Video Article

Key Factors Affecting the Performance of Sb_2S_3-sensitized Solar Cells During an Sb_2S_3 Deposition *via* $SbCl_3$-thiourea Complex Solution-processing

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URL: https://www.jove.com/video/58062
DOI: doi:10.3791/58062

Keywords: Chemistry, Issue 137, Sb_2S_3, thiourea complex solution, solution-processing, chalcogenides, solar cells, inorganic sensitizer

Date Published: 7/16/2018

Citation: Choi, Y.C., Seok, S.I., Hwang, E., Kim, D.H. Key Factors Affecting the Performance of Sb_2S_3-sensitized Solar Cells During an Sb_2S_3 Deposition *via* $SbCl_3$-thiourea Complex Solution-processing. *J. Vis. Exp.* (137), e58062, doi:10.3791/58062 (2018).

Abstract

Sb_2S_3 is considered as one of the emerging light absorbers that can be applied to next-generation solar cells because of its unique optical and electrical properties. Recently, we demonstrated its potential as next-generation solar cells by achieving a high photovoltaic efficiency of > 6% in Sb_2S_3-sensitized solar cells using a simple thiourea (TU)-based complex solution method. Here, we describe the key experimental procedures for the deposition of Sb_2S_3 on a mesoporous TiO_2 (mp-TiO_2) layer using a $SbCl_3$-TU complex solution in the fabrication of solar cells. First, the $SbCl_3$-TU solution is synthesized by dissolving $SbCl_3$ and TU in *N,N*-dimethylformamide at different molar ratios of $SbCl_3$:TU. Then, the solution is deposited on as-prepared substrates consisting of mp-TiO_2/TiO_2-blocking layer/F-doped SnO_2 glass by spin coating. Finally, to form crystalline Sb_2S_3, the samples are annealed in an N_2-filled glove box at 300 °C. The effects of the experimental parameters on the photovoltaic device performance are also discussed.

Video Link

The video component of this article can be found at https://www.jove.com/video/58062/

Introduction

Antimony-based chalcogenides (Sb-Chs), including Sb_2S_3, Sb_2Se_3, $Sb_2(S,Se)_3$, and $CuSbS_2$, are considered to be emerging materials that can be used in next-generation solar cells[1,2,3,4,5,6,7,8]. However, photovoltaic devices based on Sb-Chs light absorbers have not yet reached the 10% power conversion efficiency (PCE) required to demonstrate feasible commercialization.

To overcome these limitations, various methods and techniques have been applied, such as a thioacetamide-induced surface treatment[1], a room temperature deposition method[4], an atomic layer deposition technique[2], and the use of colloid dot quantum dots[6]. Among these various methods, the solution-processing based on a chemical bath decomposition exhibited the highest performance[1]. However, a precise control of the chemical reaction and the post-treatment are required to achieve the best performance[1,3].

Recently, we developed a simple solution-processing for high-performance Sb_2S_3-sensitized solar cells using a $SbCl_3$-thiourea (TU) complex solution[3]. Using this method, we were able to fabricate a quality Sb_2S_3 with a controlled Sb/S ratio, which was applied to a solar cell to achieve a comparable device performance of 6.4% PCE. We were also able to effectively reduce the processing time since the Sb_2S_3 was fabricated by a single-step deposition.

In this work, we describe the detailed experimental procedure for an Sb_2S_3 deposition on the substrate consisting of mesoporous TiO_2 (mp-TiO_2)/TiO_2 blocking layer (TiO_2-BL)/F-doped SnO_2 (FTO) glass for the fabrication of Sb_2S_3-sensitized solar cells *via* $SbCl_3$-TU complex solution-processing[3]. In addition, three key factors affecting the photovoltaic performance in the course of an Sb_2S_3 deposition were identified and discussed. The concept of the method can be easily applied to other sensitizer-type solar cells based on metal sulfides.

Protocol

1. Synthesis of the TiO_2-BL Solution

1. Prepare 2 transparent vials with a 50 mL volume.
2. Add 20 mL of ethanol to 1 vial (V1) and seal V1.
3. Transfer V1 to an N_2-filled glove box with a moisture-controlled system of an H_2O level of < 1 ppm.
4. Add 1.225 mL of titanium (IV) isopropoxide (TTIP) to V1 using a syringe with a 0.45 µm PVDF filter and gently stir the mixture for at least 30 min.

NOTE: This step must be performed in a glove box (or under very low humidity conditions) since TTIP is highly sensitive to moisture. If the TTIP solution is not transparent or white precipitates are observed inside the solution, it should not be used, because an undesirable reaction has already occurred inside the solution.

5. In the other prepared vial (V2), add 18 µL of HNO_3 (70%) and 138 µL of H_2O to 20 mL of ethanol using a micropipette and gently stir the mixture for at least 30 min.
   NOTE: This step must not be performed in a glove box, because H_2O is used.
6. Mix the 2 solutions by pouring the V2 solution into the V1 solution and stir for more than 2 h to synthesize the transparent 0.1 M TiO_2-BL solution.
   NOTE: The final solution must be transparent. If the solution is not transparent, resynthesize it until a transparent solution is obtained. Successfully prepared TiO_2-BL solutions are stable for several days at humidity conditions of < 50%.

2. Synthesis of the $SbCl_3$-TU Solutions with Various $SbCl_3$/TU Molar Ratios

NOTE: The synthesis must be performed in the glove box because of the very high sensitivity of $SbCl_3$ to moisture.

1. Prepare the $SbCl_3$ stock solution [1 mmol of $SbCl_3$ in 1 mL of *N,N*-dimethylformamide (DMF)] inside the glove box. For example, add 6.486 g of $SbCl_3$ to 30 mL of DMF for a 32.2 mL stock solution.
2. Add a proper amount of stock solution to a vial containing a given amount of TU to synthesize the $SbCl_3$-TU solution with the desired molar ratio of $SbCl_3$/TU. For example, suppose the 2 vials each contain 0.1 g of TU, add 0.9394 mL of the stock solution to one vial and 0.5637 mL to the other, to synthesize solutions with $SbCl_3$/TU ratios of 1/1.5 and 1/2.5, respectively.

3. Preparation of the Substrate Consisting of mp-TiO_2/TiO_2-BL/FTO Glass

1. Wash the FTO-coated glass (FTO glass) of 25 mm x 25 mm in an ultrasonic bath with acetone for 10 min, followed by ethanol.
   NOTE: To fabricate the photovoltaic device, use pre-patterned FTO glass, where the 5 - 10 mm x 25 mm FTO surface is completely etched.
2. Instantly dry the FTO glass by blowing compressed air over the sample.
3. Treat the FTO glass with a UV/O_3 cleaner for 20 min.
4. Spin coat ethanol on the FTO glass at 5,000 rpm for 60 s.
5. Immediately spin coat again with the prepared TiO_2-BL solution under the same conditions of step 3.4.
6. Dry the FTO glass for 2 min by placing it on a preheated hot plate at 200 °C.
7. Repeat steps 3.5 and 3.6 to obtain the desired TiO_2-BL thickness.
8. Deposit the mp-TiO_2 layer on the TiO_2-BL/FTO glass using the screen printing method with TiO_2 paste (50 nm TiO_2 particles) and a polyester mask.
9. Anneal the mp-TiO_2/TiO_2-BL/FTO glass at 500 °C for 30 min.
10. Dip the annealed substrates in a transparent aqueous 40 mM $TiCl_4$ solution after cooling them to room temperature.
    NOTE: The 40 mM $TiCl_4$ solution must be transparent. If the substrates are dipped in the $TiCl_4$ solution before they are cooled, they can easily break because of the large temperature difference between the substrate and the solution.
11. Transfer the substrates to an oven at 60 °C and store them for 1 h.
12. Rinse the substrates several times with warm water and instantly dry them by blowingcompressed air on them.
    NOTE: To prevent any cracking of the substrates, use warm water (approximately 60 °C) when rinsing.
13. Anneal the substrates again at 500 °C for 30 min.

4. Deposition of Sb_2S_3 on the Substrate of mp-TiO_2/TiO_2-BL/FTO Glass

1. Treat the substrates with a UV/O_3 cleaner for 20 min to clean the surface, and transfer them to the glove box.
2. Spin coat a DMF solvent on the substrates at 3,000 rpm for 60 s prior to spin coating them with the $SbCl_3$-TU solution.
3. Heat the as-coated substrates for 5 min by placing them on a hot plate at 150 °C for a partial thermal decomposition and the amorphous phase formation.
4. Place the samples on a preheated hot plate at 300 °C for 10 min for the crystalline phase formation.
5. After cooling the samples to room temperature, remove them from the glove box.

5. Fabrication of Sb_2S_3-sensitized Solar Cells

1. Add 15 mg of poly(3-hexylthiophene) (P3HT) to 1 mL of chlorobenzene and gently stir them until a clear reddish solution is obtained.
2. Spin coat chlorobenzene on the Sb_2S_3-deposited substrate at 3,000 rpm for 60 s.
3. Immediately spin coat again with the prepared P3HT solution under the same conditions as used in step 5.2.
4. Transfer the samples into a vacuum chamber of the evaporator.
5. Deposit 100 nm gold with a rate of 1.0 Å/s.

Representative Results

Figure 1 shows a schematic representation of the experimental procedure for the Sb_2S_3 deposition on the substrate of mp-TiO_2/TiO_2-BL/FTO glass. **Figure 1d** shows the basic properties and scheme of a typical product fabricated by the method described herein. The main X-ray diffraction (XRD) pattern is well matched with that of a stibnite Sb_2S_3 structure[1,3,4] and impurity phases, such as Sb_2O_3, are not visible except for substrate phases (denoted as T and F). In addition, the absorption edge at approximately 730 nm, as shown in the inset of the XRD pattern, is consistent with the band gap (E_g) of Sb_2S_3 (1.7 eV)[1,3,4,9]. These results confirm that quality Sb_2S_3 can be successfully fabricated through the method presented herein.

To fabricate high-performance Sb_2S_3-sensitized solar cells with a > 5% efficiency using this method, three key deposition steps that significantly affect the quality of the final product should be considered during the Sb_2S_3 deposition. These steps are the TiO_2-BL deposition, the mp-TiO_2 deposition, and the $SbCl_3$-TU solution deposition. Here, we show the factors during the Sb_2S_3 deposition that affect the photovoltaic (PV) performance.

In the step of the TiO_2-BL deposition (key step 1), the thickness of TiO_2-BL can be controlled by repeating the two steps of spin coating with the TiO_2-BL solution and drying the substrate. **Figure 2a** shows the cross-sectional field emission scanning electron spectroscopy (FESEM) images of the devices fabricated with different TiO_2-BL thicknesses. The TiO_2-BL thickness linearly increases from 46 to 260 nm as the number of repetition times from 1 to 6 increases, as shown in **Figure 2a** and **2b**. In terms of the PV device performance, as measured by PCE, the highest PCE values were observed at a BL thickness of approximately 130 nm (repetition times of 3).

Figure 3a and **3b** show the cross-sectional FESEM images of substrates with different mp-TiO_2 thickness and their current density-voltage (J-V) curves as a function of mp-TiO_2 thickness, respectively. The mp-TiO_2 thickness is controlled by choosing different mesh types of the polyester mask. As the mesh count (per inch) of the mask increases from 250 to 460, the mp-TiO_2 thickness decreases from 1600 to 830 nm, as shown in **Figure 3a**. The PV performance remained similar in the mp-TiO_2 thickness range of 830 - 1200 nm, but further thickness increase led to a reduced efficiency (**Figure 3b**).

In order to investigate the effects of the $SbCl_3$:TU molar ratio in key step 3, the absorption properties of the samples prepared with different molar ratios of the $SbCl_3$-TU precursor solutions were examined. As shown in **Figure 4a**, the absorption remarkably increased with a TU increase in ratio to 1:2.0; however, it gradually decreased with further TU content increases. To investigate the change of E_g, Tauc plots derived from the absorption spectra were investigated[10]. The result indicates a different $(\alpha h\nu)^2$ value but the same E_g of 1.7 eV. The best device performance was obtained around the molar ratio of $SbCl_3$:TU = 1:2.0[3], as shown in **Table 1**.

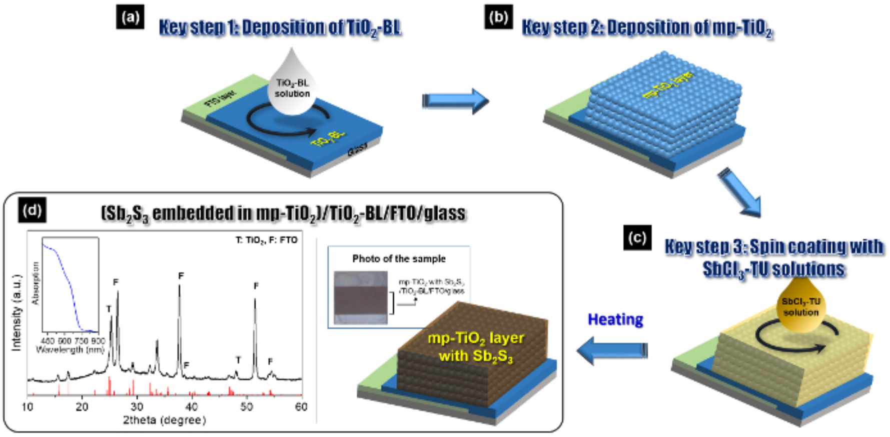

Figure 1: A schematic diagram of the deposition procedure for the Sb_2S_3 deposition on the substrate. (**a**), (**b**), and (**c**) These panels shows the three key experimental steps. (**d**) This panel shows the resultant sample composed of (mp-TiO_2 with Sb_2S_3)/TiO_2-BL/FTO glass. In the XRD pattern, the standard stibnite Sb_2S_3 structure (JCPDS No. 42-1393) is plotted as the red column. This figure has been modified from Choi *et al.*[3]. Please click here to view a larger version of this figure.

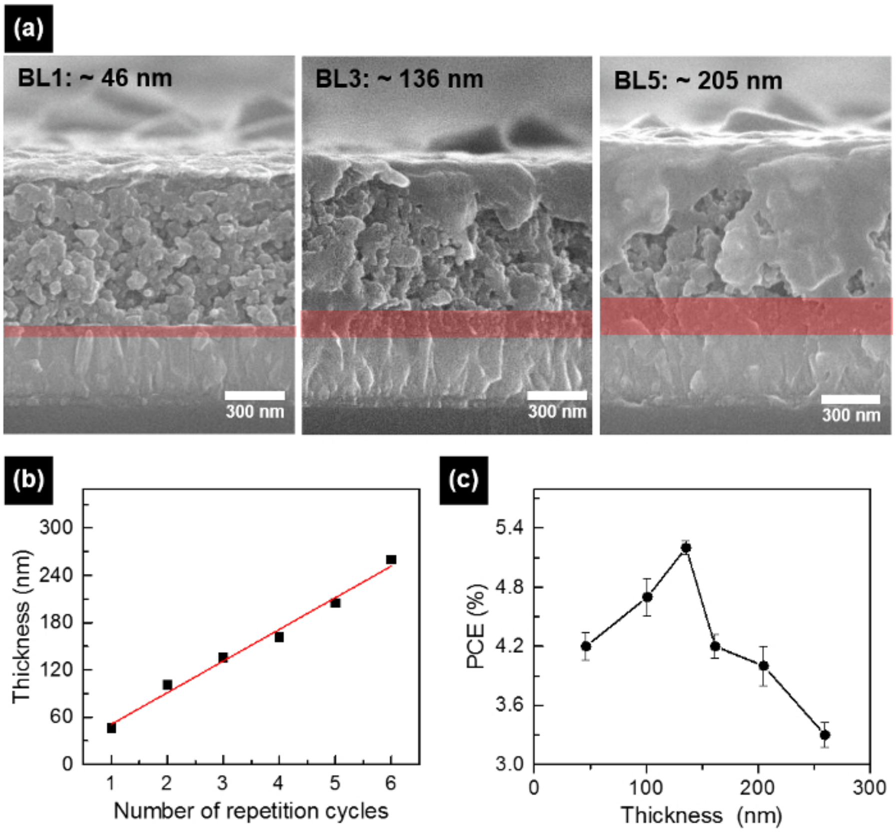

Figure 2: The effects of TiO_2-BL thickness in key step 1. (**a**) This panel shows cross-sectional FESEM images of photovoltaic devices fabricated with different TiO_2-BL thicknesses. In the images, BL# means the TiO_2-BL fabricated by # of times repetition, and the part of TiO_2-BL is marked with a red rectangle. (**b**) This graph shows the TiO_2-BL thickness as a function of the repetition number. (**c**) This panel shows a PCE graph as a function of TiO_2-BL thickness. The symbols and error bars in panel **c** are averages and standard deviations, respectively, obtained from the PCE data of ten devices. Please click here to view a larger version of this figure.

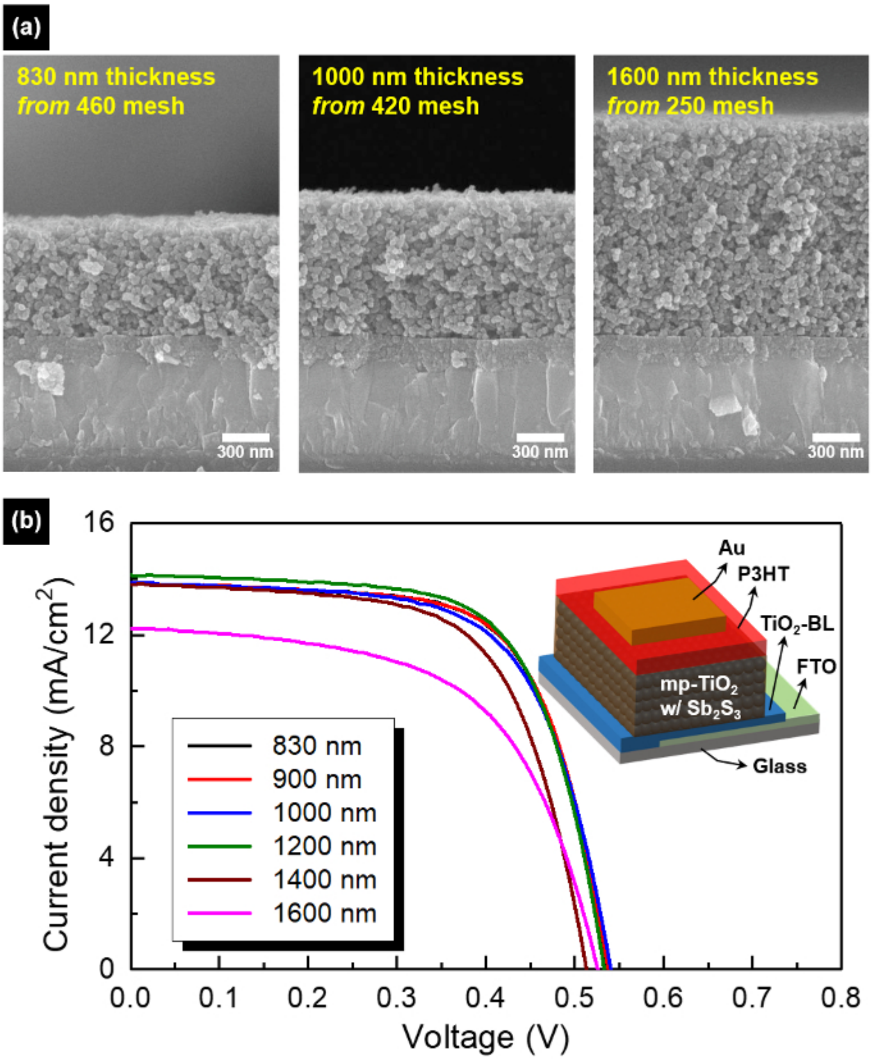

Figure 3: The effects of mp-TiO$_2$ thickness in key step 2. (**a**) This panel shows cross-sectional FESEM images of the substrates with different mp-TiO$_2$ thicknesses. (**b**) This panel shows a variation of the J-V curves as a function of mp-TiO$_2$ thickness. Please click here to view a larger version of this figure.

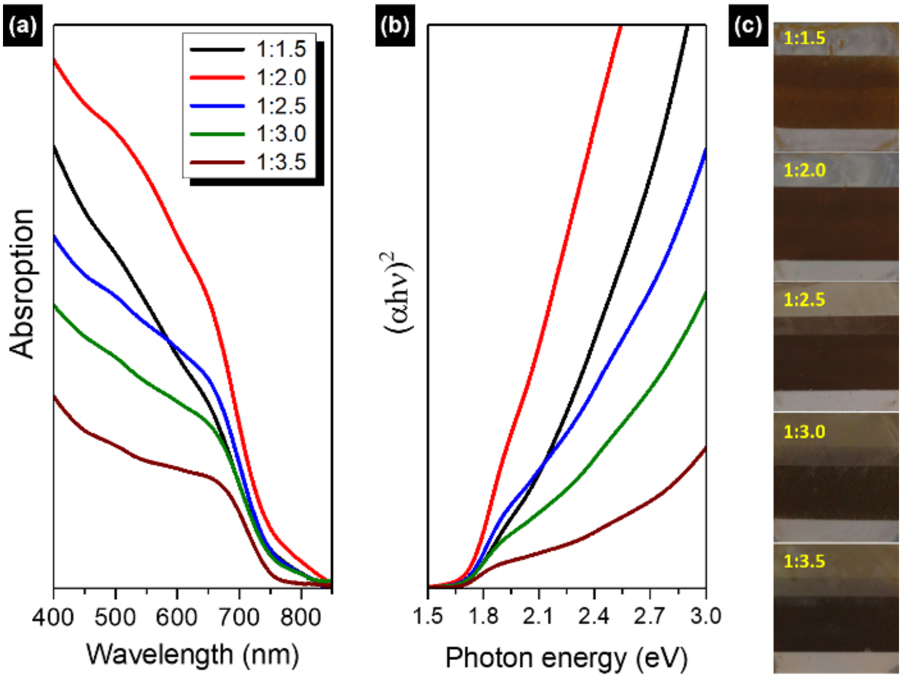

Figure 4: The effects of the molar ratio of $SbCl_3$/TU in key step 3. These panels show (**a**) the absorption, (**b**) the graph of a Tauc plot, and (**c**) photos of samples fabricated with different $SbCl_3$:TU molar ratios. The Tauc plot was obtained by assuming that Sb_2S_3 has a direct E_g. Please click here to view a larger version of this figure.

$SbCl_3$:TU Ratio	J_{SC} (mA cm^{-2})	V_{OC} (mV)	FF (%)	PCE (%)	R_{SH}/R_S (Ω cm^2)
1:1.4	12.2	475.4	61.7	3.8	582.4/7.1
1:1.6	12	487.4	66.4	4.1	1135.4/6.5
1:1.8	12.7	493.4	66.5	4.4	1217.3/6.8
1:2.0	13.1	493.4	61.6	4.2	644.7/7.8
1:2.2	13	487.4	59.4	3.9	541.8/8.9

Table 1: The effects of the molar ratio of $SbCl_3$/TU on the photovoltaic performance. J_{SC}, V_{OC}, and FF indicate the short-circuit current density, open-circuit voltage, and fill factor, respectively. The table has been reproduced from Choi *et al.*[3].

Supplementary Figure S1: The effects of the presence of mp-TiO_2. These panels show the typical (**a**) device performance and (**b**) absorption properties depending on the presence of mp-TiO_2. The samples were fabricated under the same conditions as those used for **Figure 2**. Mp-TiO_2 with a 1 µm thickness was used for the comparison. Please click here to download this file.

Discussion

TiO_2-BL is widely used as a hole-blocking layer in solar cells. As shown in **Figure 2**, a large difference was observed in the device performance depending on the TiO_2-BL thickness. Therefore, its thickness should be optimized to obtain the best overall device performance, because it critically acts as a hole-blocking layer to prevent any direct contact between FTO and hole-transporting materials[11]. It should be noted that the optimum thickness varies depending on the TiO_2-BL solution species, FTO types, method, light absorbers, and device architectures. In addition to the TiO_2-BL thickness, it should be scanned for annealing conditions including temperature and time in terms of the defect control of TiO_2[12].

In the device created with this protocol, the mp-TiO_2 plays a crucial role in achieving a high performance for two reasons. First, devices with mp-TiO_2 generally have higher J_{SC} values than those without mp-TiO_2, due to the higher absorption characteristics obtained from the Sb_2S_3 deposited on mp-TiO_2, as shown in **Supplementary Figure S1**. Second, the Sb_2S_3 fabricated *via* this protocol is easily formed into an island shape rather than a compact thin film on a planar surface[13]. This leads to an undesirable direct contact between the HTM and the TiO_2-BL in planar solar cells. Therefore, it is essential to use mp-TiO_2 in the device introduced here and to find the optimum thickness of mp-TiO_2 for achieving a high performance. For the solar cells fabricated with mp-TiO_2, the mp-TiO_2 thickness is considered as a key factor for obtaining solar cells of high performance and varies depending on the types of materials deposited on the surface of mp-TiO_2. For example, mp-TiO_2 with a thickness of 5 - 30 µm and < 200 nm is typically applied in dye-sensitized[14] and hybrid perovskite solar cells[15,16,17], respectively, to achieve a good device performance. In the current Sb_2S_3-sensitized solar cells, the thickness of mp-TiO_2 of approximately 1 µm is more suitable for the best performance[3], but the optimum thickness may vary and mp-TiO_2 may not be needed depending on the method[2].

Determining the ideal $SbCl_3$:TU molar ratio is critically important because it strongly affects the absorption properties of the light sensitizer, which are closely related to J_{SC}, as shown in **Figure 4**. In addition, an optimized ratio can aid in forming high-purity Sb_2S_3 without impurities or residues. For the samples fabricated with higher TU ratios, elemental sulfur is formed on the surface, which interrupts the charge flow in the device[3]. Therefore, to obtain improved devices, the molar ratio should be optimized.

In this study, we have demonstrated three key experimental factors in the course of an Sb_2S_3 deposition and their effects on the PV device performance of Sb_2S_3-sensitized solar cells. The protocol presented here can be applied to other sensitizer type PV systems based on Sb_2Se_3[5], $Sb_2(S/Se)_3$[7], and $CuSbS_2$[8]. We strongly believe that this method provides guidance on accessing novel materials for PV systems.

Disclosures

The authors have nothing to disclose.

Acknowledgements

This work was supported by the Daegu Gyeongbuk Institute of Science and Technology (DGIST) R&D Programs of the Ministry of Science and ICT, Republic of Korea (Grants No. 18-ET-01 and 18-01-HRSS-04).

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