

Comb-shaped Sb_2S_3 nanorod arrays on ZnO nanofibers for thin-film photovoltaics

Cite as: AIP Advances **12**, 115119 (2022); <https://doi.org/10.1063/5.0124401>

Submitted: 12 September 2022 • Accepted: 24 October 2022 • Published Online: 11 November 2022

 Boyang Zhou and  Takashi Sagawa



View Online



Export Citation



CrossMark

ARTICLES YOU MAY BE INTERESTED IN

[Engineering the charge extraction and trap states of \$\text{Sb}_2\text{S}_3\$ solar cells](#)

Applied Physics Letters **120**, 221102 (2022); <https://doi.org/10.1063/5.0094091>

[Scalable and efficient \$\text{Sb}_2\text{S}_3\$ thin-film solar cells fabricated by close space sublimation](#)

APL Materials **7**, 041105 (2019); <https://doi.org/10.1063/1.5090773>

[Solution processed \$\text{AgSbS}_2\$ film for efficient planar heterojunction solar cells](#)

Applied Physics Letters **119**, 151906 (2021); <https://doi.org/10.1063/5.0064802>



Comb-shaped Sb_2S_3 nanorod arrays on ZnO nanofibers for thin-film photovoltaics

Cite as: AIP Advances 12, 115119 (2022); doi: 10.1063/5.0124401

Submitted: 12 September 2022 • Accepted: 24 October 2022 •

Published Online: 11 November 2022



Boyang Zhou and Takashi Sagawa^{a)}

AFFILIATIONS

Graduate School of Energy Science, Kyoto University, Yoshida-Honmachi, Sakyo-Ku, Kyoto 606-8501, Japan

^{a)} Author to whom correspondence should be addressed: sagawa.takashi.6n@kyoto-u.ac.jp

ABSTRACT

A hierarchical composite of Sb_2S_3 nanorods grown on zinc oxide (ZnO) nanofiber was prepared, and the formation of comb-shaped Sb_2S_3 nanorod arrays on the ZnO nanofibers was confirmed. It was found that the size of the diameter and the density of the nanorods are regulatable by changing the concentration of polyvinyl pyrrolidone as an additive for the growth of Sb_2S_3 nanorod on ZnO nanofiber. The obtained Sb_2S_3 nanorod arrays were applied as a light absorber for thin-film solar cells composed of glass-fluorine-doped tin oxide/compact ZnO/ZnO nanofibers– $\text{ZnS}/\text{Sb}_2\text{S}_3$ nanorod arrays/poly(3-hexylthiophene-2,5-diyl)/ MoO_x/Ag . The rectification ratio and photocurrent generation efficiency of the comb-shaped Sb_2S_3 nanorod arrays were improved as compared with the heterojunction of randomly stacked Sb_2S_3 nanorods. Smaller series resistance (R_s) of $8.13 \, \Omega \, \text{cm}^{-2}$ and an ideality factor (n) of 2.84 with the comb-shaped Sb_2S_3 nanorod arrays than those of the randomly stacked ones of $R_s = 15.01 \, \Omega \, \text{cm}^{-2}$ and $n = 3.83$ also indicated superior charge extraction property and suppressed recombination of the comb-shaped Sb_2S_3 nanorod arrays at the interface.

© 2022 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/5.0124401>

I. INTRODUCTION

Research on thin-film solar cells that use copper indium gallium selenide (Sulfide) (CuInGeSe or CuInGeS), cadmium telluride (CdTe), and antimony sulfide (Sb_2S_3) to replace silicon has been developed, and Sb_2S_3 as a binary chalcogenide has recently become one of the promising materials for the photovoltaic light absorber.

Sb_2S_3 has a bandgap of $\sim 1.7 \, \text{eV}$ and a large absorption coefficient ($> 10^5 \, \text{cm}^{-1}$) in visible light,^{1,2} together with its low toxicity, stability, and abundance on earth, making it a potential material for the photovoltaic light absorber. The power conversion efficiency (PCE) of 7.5% was obtained in the bulk heterojunction solar cells based on the Sb_2S_3 -sensitized mesoporous TiO_2 films.³

The most commonly discovered Sb_2S_3 solid state solar cell architecture consists of a transparent conducting oxide coated glass substrate, a compact semiconductor metal oxide layer, an Sb_2S_3 layer, a hole transporting layer, and metal contacts.^{3–16} The working principle of such sort of solar cells can be illustrated as follows: under illumination, the active layer— Sb_2S_3 layer is excited, producing exciton pair. Thereafter, the electrons are injected into the conduction band of n-type semiconduction oxides, such as titanium

dioxide (TiO_2) or zinc oxide (ZnO), while the holes are transported to the opposite direction into the p-type hole transporting materials, such as poly[3-hexylthiophene-2,5-diyl (P3HT)] or 2,2',7,7'-tetrakis (N,N -di- p -methoxyphenyl-amine)9,9'-spirobifluorene (Spiro-OM-eTAD). Finally, the electrons and holes are collected at conductive electrodes, usually fluorine doped tin oxide (FTO) or indium doped tin oxide (ITO) and metal electrode, respectively.¹⁶ However, for planar structure devices, relatively small hole diffusion length ($L_D = 180 \pm 60 \, \text{nm}$) in Sb_2S_3 restricted the injection of holes into hole transport materials.¹⁷ Moreover, a large number of grain boundaries in the nanocrystalline films will lead to charge recombination, resulting in reduced performance.^{2,16,18} These issues have led to the exploration of solar cell structures to enhance the charge transport properties.

Using one dimensional (1D) nanostructure as a substitution for the planar contact between the active layer and hole or electron transport layer is one of the promising strategies to suppress the charge recombination and provide a direct pathway along the long axis of 1D nanostructure for electron transport.^{18–24} Electrons are considered to be several orders of magnitude faster to transport in 1D nanostructures, such as nanorods, nanowires, nanofibers, and

nanocolumns.^{25–28} In this context, a combination of Sb_2S_3 with 1D electron transport material has been developed; for example, Ying *et al.* used Sb_2S_3 -sensitized TiO_2 nanorod arrays and prepared solid state solar cells with a PCE of 5.37%.²⁹ Sun *et al.* designed ZnO nanorod arrays with Cu-doped Sb_2S_3 quantum dot and prepared an Sb_2S_3 quantum dot sensitized solar cell with a PCE of 3.14%.³⁰ Parize *et al.* reported a chemical spray pyrolysis method to cover uniform ultra-thin Sb_2S_3 as a light absorbing shell on ZnO/ TiO_2 core-shell nanowire and achieved a PCE of 2.3%.³¹ Li *et al.* prepared an Sb_2S_3 nanocrystal coated TiO_2 dendritic structure for a hybrid solar cell and achieved a PCE of 1.56%.^{32,33}

On the other hand, antimony chalcogenides, such as Sb_2S_3 and Sb_2Se_3 with an orthorhombic structure, have inherent anisotropic crystal structures.² However, only a few studies have reported on the application of those inherent anisotropic properties of the Sb_2S_3 crystal structure for photovoltaics. The Sb_2S_3 crystal is constructed by 1D ribbon like $(\text{Sb}_4\text{S}_6)_n$ chains, and it has been proved that the carrier can easily transport along the ribbon but is hard to jump between ribbons.^{2,16} In order to apply the anisotropic properties of Sb_2S_3 crystal structure and advantages of 1D nanostructure for improvement of electron transport in solar cells, we designed a comb-shaped Sb_2S_3 nanorod array on ZnO nanofibers as a light absorber for the photovoltaic device. Electrospun ZnO nanofiber scaffold was coated on compact ZnO, and Sb_2S_3 nanorod was grown on ZnO nanofibers by hydrothermal method.

II. MATERIALS AND METHODS

Preparation of glass-FTO/compact-ZnO (c-ZnO)/ZnO nanofibers-ZnS, the chemical bath deposition of Sb_2S_3 seed layer, electron spinning method for preparation of ZnO nanofiber, hydrothermal method for the growth of Sb_2S_3 nanorod arrays, and the preparation procedures of thin-film solar cells are described in the [supplementary material](#).^{34,35–37}

III. MEASUREMENTS

Measurement of x-ray diffraction (XRD) patterns, observation of scanning electron microscope (SEM) images and energy dispersive spectroscopy (EDS) mappings, measurement of x-ray photoelectron spectra (XPS), UV-visible absorption spectra, and photoemission yield, and measurement of current density-voltage (J - V) curves and external quantum efficiency (EQE) were carried out using previously reported apparatuses.³⁴

IV. RESULTS AND DISCUSSION

A. Morphology of Sb_2S_3 nanorod arrays on ZnO nanofibers

The optical image and SEM images of the pristine ZnO nanofibers and the Sb_2S_3 seeds deposited on the ZnO nanofibers are shown in Figs. 1(a)–1(d). Rod like parts of the Sb_2S_3 seeds were observed in Fig. 1(d). Sb_2S_3 nanorods were grown on ZnO nanofibers in the presence of 8 mg ml⁻¹ polyvinylpyrrolidone (PVP, Molecular Weight = 1300000, 0.4 g PVP in 50 ml precursor solution), and the composite structure was confirmed in SEM images in Figs. 1(e) and 1(f).

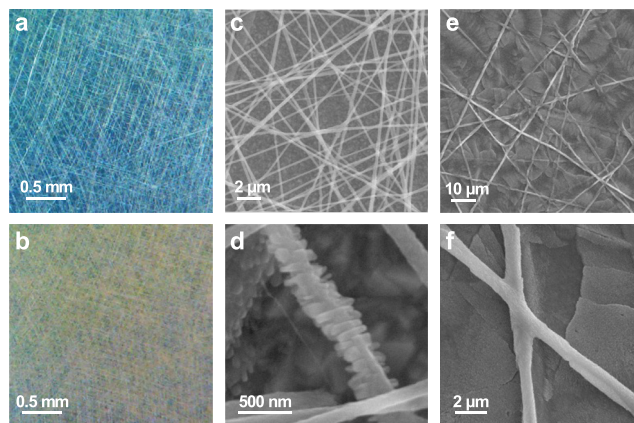


FIG. 1. Optical photo images of (a) ZnO nanofibers, (b) Sb_2S_3 seed layer coated on ZnO nanofibers, and SEM images of (c) ZnO nanofibers, (d) Sb_2S_3 seed layer coated on ZnO nanofibers, and (e) and (f) Sb_2S_3 nanorod arrays grown on ZnO nanofibers.

Sb_2S_3 compounds with an orthorhombic structure have an inherent anisotropic crystal structure. The Sb_2S_3 crystal is formed by $(\text{Sb}_4\text{S}_6)_n$ chains, and each chain is combined together by Van der Waals force as shown in Fig. 2(a), causing the carrier easier to transport through the chains rather than hopping through the inter-chains. Surfaces of Sb_2S_3 , which are parallel to the [001] direction, such as (100), (010), (110), and (120) surfaces, have no dangling bonds and have lower formation energies than (hk1) surfaces. It has also been confirmed by a computational study that, as long as the ribbons are suitably oriented, the grain boundaries will be terminated by the intrinsically benign surfaces [for example, (100), (010), (110), and (120) planes], and the recombination loss would be minimized,² as shown in Fig. 2(b). This effective carrier transport ability along the $(\text{Sb}_4\text{S}_6)_n$ ribbon and suppressed recombination nature makes the 1D Sb_2S_3 nanostructure an excellent light absorber, and it is to offer photo response and device performance.⁹

B. Morphological changes of Sb_2S_3 nanorod arrays on ZnO nanofibers by changing the concentration of PVP in the precursor solution for hydrothermal process

PVP is used for the preparation of metal-based nanomaterials since the oxygen atom in PVP can coordinate with metal and

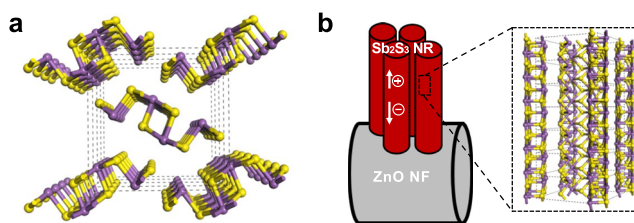


FIG. 2. Schematic diagram of (a) four Sb_2S_3 prime cells stacking along [001] direction and (b) comb-shaped Sb_2S_3 nanorod arrays on ZnO nanofiber. Note that all the atoms at the edge of these ribbons are saturated and introduce no recombination loss at the grain boundaries once they are oriented vertically onto the substrates.

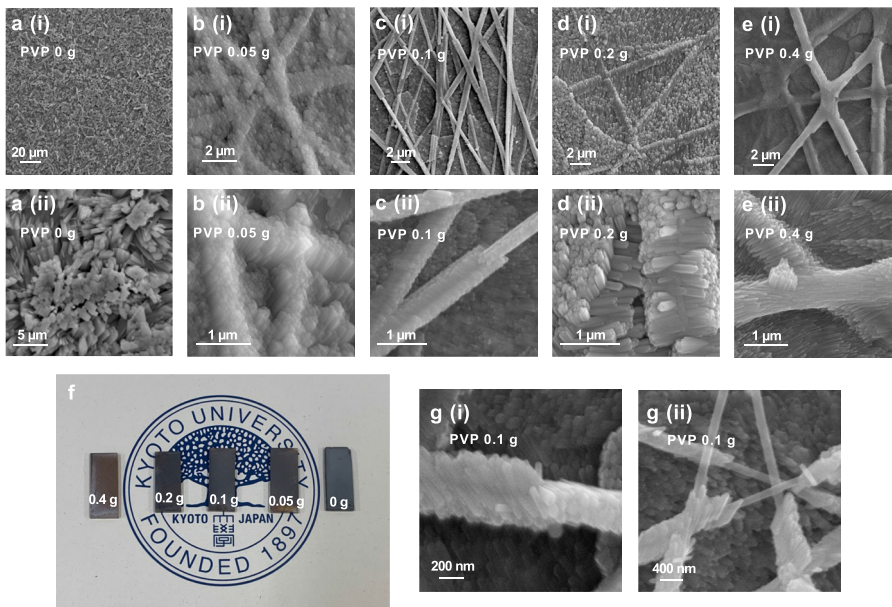


FIG. 3. SEM images of comb-shaped Sb_2S_3 nanorod arrays grown on ZnO nanofibers prepared with (a) 0 g, (b) 0.05 g, (c) 0.1 g, (d) 0.2 g, and (e) 0.4 g of PVP in 50 ml of the precursor solution during the hydrothermal process at (i) lower, (ii) higher magnifications, (f) optical image of the above five samples, and (g) SEM images of Sb_2S_3 nanorod arrays grown on ZnO nanofibers prepared with 0.1 g of PVP through hydrothermal reaction for 2 h in two different positions where Sb_2S_3 nanorod arrays are (i) fully and (ii) not fully covered ZnO nanofibers.

act as a capping ligand, which will restrict the growth of nanocrystals in a certain direction. In this context, different amount (0, 1, 2, 4, and 8 mg ml^{-1}) of PVP was added to the precursor solution for the hydrothermal process, and the morphological changes of Sb_2S_3 nanorod arrays on ZnO nanofiber composites were observed by SEM as indicated in Figs. 3(a)–3(e), and their corresponding optical

photos are shown in Fig. 3(f). It can be observed that the thickness of Sb_2S_3 nanorods covered on the ZnO nanofibers is $\sim 1 \mu\text{m}$, which is several times larger than the diameter of ZnO nanofiber, and the ZnO nanofiber scaffold could not be observed since it has been hidden by Sb_2S_3 nanorods. With the increasing amount of PVP used in the hydrothermal synthesis, the aspect ratios of the

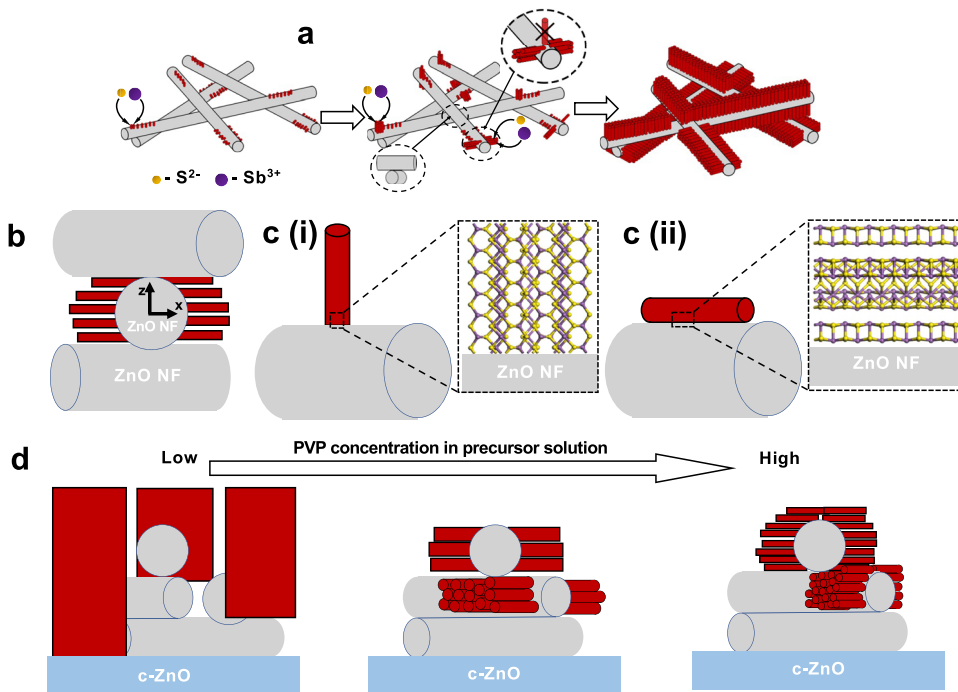


FIG. 4. Schematic diagram of (a) growth mechanisms of comb-shaped Sb_2S_3 nanorod arrays on ZnO nanofibers, (b) cross-sectional view of one ZnO nanofiber attached with comb-shaped Sb_2S_3 nanorod arrays, in which the Sb_2S_3 nanorods can only grow along x axis instead of z axis because of steric hindrance, (c-i) Sb_2S_3 nanorod vertically grown on ZnO nanofiber, (c-ii) parallel growth of Sb_2S_3 nanorod on ZnO nanofiber, and (d) comb-shaped Sb_2S_3 nanorod arrays with different diameters on ZnO nanofibers with different concentration of PVP in the precursor solution.

ZnO nanofiber increased. When the PVP concentration used was 2 and 4 mg ml⁻¹, comb-shaped structures were obtained. As shown in Fig. 3(g), Sb₂S₃ nanorods grown on ZnO nanofibers have two predominant orientations, while these two orientations are vertical to each other. This unique structure disappears when the PVP amount was increased to 8 mg ml⁻¹. When the PVP concentration was 8 mg ml⁻¹, the Sb₂S₃ nanorods covered densely on the ZnO nanofibers and it is hard to tell the predominant orientation of Sb₂S₃ nanorods.

The mechanisms of the formation of such a hierarchical structure can be supposed as follows: As shown in Fig. 4(a), the precursor of S and Sb started to react with each other and formed Sb₂S₃ nanocrystals randomly on the seed layer, which has already been coated on ZnO nanofibers. Since the (hk0) faces have no dangling bonds as mentioned above and have smaller formation energy than (hk1), Sb₂S₃ nanocrystals will naturally grow to be rod like structures. It also indicates that the Sb₂S₃ nanorod is less likely to grow parallel along the central axis of one nanofiber [Fig. 4(c-ii)] but grow vertically to the central axis of one nanofiber [Fig. 4(c-i)] because of no dangling bonds in (hk0) faces and no covalent bond between Sb₂S₃ and ZnO.

Initially formed Sb₂S₃ nanorods have a predominant growth orientation along with the seeds coated on the nanofibers as shown in Fig. 5(a). In some areas, the Sb₂S₃ nanorods can grow along only with some certain direction because other directions are blocked by other ZnO nanofibers (steric hindrance) as shown in Fig. 4(b). However, once some Sb₂S₃ nanorods are formed on nanofiber, subsequent Sb₂S₃ nanorods are preferred to grow nearby because of lower formation energy and Ostwald Ripening effect³⁸ and preferred to form locally aligned orientation, which can be confirmed by the SEM image of the intermediate state of comb-shaped Sb₂S₃ nanorod arrays on ZnO nanofibers as shown in Fig. 3(g). The hydrothermal reaction was terminated at a different time, and the SEM images of those samples are shown in Figs. 5(b)–5(f). It can be concluded that the nanorods start to form at 30 min and the predominant growth directions are limited by the seeds layer, and the nanorods are

preferred to grow aligned next to each other. EDS mapping and line scanning were characterized as indicated in Fig. S2 as proof of the composite nanostructure.

As presented in Fig. 4(d), when the PVP concentration in precursor solution was low, obtained Sb₂S₃ nanorods were large in both radius and length, and it can not be observed hierarchical nanostructure. With the increment of PVP concentration, the Sb₂S₃ nanorods were smaller and grew vertically on the nanofiber to the central axis of that nanofiber. This phenomenon can be ascribed to the steric hindrance, which prohibits the growth caused by the capping effect from PVP molecules,³⁹ as presented in Fig. S3.

C. Predominant orientation and crystal structure of the comb-shaped Sb₂S₃ nanorod arrays on ZnO nanofibers under various PVP concentrations

XRD patterns were characterized to figure out the predominant orientation of comb-shaped Sb₂S₃ nanorod arrays on ZnO nanofibers as shown in Fig. 6.

The texture coefficient of each (hk0) and (hk1) face is calculated by the following equation:

$$TC_{hkl} = \frac{I_{(hkl)}/I_{0(hkl)}}{\frac{1}{N} \sum_N I_{(hkl)}/I_{0(hkl)}}. \quad (1)$$

Those values of the samples prepared with various amounts of PVP used in the hydrothermal reaction are plotted in Figs. 6(b) and 6(c). In terms of (hk0) faces, the samples prepared with 0.1 g PVP have the highest texture coefficient, while increasing or decreasing the PVP concentration will induce a lower texture coefficient of (hk0) faces. Since the (hk0) faces are vertical to (hk1) faces, the texture coefficients of (hk1) peaks have an opposite trend.

This can be explained by the growth mechanisms of such comb-shaped Sb₂S₃ nanorod arrays on ZnO nanofibers as mentioned above in Fig. 4. Since the ZnO nanofibers are likely to stack on each other and cause steric hindrance for the growth of Sb₂S₃ nanorods

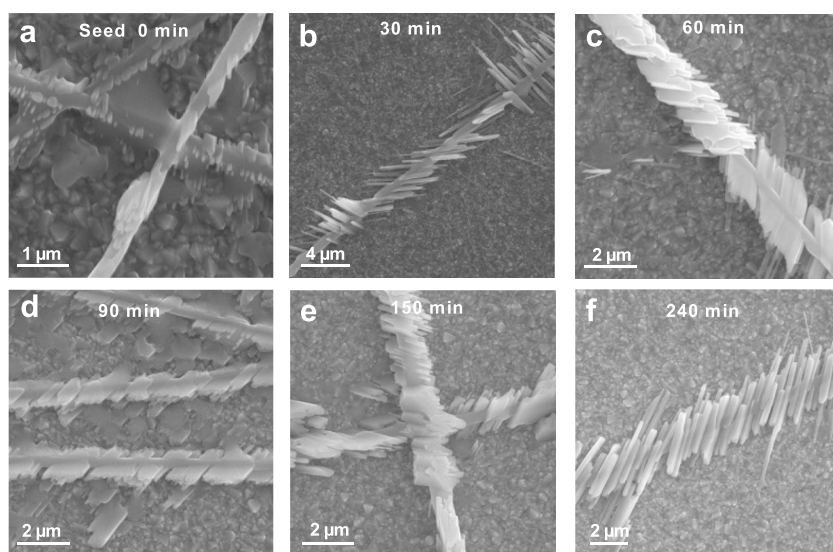


FIG. 5. SEM images of comb-shaped Sb₂S₃ nanorod arrays on ZnO nanofibers obtained with different hydrothermal reaction times for (a) 0 min, (b) 0.5 h, (c) 1 h, (d) 1.5 h, (e) 2.5 h, and (f) 4 h.

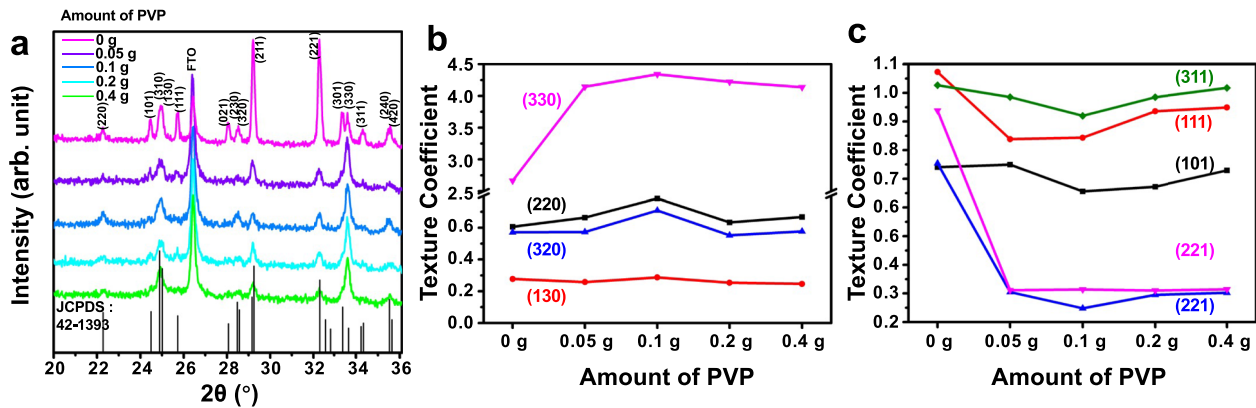


FIG. 6. (a) XRD patterns and (b) texture coefficient of (hk0) faces, and (c) texture coefficient of (hk1) faces of comb-shaped Sb_2S_3 nanorod arrays on ZnO nanofibers prepared with 0, 0.05, 0.1, 0.2, and 0.4 g of PVP in 50 ml of the precursor solution in the hydrothermal reaction.

as shown in Fig. 4(b), Sb_2S_3 nanorods predominantly grow along the x-axis instead of the z-axis. Moreover, when the PVP concentration was too low, the nanocrystals were larger and ZnO nanofibers were submerged under Sb_2S_3 nanorods, while the size of nanocrystals was smaller and diminish the influence of steric hindrance.

It can be confirmed that PVP concentration affects the nanocrystal size of Sb_2S_3 by the values of FWHM of some certain peaks of the XRD patterns as shown in Figs. S4 and S5. The (330) peaks of each sample were fitted by the gaussian method and compared in Fig. S6a. The respective grain sizes were estimated by using Scherrer's equation,

$$D = \frac{K\lambda}{\beta \cos \theta}, \quad (2)$$

where D is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size and may be smaller or equal to the particle size; K is a dimensionless shape factor, with a value close to unity. λ is the x-ray wavelength, β is FWHM in radians, and θ is the Bragg angle. The calculated crystalline sizes are plotted in Fig. S6b. It can be found that the crystalline sizes of Sb_2S_3 nanocrystals decreased as the PVP concentration used in the precursor solution increased. A similar trend also exists in the (130) peak as depicted in Figs. S6c and S6d.

D. Spectral characterization of Sb_2S_3 nanorod array on ZnO nanofiber composites

Figure 7(d) indicates that the band energy level diagram of five samples of Sb_2S_3 nanorod arrays on ZnO nanofibers prepared with different concentrations of PVP and was estimated from the absorption edges of their UV-visible absorption spectra [Fig. 7(a)], the Tauc's plots [Fig. 7(b)], and the plots of the emission yield vs photoenergy profiles [Fig. 7(c)].

XPS of the above five samples of Sb_2S_3 nanorod arrays on ZnO nanofibers prepared with different concentrations of PVP was characterized as shown in Fig. S7. The spin-orbit coupled doublet Sb 3d core level was split into $3d_{5/2}$ and $3d_{3/2}$, and the separation of the 3d doublet by 9.3 eV can be attributed to the charge state of Sb^{3+} .⁴⁰ The

Sb 3d peak in the XPS spectrum of the Sb_2S_3 crystals can be deconvoluted into several peaks. It is worth noticing that the FWHM of Sb 3d peaks are fixed to be 0.86 eV for all spectra in the fitting process. It has already been confirmed that the signal of the Sb $3d_{5/2}$ peak and $\text{Sb}_{3/2}$ is composed of Sb-S bonds from Sb_2S_3 and Sb-O from Sb_2O_3 defects.⁴¹ It is also confirmed that a non-negligible O 1s peak was observed in the Sb_{3d} orbitals of the samples, which was caused by the existence of the -OH group.⁴²⁻⁴⁴ The Sb-O defects were caused by non-radiative recombination, which will be resulted in PCE loss when used in photovoltaic devices. The spectra of Sb 3d of five tested samples show clear Sb-O defects. The lower Sb-S to Sb-O atomic ratio indicates more defects; hence, the comb-shaped Sb_2S_3 nanorod arrays on ZnO nanofibers prepared with 0.1 g PVP had fewer defects than others as shown in Fig. S7f.

E. Photovoltaic characteristics of Sb_2S_3 nanorod array on ZnO nanofiber composite-based thin film solar cells

Thin film solar cells composed of glass-FTO/c-ZnO/ZnO nanofibers- $\text{ZnS}/\text{Sb}_2\text{S}_3$ nanorod arrays/P3HT/MoO_x/Ag were prepared with the above five samples of Sb_2S_3 nanorod arrays on ZnO nanofibers obtained with different concentrations of PVP, and the J - V curves of the best performed solar cells were indicated in Fig. 7(e). Short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), PCE, series resistance (R_s), and shunt resistance (R_{sh}) of the champion device were summarized in Table I.

It can be found that the lowest PCE was attained when the Sb_2S_3 nanorod arrays on ZnO nanofibers prepared without PVP were used. This is mainly caused by the high leakage current as shown in the dark J - V curves in Fig. 7(f). As the SEM image and schematic diagram shown in Figs. 3(a) and 4(d), the radius of Sb_2S_3 nanorods is larger than that of ZnO nanofiber, and the gap between the nanorods is quite large, which may be induced by the direct contact between P3HT and ZnO nanofiber. On the other hand, the device using comb-shaped Sb_2S_3 nanorod arrays on ZnO nanofibers prepared with 0.1 g PVP showed the highest PCE, which may be attributed to its relatively high carrier transport ability and relatively fewer Sb-O defects (Fig. S7f).

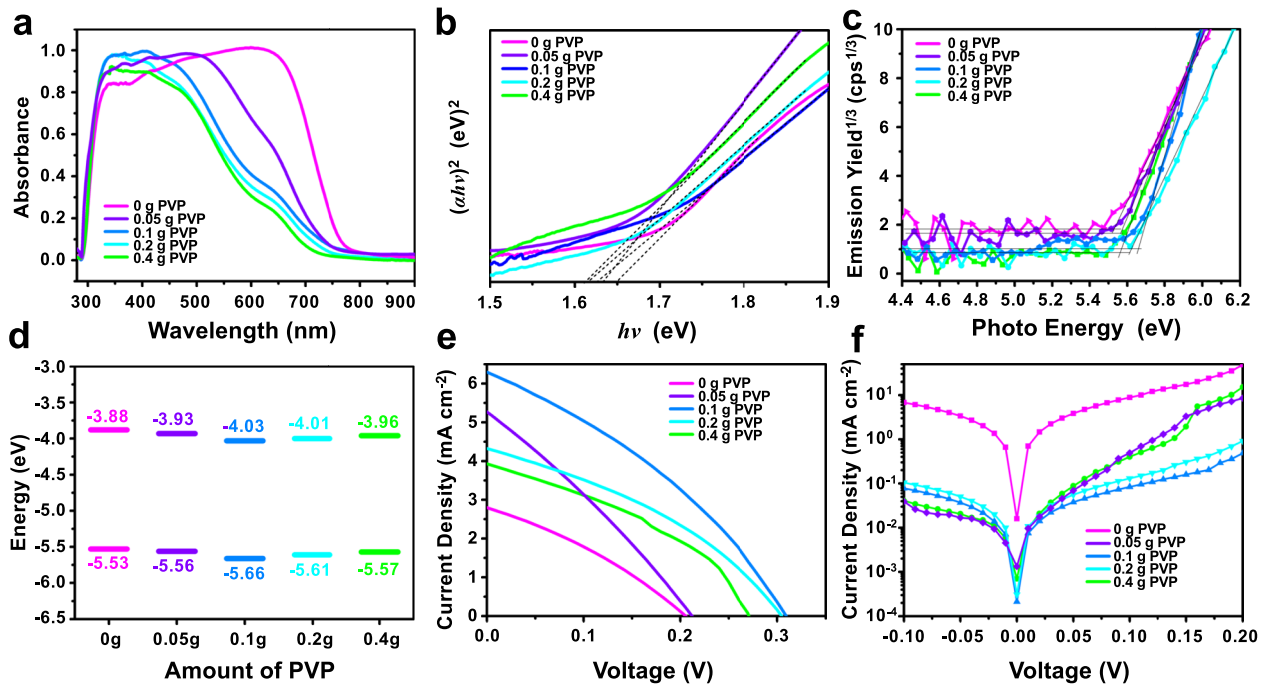


FIG. 7. (a) Absorption spectra, (b) Tauc's plots of $(\alpha h\nu)^{1/2}$ vs photo energy, (c) emission yield vs photo energy profiles, (d) band energy level diagram of Sb_2S_3 nanorod arrays grown on ZnO nanofibers with different amounts of PVP in the precursor solution, and (e) J - V curves and (f) dark J - V curves of solar cells composed of glass-FTO/c-ZnO/ZnO nanofibers- $\text{ZnS}/\text{Sb}_2\text{S}_3$ nanorod arrays/P3HT/MoO_x/Ag, in which the Sb_2S_3 nanorod arrays grown on ZnO nanofibers were prepared with different amount of PVP in the precursor solution.

The champion device of using the comb-shaped Sb_2S_3 nanorod arrays on ZnO nanofibers as a light absorbing layer was also compared with devices using planar Sb_2S_3 layer and randomly stacked Sb_2S_3 nanorods as a light absorber, and the J - V characterization of the champion devices are shown in Figs. 8(a) and 8(b) and Table II.

It was found that the device using planar Sb_2S_3 as a light absorbing layer showed the lowest PCE. It can also be found that the device using the comb-shaped Sb_2S_3 nanorod arrays on ZnO nanofibers exhibit better performance than planar absorber as well as randomly stacked Sb_2S_3 nanorods. From the EQE curves as shown in Fig. 8(c), the randomly stacked nanorods-based device showed higher EQE

than that of the comb-shaped Sb_2S_3 nanorod arrays on ZnO nanofibers in the region from 310 to 330 nm, while the comb-shaped Sb_2S_3 nanorod arrays on ZnO nanofibers-based device showed much higher EQE from 330 to 750 nm. The absorption spectra of the above three light absorbing layers-based solar cells were also compared as depicted in Fig. 8(d), and the cross-sectional SEM images of those tested light absorbers-based solar cells were shown in Fig. S8. It is clear that the profiles of the EQE curves in Fig. 8(c) are reflected by the absorbance in Fig. 8(d), which was directly reflected by the total thickness of the layers of each component. The higher EQE of the device using Sb_2S_3 nanorods on ZnO nanofibers as light absorbers might be ascribed to the fast carrier transport from Sb_2S_3 to ZnO.

TABLE I. Photovoltaic characteristics of solar cells composed of glass-FTO/c-ZnO/ZnO nanofibers- $\text{ZnS}/\text{Sb}_2\text{S}_3$ nanorod arrays/P3HT/MoO_x/Ag (champion device).

PVP (g)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)	R_s (Ω)	R_{sh} (Ω)
0	2.767	0.203	0.317	0.178	1148.0	2153.2
0.05	5.355	0.217	0.285	0.331	781.5	3332.9
0.1	6.293	0.309	0.340	0.662	646.3	3513.8
0.2	4.322	0.305	0.473	0.473	747.0	3473.2
0.4	3.929	0.271	0.379	0.403	701.1	3403.5

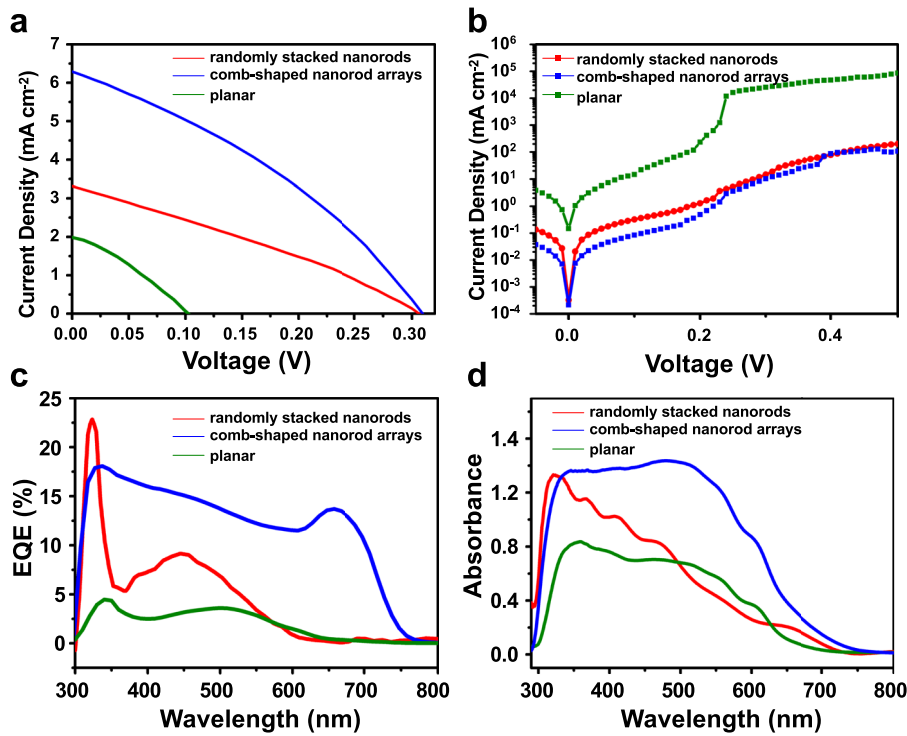


FIG. 8. (a) J - V curves, (b) dark J - V curves, (c) EQE profiles, and (d) absorption spectra of the light absorber of the solar cells using randomly stacked Sb_2S_3 nanorods, comb-shaped Sb_2S_3 nanorod arrays on ZnO nanofibers, and planar Sb_2S_3 as the light absorber.

An equivalent circuit model of the solar cells was introduced to evaluate the improvement of electron transport efficiency by Eq. (3),

$$J = J_0 \exp\left[\frac{V - R_s J}{nV_{th}}\right] + GV - J_L. \quad (3)$$

V_{th} was obtained from thermal energy $k_B T/e$, where k_B is the Boltzmann constant, T is the absolute temperature, and e is the elementary charge, which is generally considered to be 0.0257 V at 298 K. J_L is the photocurrent density, which can be directly approximated as the current density of the device when voltage is 0 V ($J_L = J_{sc}$). R_s is the series resistance and $G (=R_{sh}^{-1})$ is the parallel conductance. J_0 and n are the reversed saturation current density at the dark state and ideality factor of the diodes, respectively. These parameters can be solved separately by transforming Eq. (3) into the three following Eqs. (4)–(6):

$$\frac{dJ}{dV} = \frac{1}{nV_{th}} \times J_0 \exp\left[\frac{V - R_s J}{nV_{th}}\right] + G, \quad (4)$$

$$\frac{dV}{dJ} = R_s + \frac{nV_{th}}{J + J_L - GV}, \quad (5)$$

$$\ln(J + J_L - GV) = \frac{1}{nV_{th}} \times (V - R_s J) + \ln J_0. \quad (6)$$

The parallel conductance G calculated by Eq. (4) is shown in Fig. 9(a), and the randomly stacked Sb_2S_3 nanorods device has the smallest parallel conductance of 8.40 mS cm^{-2} compared to that of 10.85 and 11.23 mS cm^{-2} for Sb_2S_3 nanorod decorated ZnO nanofiber solar cell and planar Sb_2S_3 device, respectively.

The series resistance R_s calculated by Eq. (5) is shown in Fig. 9(b) with 8.13, 15.01, and $13.46 \Omega \text{ cm}^{-2}$ for Sb_2S_3 nanorod

TABLE II. Photovoltaic characteristics of solar cells with three different light absorbers (champion device).

Light absorber	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)	R_s (Ω)	R_{sh} (Ω)
Randomly stacked Sb_2S_3 nanorods	3.315	0.302	0.321	0.374	1075.4	1784.5
Comb-shaped Sb_2S_3 nanorod arrays	6.293	0.309	0.340	0.662	646.28	3513.8
Planar Sb_2S_3 layer	1.952	0.095	0.372	0.060	1132.4	1341.2

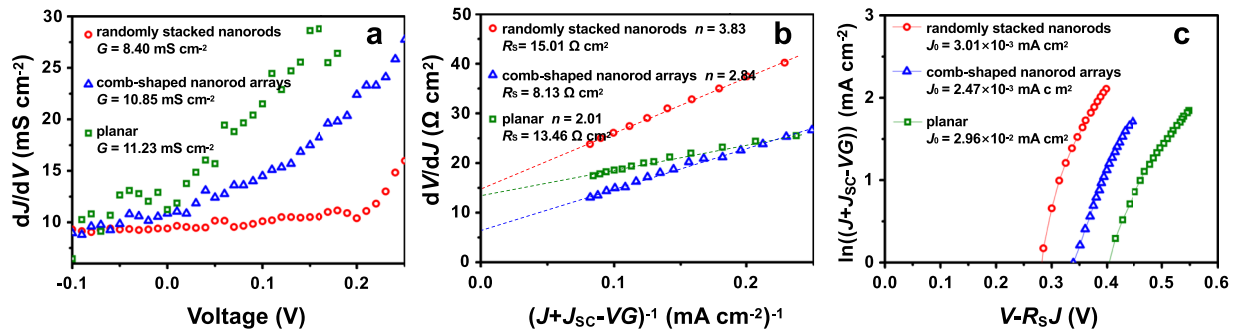


FIG. 9. Calculation of characteristic parameters in the equivalent circuit: (a) shunt conductance, G ; (b) series, R_s , and ideality factor, n ; and (c) dark state saturation current, J_0 .

decorated ZnO nanofiber solar cell, randomly stacked Sb₂S₃ nanorods and planar Sb₂S₃ devices, respectively. It was found that the Sb₂S₃ nanorod decorated ZnO nanofiber based device showed the smallest R_s , implying the improvement in charge extraction capability. The value of ideality factor n is obtained from Eq. (5) by the slope of the dashed line in Fig. 9(b), reflects the recombination in the diode, with n being 2.84, 3.83, and 2.01 for Sb₂S₃ nanorod decorated ZnO nanofiber solar cell, randomly stacked Sb₂S₃ nanorods, and planar Sb₂S₃ devices, respectively. The smaller n indicates the more suppression of recombination at the interface. In other words, there is still quite a lot of recombination occurring in the interface for Sb₂S₃ nanorods on ZnO nanofibers-based solar cells, which might be caused by the insufficient contact between each component. The maximum V_{oc} could be predicted by Shockley–Queisser limit model⁴⁵ as can be expressed by Eq. (7),

$$V_{oc}^{SQ} = V_{th} \ln \left(\frac{J_{sc}^{SQ}}{J_0^{BB}} + 1 \right), \quad (7)$$

where J_0^{BB} is the reverse saturation current density calculated by considering merely the black body radiation of the solar cell at room temperature. The trapping and re-emission process of non-equilibrium carriers by deep-level defects in the device can cause severe recombination current and boost the J_0 , which can be considered to be the loss in V_{oc} .⁴⁶ The values of J_0 of each device were also calculated by Eq. (6) as indicated in Fig. 9(c). Calculated J_0 of Sb₂S₃ nanorods ZnO nanofibers-based solar cell was 2.47×10^{-5} mA cm⁻², which is smaller than that of the other two devices, one order smaller than that of the planar device, indicating that the trap-mediated recombination was effectively suppressed and resulted in a much larger V_{oc} .

Low PCE of a such device using the comb-shaped Sb₂S₃ nanorod arrays on ZnO nanofibers as light absorbers may be brought by the insufficient contact between ZnO nanofibers and compact ZnO layer after the growth of Sb₂S₃ nanorods as shown in Fig. S9. Some nanofibers as marked in the red dashed circle cannot contact directly with the compact ZnO layer. These parts were occupied by Sb₂S₃ nanorods as confirmed by the cross-sectional SEM image and EDS mapping as shown in Fig. S10. It is difficult for free carriers generated from these parts to travel through a long path

and overcome a huge barrier to the FTO electrode. Those parts also blocked contact with other parts, like P3HT, which may also reduce the quantum efficiency.

V. CONCLUSION

Preparation for comb-shaped Sb₂S₃ nanorod arrays on ZnO nanofibers through hydrothermal growth of Sb₂S₃ nanorods on ZnO nanofiber was proposed. The size of the diameter of the nanorod and the extent of formation of comb-shaped Sb₂S₃ nanorod arrays on ZnO nanofibers were controlled by changing the concentration of PVP as the additive in the precursor solution. Spectral properties of Sb₂S₃ nanorod arrays on ZnO nanofibers were characterized, and the photovoltaic characteristics of thin-film solar cells were evaluated with the device structure of glass-FTO/c-ZnO/ZnO nanofibers–ZnS/Sb₂S₃ nanorod arrays/P3HT/MoO_x/Ag. It was found that the rectification ratio and photocurrent generation efficiency of the comb-shaped Sb₂S₃ nanorod arrays on ZnO nanofibers were improved as compared with those of randomly stacked Sb₂S₃ nanorods. Smaller series resistance and ideality factor of the comb-shaped Sb₂S₃ nanorod arrays than those of the randomly stacked ones also indicated superior charge extraction properties and suppressed recombination at the interface.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for experimental detail and the corresponding other experimental data.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan as the MEXT KAKENHI (Grant Number: 17H03536).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

B. Zhou: Conceptualization (lead); Data curation (equal); Writing – original draft (equal). **T. Sagawa:** Conceptualization (supporting); Supervision (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- M. Y. Versavel and J. A. Haber, "Structural and optical properties of amorphous and crystalline antimony sulfide thin-films," *Thin Solid Films* **515**(18), 7171–7176 (2007).
- R. Kondrotas, C. Chen, and J. Tang, "Sb₂S₃ solar cells," *Joule* **2**(5), 857–878 (2018).
- J. Han, X. Pu, H. Zhou, Q. Cao, S. Wang, Z. He, B. Gao, T. Li, J. Zhao, and X. Li, "Synergistic effect through the introduction of inorganic zinc halides at the interface of TiO₂ and Sb₂S₃ for high-performance Sb₂S₃ planar thin-film solar cells," *ACS Appl. Mater. Interfaces* **12**(39), 44297–44306 (2020).
- L. Wang, D. Li, K. Li, C. Chen, H. Deng, L. Gao, Y. Zhao, F. Jiang, L. Li, F. Huang, Y. He, H. Song, G. Niu, and J. Tang, "Stable 6%-efficient Sb₂Se₃ solar cells with a ZnO buffer layer," *Nat. Energy* **2**(4), 1–9 (2017).
- X. Wen, C. Chen, S. Lu, K. Li, R. Kondrotas, Y. Zhao, W. Chen, L. Gao, C. Wang, and J. Zhang, "Vapor transport deposition of antimony selenide thin film solar cells with 7.6% efficiency," *Nat. Commun.* **9**(1), 2179 (2018).
- H. Deng, Y. Zeng, M. Ishaq, S. Yuan, H. Zhang, X. Yang, M. Hou, U. Farooq, J. Huang, K. Sun, R. Webster, H. Wu, Z. Chen, F. Yi, H. Song, X. Hao, and J. Tang, "Quasiepitaxy strategy for efficient full-inorganic Sb₂S₃ solar cells," *Adv. Funct. Mater.* **29**(31), 1901720 (2019).
- R. Nie, H. S. Yun, M. J. Paik, A. Mehta, B. W. Park, Y. C. Choi, and S. I. Seok, "Efficient solar cells based on light-harvesting antimony sulfoiodide," *Adv. Energy Mater.* **8**(7), 1701901 (2018).
- R. Tang, X. Wang, C. Jiang, S. Li, W. Liu, H. Ju, S. Yang, C. Zhu, and T. Chen, "n-type doping of Sb₂S₃ light-harvesting films enabling high-efficiency planar heterojunction solar cells," *ACS Appl. Mater. Interfaces* **10**(36), 30314–30321 (2018).
- Z. Li, X. Liang, G. Li, H. Liu, H. Zhang, J. Guo, J. Chen, K. Shen, X. San, W. Yu, R. Schropp, and Y. Mai, "9.2%-efficient core-shell structured antimony selenide nanorod array solar cells," *Nat. Commun.* **10**(1), 125 (2019).
- Y. Zeng, K. Sun, J. Huang, M. P. Nielsen, F. Ji, C. Sha, S. Yuan, X. Zhang, C. Yan, X. Liu, H. Deng, Y. Lai, J. Seidel, N. Ekins-Daukes, F. Liu, H. Song, M. Green, and X. Hao, "Quasi-vertically-orientated antimony sulfide inorganic thin-film solar cells achieved by vapor transport deposition," *ACS Appl. Mater. Interfaces* **12**(20), 22825–22834 (2020).
- S.-J. Lee, S.-J. Sung, K.-J. Yang, J.-K. Kang, J. Y. Kim, Y. S. Do, and D.-H. Kim, "Approach to transparent photovoltaics based on wide band gap Sb₂S₃ absorber layers and optics-based device optimization," *ACS Appl. Energy Mater.* **3**(12), 12644–12651 (2020).
- X. Jin, Y. Fang, T. Salim, M. Feng, S. Hadke, S. W. Leow, T. C. Sum, and L. H. Wong, "In situ growth of [hk1]-oriented Sb₂S₃ for solution-processed planar heterojunction solar cell with 6.4% efficiency," *Adv. Funct. Mater.* **30**(35), 2002887 (2020).
- W. Lin, W.-T. Guo, L. Yao, J. Li, L. Lin, J.-M. Zhang, S. Chen, and G. Chen, "Zn(O,S) buffer layer for in situ hydrothermal Sb₂S₃ planar solar cells," *ACS Appl. Mater. Interfaces* **13**(38), 45726–45735 (2021).
- W. Wang, X. Wang, G. Chen, L. Yao, X. Huang, T. Chen, C. Zhu, S. Chen, Z. Huang, and Y. Zhang, "Over 6% certified Sb₂(S,Se)₃ solar cells fabricated via in situ hydrothermal growth and postselenization," *Adv. Electron. Mater.* **5**(2), 1800683 (2018).
- Y. Zhao, S. Wang, C. Jiang, C. Li, P. Xiao, R. Tang, J. Gong, G. Chen, T. Chen, and J. Li, "Regulating energy band alignment via alkaline metal fluoride assisted solution post-treatment enabling Sb₂(S,Se)₃ solar cells with 10.7% efficiency," *Adv. Energy Mater.* **12**(1), 2103015 (2022).
- U. A. Shah, S. Chen, G. M. G. Khalaf, Z. Jin, and H. Song, "Wide bandgap Sb₂S₃ solar cells," *Adv. Funct. Mater.* **31**(27), 2100265 (2021).
- J. A. Christians, D. T. Leighton, and P. V. Kamat, "Rate limiting interfacial hole transfer in Sb₂S₃ solid-state solar cells," *Energy Environ. Sci.* **7**(3), 1148–1158 (2014).
- M. Batmunkh, T. J. Macdonald, C. J. Shearer, M. Bat-Erdene, Y. Wang, M. J. Biggs, I. P. Parkin, T. Nann, and J. G. Shapter, "Carbon nanotubes in TiO₂ nanofiber photoelectrodes for high-performance perovskite solar cells," *Adv. Sci.* **4**(4), 1600504 (2017).
- L. E. Greene, M. Law, B. D. Yuhas, and P. Yang, "ZnO–TiO₂ core–shell nanorod/P3HT solar cells," *J. Phys. Chem. C* **111**(50), 18451–18456 (2007).
- Y.-J. Lee, D. S. Ruby, D. W. Peters, B. B. McKenzie, and J. W. P. Hsu, "ZnO nanostructures as efficient antireflection layers in solar cells," *Nano Lett.* **8**(5), 1501–1505 (2008).
- Y. Hames, Z. Alpaslan, A. Kösemen, S. E. San, and Y. Yerli, "Electrochemically grown ZnO nanorods for hybrid solar cell applications," *Solar Energy* **84**(3), 426–431 (2010).
- D. Y. Son, J. H. Im, H. S. Kim, and N. G. Park, "11% efficient perovskite solar cell based on ZnO nanorods: An effective charge collection system," *J. Phys. Chem. C* **118**(30), 16567–16573 (2014).
- E. Galoppini, J. Rochford, H. Chen, G. Saraf, Y. Lu, A. Hagfeldt, and G. Boschloo, "Fast electron transport in metal organic vapor deposition grown dye-sensitized ZnO nanorod solar cells," *J. Phys. Chem. B* **110**(33), 16159–16161 (2006).
- K. Mahmood, A. Khalid, S. W. Ahmad, and M. T. Mehran, "Indium-doped ZnO mesoporous nanofibers as efficient electron transporting materials for perovskite solar cells," *Surf. Coat. Technol.* **352**, 231–237 (2018).
- G. S. Han, H. S. Chung, D. H. Kim, B. J. Kim, J.-W. Lee, N.-G. Park, I. S. Cho, J.-K. Lee, S. Lee, and H. S. Jung, "Epitaxial 1D electron transport layers for high-performance perovskite solar cells," *Nanoscale* **7**(37), 15284–15290 (2015).
- L. Yang and W. W.-F. Leung, "Application of a bilayer TiO₂ nanofiber photoanode for optimization of dye-sensitized solar cells," *Adv. Mater.* **25**(12), 1792–1795 (2013).
- F. J. Ramos, M. Oliva-Ramirez, M. K. Nazeeruddin, M. Grätzel, A. R. González-Elipe, and S. Ahmad, "Nanocolumnar 1-dimensional TiO₂ photoanodes deposited by PVD-OAD for perovskite solar cell fabrication," *J. Mater. Chem. A* **3**(25), 13291–13298 (2015).
- L. Yang and W. W.-F. Leung, "Application of a bilayer TiO₂ nanofiber photoanode for optimization of dye-sensitized solar cells," *Adv. Mater.* **23**(39), 4559–4562 (2011).
- C. Ying, F. Guo, Z. Wu, K. Lv, and C. Shi, "Influence of surface modifier molecular structures on the photovoltaic performance of Sb₂S₃-sensitized TiO₂ nanorod array solar cells," *Energy Technol.* **8**(6), 1901368 (2020).
- Z. Sun, Z. Peng, Z. Liu, J. Chen, W. Li, W. Qiu, and J. Chen, "Band energy modulation on Cu-doped Sb₂S₃-based photoelectrodes for charge generation and transfer property of quantum dot-sensitized solar cells," *J. Nanoparticle Res.* **22**(9), 1–9 (2020).
- R. Parize, A. Katerski, I. Gromyko, L. Rapenne, H. Roussel, E. Kärber, E. Appert, M. Krunk, and V. Consonni, "ZnO/TiO₂/Sb₂S₃ core-shell nanowire heterostructure for extremely thin absorber solar cells," *J. Phys. Chem. C* **121**(18), 9672–9680 (2017).
- Y. Li, Y. Wei, K. Feng, Y. Hao, J. Pei, and B. Sun, "Preparation of Sb₂S₃ nanocrystals modified TiO₂ dendritic structure with nanotubes for hybrid solar cell," *Mater. Res. Express* **5**(6), 065903 (2018).
- Y. Li, Y. Wei, K. Feng, Y. Hao, J. Pei, Y. Zhang, and B. Sun, "Introduction of PCPDTBT in P3HT: Spiro-OMeTAD blending system for solid-state hybrid solar cells with dendritic TiO₂/Sb₂S₃ nanorods composite film," *J. Solid State Chem.* **276**, 278–284 (2019).
- B. Zhou, T. Hayashi, K. Hachiya, and T. Sagawa, "Preparation of Sb₂S₃ nanorod arrays by hydrothermal method as light absorbing layer for Sb₂S₃-based solar cells," *Thin Solid Films* **757**, 139389 (2022).

- ³⁵R. Chen, J. Cao, Y. Duan, Y. Hui, T. T. Chuong, D. Ou, F. Han, F. Cheng, X. Huang, B. Wu, and N. Zheng, "High-efficiency, hysteresis-less, UV-stable perovskite solar cells with cascade ZnO–ZnS electron transport layer," *J. Am. Chem. Soc.* **141**(1), 541–547 (2019).
- ³⁶S. Messina, M. T. S. Nair, and P. K. Nair, "All-chemically deposited solar cells with antimony sulfide-selenide/lead sulfide thin film absorbers," *MRS Online Proc. Libr.* **1012**, 413–418 (2007).
- ³⁷Q. Han, L. Chen, M. Wang, X. Yang, L. Lu, and X. Wang, "Low-temperature synthesis of uniform Sb₂S₃ nanorods and its visible-light-driven photocatalytic activities," *Mater. Sci. Eng., B* **166**(1), 118–121 (2010).
- ³⁸B. Jia and L. Gao, "Growth of well-defined cubic hematite single crystals: Oriented aggregation and Ostwald ripening," *Cryst. Growth Des.* **8**(4), 1372–1376 (2008).
- ³⁹I. A. Safo, M. Werheid, C. Dosche, and M. Oezaslan, "The role of polyvinylpyrrolidone (PVP) as a capping and structure-directing agent in the formation of Pt nanocubes," *Nanoscale Adv.* **1**(8), 3095–3106 (2019).
- ⁴⁰G.-X. Liang, Z.-H. Zheng, P. Fan, J.-T. Luo, J.-G. Hu, X.-H. Zhang, H.-L. Ma, B. Fan, Z.-K. Luo, and D.-P. Zhang, "Thermally induced structural evolution and performance of Sb₂Se₃ films and nanorods prepared by an easy sputtering method," *Sol. Energy Mater. Sol. Cells* **174**, 263–270 (2018).
- ⁴¹Q. Wang, Z. Chen, J. Wang, Y. Xu, Y. Wei, Y. Wei, L. Qiu, H. Lu, Y. Ding, and J. Zhu, "Sb₂S₃ solar cells: Functional layer preparation and device performance," *Inorg. Chem. Front.* **6**(12), 3381–3397 (2019).
- ⁴²T. J. Whittles, T. D. Veal, C. N. Savory, A. W. Welch, F. W. de Souza Lucas, J. T. Gibbon, M. Birkett, R. J. Potter, D. O. Scanlon, A. Zakutayev, and V. R. Dhanak, "Core levels, band alignments, and valence-band states in CuSbS₂ for solar cell applications," *ACS Appl. Mater. Interfaces* **9**(48), 41916–41926 (2017).
- ⁴³P. Büttner, F. Scheler, C. Pointer, D. Döhler, M. K. S. Barr, A. Koroleva, D. Pankin, R. Hatada, S. Flege, A. Manshina, E. R. Young, I. Mínguez-Bacho, and J. Bachmann, "Adjusting interfacial chemistry and electronic properties of photovoltaics based on a highly pure Sb₂S₃ absorber by atomic layer deposition," *ACS Appl. Energy Mater.* **2**(12), 8747–8756 (2019).
- ⁴⁴Z. Deng, D. Chen, F. Tang, J. Ren, and A. J. Muscat, "Synthesis and purple-blue emission of antimony trioxide single-crystalline nanobelts with elliptical cross section," *Nano Res.* **2**(2), 151–160 (2009).
- ⁴⁵W. Shockley and H. J. Queisser, "Detailed balance limit of efficiency of p-n junction solar cells," *J. Appl. Phys.* **32**(3), 510–519 (1961).
- ⁴⁶Y. Qi, Y. Li, and Q. Lin, "Engineering the charge extraction and trap states of Sb₂S₃ solar cells," *Appl. Phys. Lett.* **120**(22), 221102 (2022).