increased charge separation efficiencies as a result of improved photoexcited carrier lifetime by the sulfur vapor annealing. Additionally,  $\eta_{sep}$  at 0.6 V vs. RHE are calculated to be 26.8% for the S-annealed Bi<sub>2</sub>S<sub>3</sub> and 10.1% for the un-annealed (Figure 5d).



**Figure 5.** (a) IPCE and (c) APCE of 10 layers of un-annealed and S-annealed Bi<sub>2</sub>S<sub>3</sub> thin films measured at 0.6 V<sub>RHE</sub> in 0.3 M Na<sub>2</sub>S aqueous electrolyte at pH 13. (b) Products of  $\eta_{abs}$  and  $\eta_{sep}$ , and (d)  $\eta_{sep}$  of 10 layers of un-annealed and S-annealed Bi<sub>2</sub>S<sub>3</sub> thin films at different potentials measured in 0.3 M Na<sub>2</sub>S aqueous electrolyte.

# 4.2. Sulfide Surface Treatment

The PEC performance of S-annealed Bi<sub>2</sub>S<sub>3</sub> thin films was also evaluated by measuring the threeelectrode *J-V* and *J-t* curves in aqueous Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> electrolytes (Figure 6). During the first *J-V* measurements, the photocurrent of S-annealed Bi<sub>2</sub>S<sub>3</sub> reaches ~3.93 mA/cm<sup>2</sup> in 0.3 M Na<sub>2</sub>S aqueous electrolyte at 1.0 V<sub>RHE</sub> as compared to ~0.31 mA/cm<sup>2</sup> in 0.3 M Na<sub>2</sub>SO<sub>3</sub> aqueous electrolyte (Figure 6 a and b). This indicates that the charge separation efficiencies of S-annealed Bi<sub>2</sub>S<sub>3</sub> thin film in Na<sub>2</sub>S

electrolyte are significantly higher than those in Na<sub>2</sub>SO<sub>3</sub> electrolyte, considering that the absorption efficiencies remain the same and that the surface charge transfer efficiencies are comparable for these two electrolytes. When Bi<sub>2</sub>S<sub>3</sub> is measured in Na<sub>2</sub>S electrolyte, the sulfide ions may fill in sulfur vacancies on the surface of Bi<sub>2</sub>S<sub>3</sub> to reduce the active charge recombination sites at the semiconductor/electrolyte interface, which will lead to improved charge separation efficiencies. However, when  $Bi_2S_3$  is measured in Na<sub>2</sub>SO<sub>3</sub> electrolyte, the material might be oxidized during the measurements by  $S^{2-} + SO_3^{2-} + 2h^+ \rightarrow$  $S_2O_3^{2-}$ . The oxidation may create more sulfur vacancies and oxide impurities on the surface of  $Bi_2S_3$ , which introduce a higher concentration of recombination sites at the semiconductor/electrolyte interface. This can be further supported by J-t measurements at 0.6 V<sub>RHE</sub> and consecutive J-V measurements in Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> electrolytes. The photocurrent of S-annealed Bi<sub>2</sub>S<sub>3</sub> increases between the first and third J-Vmeasurements and during the J-t measurement in Na<sub>2</sub>S electrolyte (Figure 6 a and c), while it drastically decreases in Na<sub>2</sub>SO<sub>3</sub> electrolyte (Figure 6 b and d). This photocurrent enhancement in Na<sub>2</sub>S electrolyte can be mainly attributed to the improved charge separation efficiencies, which are likely due to reduced recombination sites at the Bi<sub>2</sub>S<sub>3</sub>/Na<sub>2</sub>S electrolyte interface, as have been discussed. In contrast, the photocurrent degradation in Na<sub>2</sub>SO<sub>3</sub> further suggests that  $Bi_2S_3$  might undergo oxidation in the electrolyte. The high stability and photoelectrochemical performance of  $Bi_2S_3$  in Na<sub>2</sub>S electrolyte suggest that the material can be potentially applied in a liquid-junction solar cell using polysulfide electrolyte to achieve high photovoltaic performance.



**Figure 6.** Photoelectrochemical measurements of 10 layers of S-annealed Bi<sub>2</sub>S<sub>3</sub> under back illumination. (a)  $1^{\text{st}}$  and  $3^{\text{rd}}$  *J-V* measurements in 0.3 M Na<sub>2</sub>S aqueous electrolyte. (b)  $1^{\text{st}}$  and  $3^{\text{rd}}$  *J-V* measurements in 0.3 M Na<sub>2</sub>SO<sub>3</sub> aqueous electrolyte. (c) *J-t* measurement in 0.3 M Na<sub>2</sub>S aqueous electrolyte at 0.6 V<sub>RHE</sub>. (d) *J-t* measurement in 0.3 M Na<sub>2</sub>SO<sub>3</sub> aqueous electrolyte at 0.6 V<sub>RHE</sub>.

The morphologies of  $Bi_2S_3$  before and after three *J-V* measurements in  $Na_2SO_3$  electrolyte were then characterized by SEM. As shown in Figure 7a. the  $Bi_2S_3$  thin film after 3 times consecutive *J-V* measurements exhibits porous structure as compared to the nonporous structure for the as-annealed film. The drastic change in surface morphology also suggests corrosion or oxidation of the film by  $Na_2SO_3$ electrolyte during the PEC measurements. Moreover, XRD patterns show that the  $Bi_2S_3$  film after consecutive *J-V* measurements in Na<sub>2</sub>SO<sub>3</sub> do not contain bulk crystalline impurities as compared to the as-annealed film, which suggests that defects likely form on the surface of the film (Figure 7b). However, the XPS spectra of the Bi<sub>2</sub>S<sub>3</sub> films before and after 10 min *J-t* measurements in Na<sub>2</sub>SO<sub>3</sub> at 0.6 V<sub>RHE</sub> exhibit similar characteristics (Figure 7c and Figure 2). The surfaces of both films mainly contain Bi<sub>2</sub>S<sub>3</sub> with a small amount of SO<sub>x</sub> and S<sup>0</sup> species. It is likely that the amount of oxides that are formed on the surface during the *J-t* measurements are below the detection limit. Longer duration and/or higher voltages can be used to measure the *J-t* curves of Bi<sub>2</sub>S<sub>3</sub> film in Na<sub>2</sub>SO<sub>3</sub> electrolyte to study the oxidation of the film by  $SO_3^{2-}$ .



**Figure 7.** (a) and (b) SEM images and XRD patterns of S-annealed  $Bi_2S_3$  before and after 3 times *J-V* measurements in 0.3 M Na<sub>2</sub>SO<sub>3</sub> aqueous electrolyte (pH 10.2). (c) Bi 4f/S 2p and S 2s XPS spectra of S-annealed  $Bi_2S_3$  after 10 min *J-t* measurement in 0.3 M Na<sub>2</sub>SO<sub>3</sub> at 0.6 V<sub>RHE</sub>.

The influence of Na<sub>2</sub>S on the photoelectrochemical performance of Bi<sub>2</sub>S<sub>3</sub> was further evaluated by soaking the S-annealed Bi<sub>2</sub>S<sub>3</sub> in 0.3 M Na<sub>2</sub>S aqueous solution for 10 min and measuring the three-electrode *J-V* curves in 0.3 M Na<sub>2</sub>SO<sub>3</sub> aqueous electrolyte. As shown in Figure 8a, the photocurrent of the Na<sub>2</sub>S-treated Bi<sub>2</sub>S<sub>3</sub> is higher than that of as-annealed Bi<sub>2</sub>S<sub>3</sub>. This improvement in photocurrent can further support that sulfide ions fill in sulfur vacancies on the surface of the film to reduce the number of recombination sites. Moreover, by soaking Bi<sub>2</sub>S<sub>3</sub> film that was measured in Na<sub>2</sub>SO<sub>3</sub> once and then measuring the *J-V* curve of the film again, the photocurrent increases as compared to the first measurement (Figure 8b). In contrast, consecutive *J-V* measurements of Bi<sub>2</sub>S<sub>3</sub> in Na<sub>2</sub>SO<sub>3</sub> without intermediately soaking the sample in Na<sub>2</sub>S will result in decrease of the photocurrent (Figure 6b). These results suggest that the Na<sub>2</sub>S soaking treatment can also passivate the oxide impurities that are formed in the PEC measurements in Na<sub>2</sub>SO<sub>3</sub> electrolyte. Overall, these results indicate that the sulfide surface treatment can be used as a potential method to passivate surface defects of the as-annealed Bi<sub>2</sub>S<sub>3</sub> thin films. In fact, similar effects have been observed for Sb<sub>2</sub>S<sub>3</sub>, where the performance of the material increases after soaking the film in a solution containing sulfur ions.<sup>38</sup>



**Figure 8.** (a) *J-V* curves of S-annealed  $Bi_2S_3$  with and without soaking in 0.3 M Na<sub>2</sub>S measured in 0.3 M Na<sub>2</sub>SO<sub>3</sub>. (b) Blue: 1<sup>st</sup> *J-V* measurement of  $Bi_2S_3$  measured in 0.3 M Na<sub>2</sub>SO<sub>3</sub>; red: *J-V* measurement in Na<sub>2</sub>SO<sub>3</sub> of the same sample soaked in Na<sub>2</sub>S after the sample was measured three times in 0.3 M Na<sub>2</sub>SO<sub>3</sub>. Note that the  $Bi_2S_3$  samples in (a) and (b) are not synthesized under the same sulfur vapor annealing condition.

The morphologies of the  $Bi_2S_3$  film with and without  $Na_2S$  soaking were characterized by SEM.  $Na_2S$ -treated  $Bi_2S_3$  exhibits similar morphologies to the as-annealed  $Bi_2S_3$ , which indicates that the improved charge separation is not due to structural changes (Figure 9a). XRD patterns indicate that  $Na_2S$  soaking does not change the bulk crystallinity or phase purity of the  $Bi_2S_3$  film (Figure 9b). Moreover, the surface chemical compositions were characterized by XPS, which shows similar characteristics for the film with and without  $Na_2S$  soaking (Figure 9c). It is likely that the amount of defects that was passivated by  $Na_2S$  soaking is below the detection capability of the XPS. Therefore, more sensitive measurement is needed to elucidate the change in surface properties. It is also recommended that charge dynamics including photocarrier lifetime and mobility of  $Bi_2S_3$  with and without  $Na_2S$  soaking can be characterized in the future to elucidate the change in trapping site concentrations.



**Figure 9.** (a) and (b) SEM images and XRD patterns of S-annealed Bi<sub>2</sub>S<sub>3</sub> with and without soaking in Na<sub>2</sub>S. (c) Bi 4f/S 2p and S 2s XPS spectra of S-annealed Bi<sub>2</sub>S<sub>3</sub> with Na<sub>2</sub>S soaking.

## 4.3. Vacuum Annealing

Vacuum annealing of the S-annealed  $Bi_2S_3$  was attempted in 70 millitorr vacuum at five temperatures ranging from 150 °C to 445 °C to evaporate the elemental sulfur in B<sub>2</sub>S<sub>3</sub> films, which may create shallow hole trapping sites to decrease the performance of the material. Since sulfur has a relatively low melting point of 115 °C, it was expected that the elemental sulfur in the film can be removed at sufficiently high temperatures. It was also expected that with increasing vacuum annealing temperature, the amount of elemental sulfur will decrease while the amount of sulfur vacancies will increase. Thus, an optimum PEC performance of the Bi<sub>2</sub>S<sub>3</sub> films with vacuum annealing was expected to occur at an intermediate vacuum annealing temperature, at which elemental sulfur defects can be sufficiently removed without creating a large amount of sulfur vacancies. However, J-V measurements in 0.3 M Na<sub>2</sub>S aqueous electrolyte of S-annealed Bi<sub>2</sub>S<sub>3</sub> with vacuum annealing shows that the photocurrent increases as the vacuum annealing temperature increases from 150 °C to 375 °C and then decreases at 445 °C (Figure 10a). The photocurrents of Bi<sub>2</sub>S<sub>3</sub> films annealed in vacuum at 150 °C and 225 °C are lower than that of the S-annealed sample, while those annealed in vacuum at 300 °C and 375 °C are higher (Figure 10a). The S-annealed Bi<sub>2</sub>S<sub>3</sub> film annealed in vacuum at 445  $^{\circ}$ C changes from opaque black to transparent, which suggests decomposition of the film. Moreover, XPS of the S-annealed Bi<sub>2</sub>S<sub>3</sub> with vacuum annealing at 375 °C (the best-performing sample) shows that vacuum annealing introduces more  $Bi_2O_3$  impurities without removing the elemental sulfur (Figure 10b). Oxide impurities in the form of oxygen interstitials should decrease the PEC performance of  $Bi_2S_3$  by creating hole trapping sites. Thus, the present vacuum annealing results are not consistent with what we expected. One possibility is that vacuum annealing at higher temperatures introduces more hydrogen impurities to Bi<sub>2</sub>S<sub>3</sub>, which increase the conductivity of the film, as predicted by the DFT density of calculations. However, more experimental evidence is needed to elucidate the discrepancy between our expectation and measured PEC results.



**Figure 10.** (a) *J-V* measurements of as-annealed  $Bi_2S_3$  and S-annealed  $Bi_2S_3$  with vacuum annealing at 70 millitorr at different temperatures. (b) Bi 4f/S 2p and S 2s XPS spectra of S-annealed  $Bi_2S_3$  with vacuum annealing at 375 °C.

#### 5. CONCLUSIONS

We have synthesized Bi<sub>2</sub>S<sub>3</sub> thin film photoelectrode via a combination of solution deposition and sulfur vapor annealing. We have identified four major advantages of the annealing process. Firstly, the sulfur vapor annealing improves crystallinity of the solution-deposited Bi<sub>2</sub>S<sub>3</sub> nanocrystals by increasing the crystallite size from 10 nm to 50 nm. Secondly, introducing sulfur vapor during high-temperature annealing prevents formation of Bi<sub>2</sub>O<sub>3</sub> bulk crystal impurities and leads to phase-pure Bi<sub>2</sub>S<sub>3</sub>. Thirdly, sulfur vapor annealing converts the surface oxides of the un-annealed film to sulfides. Lastly, sulfur vapor annealing may fill in sulfur vacancies of the un-annealed Bi<sub>2</sub>S<sub>3</sub> to significantly reduce the concentration of mid-gap charge recombination sites, resulting in longer photoexcited carrier lifetimes. Overall, the Sannealed Bi<sub>2</sub>S<sub>3</sub> exhibits significantly enhanced light absorption and charge separation efficiencies, which makes it promising for photovoltaic and photoelectrochemical energy conversion applications. The sulfur vapor annealing method could be utilized as a general approach to process solution-deposited metal sulfide materials to enhance the optoelectronic performance of these promising materials. Moreover, DFT density of states calculations show that hydrogen doping creates effective donor levels at the conduction band edge of Bi<sub>2</sub>S<sub>3</sub>, which should increase electron conductivity without introducing recombination sites. We will explore the influence of hydrogen impurities on the optoelectronic properties and performance of the material in future work.

We have also attempted sulfide surface treatment and vacuum annealing to further improve the optoelectronic performance of the S-annealed Bi<sub>2</sub>S<sub>3</sub>. Both Na<sub>2</sub>S-treated and vacuum-annealed Bi<sub>2</sub>S<sub>3</sub> thin films demonstrate further improvement in charge separation efficiencies. For the Na<sub>2</sub>S treatment, it is likely that the sulfide ions fill in sulfur vacancies and displace anionic defects of S-annealed Bi<sub>2</sub>S<sub>3</sub> films, which may increase the photoexcited carrier lifetime and electron mobility. However, more experimental evidence is needed to support this hypothesis. For the vacuum annealing, more experiments coupled with

XPS characterizations are needed to elucidate the improvement in photoelectrochemical performance. Future work should also be focused on fabricating  $Bi_2S_3$  into solid-state or liquid-junction photovoltaic devices and studying chemical properties and charge dynamics at the interfaces.

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# 7. APPENDIX



**Figure A1.** Spectral output of illumination sources used in this work measured with calibrated spectrometers. (a) Spectral irradiance of the class-AAA Solar Simulator (81.7 mW/cm<sup>2</sup> overall intensity), compared to the air mass 1.5 global (AM1.5G, ASTM-G173-3) standard. (b) Irradiance of Xe lamp with monochromator, used for incident photon-to-current conversion efficiency (IPCE) measurements.



Figure A2. O 1s XPS of un-annealed, Ar-annealed, and S-annealed Bi<sub>2</sub>S<sub>3</sub> thin films.



Figure A3. Band Structure of pristine  $Bi_2S_3$ .



**Figure A4.** *J-V* measurements in 0.3 M Na<sub>2</sub>S aqueous electrolyte. (a) 10 layers of  $Bi_2S_3$  thin films without annealing and with sulfur vapor annealing at different temperatures. (b)  $Bi_2S_3$  thin films with different thickness annealed at 445 °C in sulfur vapor.



Figure A5. Absorption coefficients of un-annealed and S-annealed Bi<sub>2</sub>S<sub>3</sub> thin films.