Effects of Surface Blocking Layer of Sb$_2$S$_3$ on Nanocrystalline TiO$_2$ for CH$_3$NH$_3$PbI$_3$ Perovskite Solar Cells

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ABSTRACT: Sb$_2$S$_3$ layers were inserted at the interface between TiO$_2$ and CH$_3$NH$_3$PbI$_3$ perovskite to create CH$_3$NH$_3$PbI$_3$ solar cells using inorganic hole transporting material (CuSCN). The CH$_3$NH$_3$PbI$_3$ layer was spin-coated by a one-drop method onto the nanocrystalline TiO$_2$ layer. The photoenergy conversion efficiencies were improved with Sb$_2$S$_3$ layers (the best efficiency: 5.24%). During the light exposure test without encapsulation, the CH$_3$NH$_3$PbI$_3$ solar cells without Sb$_2$S$_3$ deteriorated to zero efficiency in 12 h and were completely changed from black to yellow because the perovskite CH$_3$NH$_3$PbI$_3$ was changed to hexagonal PbI$_2$. With Sb$_2$S$_3$, on the other hand, the CH$_3$NH$_3$PbI$_3$ solar cells became stable against light exposure without encapsulation, which did not change the crystal structure or the wavelength edges of absorption and IPCE. Therefore, it was believed that degradation can occur at the interface between TiO$_2$ and CH$_3$NH$_3$PbI$_3$.

INTRODUCTION

Recently, solid-state printed solar cells using CH$_3$NH$_3$PbX$_3$ (X: halide) perovskite as a photoabsorber have been intensively investigated, by performing high photoenergy-conversion efficiencies of 9.7−15.7% using low-cost processes (spin coating). However, their stability has been ambiguous. At first, the stability of CH$_3$NH$_3$PbX$_3$ solar cells have been reported without encapsulation stored in the dark. Under constant illumination at 100 mW cm$^{-2}$, the CH$_3$NH$_3$PbX$_3$ stability test was performed with encapsulation. Although the CH$_3$NH$_3$PbX$_3$ exhibited very promising long-term stability, sealing by organic materials cannot be seamless against water and oxygen. Therefore, it is important to evaluate the stability under light irradiation without encapsulation. In this work, we investigated the stability of the perovskite CH$_3$NH$_3$PbI$_3$ under one sun irradiation (AM 1.5) without encapsulation.

In order to improve the stability of solar cells against light irradiation, the passivation of the TiO$_2$ photocatalytic effect should be considered using the surface blocking layer. Moreover, in the reports of dye-sensitized solar cells (DSCs) and extremely thin absorber (ETA) solar cells, which have been composed of nanocrystalline TiO$_2$ photoelectrodes like CH$_3$NH$_3$PbX$_3$ perovskite solar cells, the surface blocking layer can improve the photovoltaic characteristics by blocking the charge recombination between electrons in TiO$_2$ and holes in hole-transporting materials (HTM). Hence, the surface blocking layer on TiO$_2$ has two blocking functions: the blockings of the TiO$_2$ photocatalytic effect and the charge recombination in TiO$_2$ and HTM.

Usually, metal oxides are utilized for DSCs and ETA cells for such a surface blocking layer. In this report, however, Sb$_2$S$_3$ has been utilized as the surface blocking layer due to the facile fabrication on the nanocrystalline TiO$_2$ layer, the photostability, and the energy diagram to transport electrons from CH$_3$NH$_3$PbI$_3$ to TiO$_2$ (Figure 1), which can extend the distance between electrons and holes. Although there is a small energy wall between the conduction bands (spike) from CH$_3$NH$_3$PbI$_3$ to Sb$_2$S$_3$ (0.2 eV), this spike is quite similar to the energy diagrams in Cu(In,Ga)(S,Se)$_2$ (CIGS) solar cells between CIGS and buffering sulfides and can enhance the photoenergy conversion efficiency. Hence, it was expected that the insertion of the Sb$_2$S$_3$ layer between TiO$_2$ and CH$_3$NH$_3$PbI$_3$ might enhance the photovoltaic characteristics.

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Figure 1. Energy diagram of materials for carbon-doublebond-free printed CH$_3$NH$_3$PbI$_3$ perovskite solar cells.
In this report, three types of inorganic printed solar cells have been fabricated for the comparison of the photovoltaic effects, as shown in Figure 2. The first type of solar cell is \(\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{CuSCN}/\text{Au}\) (Figure 2a), which was published in our recent paper.\(^8\)\(^9\) Using a \(	ext{BaTiO}_3/\text{MgO}\) blocking layer on \(	ext{TiO}_2\) and Ti doping in the \(	ext{Sb}_2\text{S}_3\) layer, the conversion efficiency can be improved. However, such modifications have not been applied in this report for simplification. The second type of solar cell is \(\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{CuSCN}/\text{Au}\) (Figure 2b). This combination with inorganic hole-transporting material (HTM) was reported as \(	ext{CH}_3\text{NH}_3\text{PbI}_3\) perovskite solar cells, which can be carbon double-bond-free inorganic printed solar cells.\(^13\) The third type of solar cell is \(\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{CuSCN}/\text{Au}\) (Figure 2c), which is the new structure of this report. The insertion of the \(	ext{Sb}_2\text{S}_3\) layer at the interface of \(	ext{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3\) can improve not only the photoenergy conversion efficiency but also the stability against light exposure (AM 1.5, 100 mW cm\(^{-2}\)) without encapsulation.

In order to analyze the effect of the \(	ext{Sb}_2\text{S}_3\) layer in the interface between \(	ext{TiO}_2\) and \(	ext{CH}_3\text{NH}_3\text{PbI}_3\) for solar cells, measurements for UV/vis absorption spectroscopy, incident photon-to-current efficiency (IPCE), X-ray diffraction (XRD), and Fourier Transform-Infrared (FT-IR) spectroscopy were performed.

### EXPERIMENTAL SECTION

\(\text{TiO}_2\) electrodes were fabricated on F-doped \(\text{SnO}_2\)-coated glass plates [\(\text{FTO}; \text{TEC}-15\) (\(t = 2\) mm), NSG-Pilkington]. The edge of the \(\text{FTO}\) layer was first etched using \(\text{Zn}\) powder and \(\text{HCl}\) to eliminate shunting of the solar cell at the edge. The etched \(\text{FTO}\) substrate was put into an ultrasonic bath containing detergent, rinsed with water and ethanol, and then treated with a \(\text{UV}/\text{O}_3\) cleaner for 15 min. Dense \(\text{TiO}_2\) layers were coated on the \(\text{FTO}\) by spray pyrolysis using a solution of titanium diisopropoxide bis(acetylacetonate) (\(\text{TAA}; 0.6\) mL) in ethanol (9 mL, Kanto Chemical Co., Inc., Japan) on a hot plate at 450 °C. The \(\text{TAA}\) was prepared by pouring acetylacetone (Wako Pure Chemical Industries, Ltd., Japan) into titanium isopropoxide (Kanto Chemical Co., Inc., Japan) with the ratio of 2:1 (mol/mol).

A nanocrystalline \(\text{TiO}_2\) layer was fabricated by screen printing \(\text{TiO}_2\) paste that was synthesized by a hydrothermal method under basic conditions and annealed at 550 °C.\(^{14}\) The thickness of the nanocrystalline \(\text{TiO}_2\) layer was ca. 2 \(\mu\)m. \(	ext{Sb}_2\text{S}_3\) was deposited on the nanocrystalline-\(\text{TiO}_2\) electrodes by the chemical bath deposition (CBD) method from a solution of \(\text{SbCl}_3\) and \(\text{Na}_2\text{S}_2\text{O}_3\).\(^9\)\(^{12}\) The as-deposited orange films of amorphous \(	ext{Sb}_2\text{S}_3\) were annealed under \(\text{N}_2\) at 320 °C for 30 min to give a dark-brown crystalline stibnite. The samples were removed from the oven immediately after annealing and were allowed to cool in air and then were dipped into a 0.5 M aqueous KSCN solution for 5 min. The excess solution wicked off and dried at 80 °C. The \(	ext{Sb}_2\text{S}_3\) layer thickness was 1–2 nm, observed by TEM.\(^7\) The effect of \(	ext{Sb}_2\text{S}_3\) thickness is very important to this report. The thickness of \(	ext{Sb}_2\text{S}_3\) can be controlled by varying the deposition time, which will be a further target of research.

The \(\text{CH}_3\text{NH}_3\text{PbI}_3\) layer was deposited by spin coating under ambient conditions. The \(\text{CH}_3\text{NH}_3\text{PbI}_3\) solution was prepared from a mixture of \(\text{PbI}_2\) (1.1453 g, Kishida Chemical Co. Ltd., Japan) and \(\text{CH}_3\text{NH}_3\text{I}\) (0.395 g) in \(\gamma\)-butyrolactone (2 mL) (Kishida Chemical Co. Ltd., Japan). The \(\text{CH}_3\text{NH}_3\text{I}\) was synthesized by mixing \(\text{HI}\) (Tokyo Chemical Industry Co., Ltd., Japan) and \(\text{CH}_3\text{NH}_2\) (Tokyo Chemical Industry Co., Ltd., Japan) according to ref 15. 40 \(\mu\)L of \(\text{CH}_3\text{NH}_3\text{PbI}_3\) solution was dropped on the porous \(\text{TiO}_2\) layer and spin coated at 2000 rpm for 30 s. The acceleration was 667 rpm/s. During the spin coating, hot air from a hair drier was applied to the substrate.\(^13\)

After the deposition of \(\text{CH}_3\text{NH}_3\text{PbI}_3\), the substrate was annealed at 100 °C for 15 min under a \(\text{N}_2\) flow. \(\text{CuSCN}\) (Kishida Chemical Co. Ltd., Japan) layers and Au back contacts were deposited using the doctor blade process and vacuum evaporation, respectively.\(^9\)\(^{12}\)

Scanning electron microscope (SEM; JSM-6510, JEOL) was employed to evaluate the morphology of the films. The crystal structure was characterized using X-ray diffraction (XRD; Miniflex II, Rigaku) with Cu \(\text{K}α\) radiation. UV/vis absorption spectra were measured using a UV/vis spectrometer (Lambda 750, PerkinElmer). FT-IR spectra were measured using an FT-IR spectrometer with a diamond ATR (Frontier Optica, PerkinElmer). The size of the samples used for photocurrent–voltage (I–V) measurements was 25 mm\(^2\) (5 × 5 mm). An AM 1.5 solar simulator equipped with a 300 W Xe lamp (YSS-80A, Yamashita Denso) was employed for photovoltaic measurements. The power of the solar simulator light was calibrated to 100 mW cm\(^{-2}\) using a reference Si photodiode (Bunkou Keiki). I–V curves were obtained by applying an external bias to the cell and measurement of the generated photocurrent with a DC voltage current source (6240, ADCMT).

### RESULTS AND DISCUSSIONS

Figure 3 shows current–voltage curves of \(\text{CH}_3\text{NH}_3\text{PbI}_3\)-printed solar cells under light irradiation (AM 1.5, 100 mW cm\(^{-2}\)). The
photovoltaic characteristics were summarized in Table 1. Although we have published 4.1% and 5.7% conversion efficiencies using Sb$_2$S$_3$/CuSCN layers, the photovoltaic effect in Table 1a (TiO$_2$/Sb$_2$S$_3$/CuSCN/Au) is not significant (just 2.6% conversion efficiency) because of the absence of the BaTiO$_3$/MgO blocking layer on TiO$_2$ and because of Ti doping in the Sb$_2$S$_3$ layer. The solar cells of (b) (TiO$_2$/CH$_3$NH$_3$PbI$_3$/CuSCN/Au) performed high open circuit photovoltage ($V_{OC}$) and fill factors (FF), indicating that the highest efficiency conversion in the series of Table 1 due to the Sb$_2$S$_3$ effect. The photovoltaic characteristics of the best-efficiency cell were $V_{OC}$: 0.57 V, $J_{SC}$: 17.23 mA cm$^{-2}$, and FF: 0.52; $\eta$: 5.12%.

The light durability of inorganic printed solar cells using the CH$_3$NH$_3$PbI$_3$/CuSCN layer has been examined without encapsulation (Figure 4). The examined solar cells were (a) (FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$/CuSCN/Au) and (b) (FTO/TiO$_2$/Sb$_2$S$_3$/CH$_3$NH$_3$PbI$_3$/CuSCN/Au). Without Sb$_2$S$_3$, the stability of the solar cell was very poor. The photoenergy conversion efficiency deteriorated drastically within 5 h and became very close to zero within 12 h. With Sb$_2$S$_3$, the other hand, the conversion efficiency was maintained 65% of the initial conversion efficiency without encapsulation after the 12 h light irradiation. Therefore, the effect of the Sb$_2$S$_3$ layer in the TiO$_2}$/CH$_3$NH$_3$PbI$_3$ interface significantly affects the photo-energy conversion efficiency (Figure 3) and the light stability (Figure 4).

Figure 4 shows IPCE spectra of printed solar cells. The IPC edge of (a) a Sb$_2$S$_3$ absorber solar cell was 740 nm. Using CH$_3$NH$_3$PbI$_3$, the IPC edge was 800 nm. The absorption wavelength edges of Sb$_2$S$_3$ and CH$_3$NH$_3$PbI$_3$ layers (Figure 5) corresponded to the IPC spectra edges of Sb$_2$S$_3$ and CH$_3$NH$_3$PbI$_3$ solar cells, respectively. The insertion of the Sb$_2$S$_3$ layer at the interface between TiO$_2$ and CH$_3$NH$_3$PbI$_3$ enhanced the IPC value of CH$_3$NH$_3$PbI$_3$ from 50–60% to 70–80%. Moreover, the IPC edge of the CH$_3$NH$_3$PbI$_3$ solar cell with Sb$_2$S$_3$ light exposure for 12 h was kept at 800 nm, as with the fresh solar cell. If the CH$_3$NH$_3$PbI$_3$ layer lost the photovoltaic function in the (TiO$_2$/Sb$_2$S$_3$/CH$_3$NH$_3$PbI$_3$/ CuSCN/Au) cell and the resulting photovoltaic performance shifted to 530 nm, which was similar to PbI$_2$. The absorption spectrum of PbI$_2$ shows a shoulder from 520 to 620 nm, maybe due to the large grain on the PbI$_2$ layer. The spectrum of Sb$_2$S$_3$/CH$_3$NH$_3$PbI$_3$ was very close to only CH$_3$NH$_3$PbI$_3$ and did not change the absorption edge after the 12 h light exposure. Although more light has been absorbed by the cells without Sb$_2$S$_3$ than by those with Sb$_2$S$_3$ (Figure 5), the short circuit current density without Sb$_2$S$_3$ was lower than that with Sb$_2$S$_3$ (Figure 3). Therefore, it can be speculated that the internal absorbed photon-to-current conversion efficiency (APCE) with Sb$_2$S$_3$ might be higher than that without Sb$_2$S$_3$.

The fresh layers of Sb$_2$S$_3$ and CH$_3$NH$_3$PbI$_3$ have absorption edges at 740 and 800 nm, respectively. However, after 12 h irradiation, the band edge of CH$_3$NH$_3$PbI$_3$ was
the interface between (e) TiO2 and CH3NH2PbI3, the CH3NH2PbI3 crystal structure was retained as perovskite under the 12 h light exposure. A small peak of PbI2 emerged again after the light exposure in the (e) Sb2S3/CH3NH2PbI3 layer, which may be due to the segregation of PbI2 by the removal of CH3NH2 and HI from the CH3NH2PbI3 layer surface.

Figure 8 shows FT-IR spectra of the CH3NH2PbI3 layer on TiO2: (a) in the fresh layer, (b) after 12 h of light exposure without Sb2S3, and (c) after 12 h of light exposure with Sb2S3. The apparent peaks by methylamine were observed as a line (a). Due to the thick layer of CH3NH2PbI3, the background of TiO2 (below 1000 nm) was depressed, which was observed as lines (b and c). After the light exposure test without Sb2S3 as line (b), the layer became yellow and the FT-IR peaks of methylamine disappeared. Hence, the CH3NH2PbI3 changed to PbI2. On the other hand, with Sb2S3, the FT-IR peaks of methylamine remained as line (c). The large increase from 1000 to 3000 nm may be attributed to H2O adsorbed into the CH3NH2PbI3 layer during the 12 h light exposure, which was not observed in the (a) fresh CH3NH2PbI3 layer without H2O adsorption or in the (b) PbI2 layer due to the absence of CH3NH2. Therefore, although the top surface of CH3NH2 was removed from the CH3NH2PbI3 layer, the Sb2S3 layer retained the CH3NH2PbI3 perovskite crystal structure.

Figure 9 shows the reaction scheme used to consider the degradation effect of the CH3NH2PbI3 layer against the light exposure without encapsulation. Without Sb2S3, the CH3NH2PbI3 layer can change to PbI2 with losing CH3NH2 and HI (eq 1) by overnight light exposure (Figure 9a).

\[
\text{CH}3\text{NH}2\text{PbI}_3 \rightleftharpoons \text{PbI}_2 + \text{CH}_3\text{NH}_2 + \text{HI}
\] (1)

On the other hand, with Sb2S3, the CH3NH2PbI3 layer can be stabilized and made durable against light exposure (Figure 9b). Therefore, the decomposition of CH3NH2PbI3 occurs at the interface between TiO2 and CH3NH2PbI3. TiO2 has a strong ability to extract electrons from organic materials as photocatalysts and from iodide (I2) as electrodes in dye-sensitized solar cells. Hence, the driving force of the decomposition may be due to the effect of electron extraction by TiO2 from an iodide anion. The possible reaction at the TiO2 surface may be as eqs 2–4:

\[
2\text{I}^- \rightleftharpoons \text{I}_2 + 2e^-
\] [at the interface between TiO2 and CH3NH2PbI3] (2)

\[
3\text{CH}_3\text{NH}_3^+ \rightleftharpoons 3\text{CH}_3\text{NH}_2^+ + 3\text{H}^+
\] (3)
The CH3NH3PbI3 perovskite crystal is composed of CH3NH3+ ions, Pb\(^{2+}\) ions, and I\(^{-}\) ions. At first, TiO\(_2\) can extract electrons from I\(^{-}\), resulting in I\(^{-}\), which deconstructs the perovskite crystal. Equation 3 is in equilibrium with water. Assisted with water, the pK\(_a\) of the equation (CH3NH3\(^{+}\) + H\(_2\)O \rightleftharpoons CH3NH\(_2\) + H\(_3\)O\(^{+}\)) is 10.8.\(^{16}\) Which suggests that the equilibrium is basically shifted to the left side but that the elimination of CH3NH\(_2\) and H\(^{+}\) (or H\(_3\)O\(^{+}\)) can shift the equilibrium to the right side. Without the perovskite structure, the equilibrium (eq 3) may shift to the right side easily. The electron extracted by TiO\(_2\) can return to the TiO\(_2\) surface, and eq 4 can occur while emitting HI and CH3NH2. Losing H\(^{+}\) by eq 4, the equilibrium of eq 3 can shift to the right side with the emission of CH3NH2 because of the low boiling point of CH3NH\(_2\) (17 °C).\(^{16}\) In contrast, the Sb\(_2\)S\(_3\) layer (Figure 9b) can deactivate the reaction of I\(^{-}/I\(^2\)) at the surface of TiO\(_2\), the electrons can shift from the conduction band of CH3NH3PbI\(_3\) and the CH3NH3PbI\(_3\) layer can be stabilized and made durable against light exposure. Although the reaction of the decomposition scheme is somewhat of a speculation, it can be deduced that the presented reaction scheme is the most probable one due to the results shown above. In order to provide concrete evidence, we are managing further research at present.

The improvement in PCE should be attributed directly to enhancement of the charge recombination and a decrease in the V\(_{OC}\). However, this prohibition of the TiO\(_2\) photocatalysis may enhance the stability of the perovskite layer.

In conclusion, CH3NH3PbI\(_3\) perovskite solar cells using an inorganic hole transporting material (CuSCN) with/without Sb\(_2\)S\(_3\) by chemical bath deposition at the interface between TiO\(_2\) and CH3NH3PbI\(_3\) were fabricated. The Sb\(_2\)S\(_3\) layer was improved for higher photovoltaic effects. Light exposure tests of CH3NH3PbI\(_3\) perovskite solar cells have been performed without encapsulation. During the light exposure test without Sb\(_2\)S\(_3\), the black CH3NH3PbI\(_3\) layers were completely changed to yellow, because the perovskite CH3NH3PbI\(_3\) was changed to hexagonal PbI\(_2\). With Sb\(_2\)S\(_3\), on the other hand, the CH3NH3PbI\(_3\) perovskite solar cells did not change structures (measured by XRD), and the wavelength edges of absorption and IPCE spectra also did not change. Therefore, it was understood that Sb\(_2\)S\(_3\) elongates the lifetime of the CH3NH3PbI\(_3\) perovskite structure during light exposure and that the degradation origin of the CH3NH3PbI\(_3\) perovskite layer is the interface between TiO\(_2\) and CH3NH3PbI\(_3\). The degradation is related to the unfixed positioning of the CH3NH3\(^{+}\) cation in the CH3NH3PbI\(_3\) perovskite crystal.\(^{17-19}\) However, the degradation effect by water is still not clear. Bromide doping enhanced the stability of the CH3NH3PbX\(_3\) solar cells against moisture.\(^{3}\) At the same time, water should affect the lithium salt doped in the HTM layer for the CH3NH3PbX\(_3\) solar cells. The photovoltaic performance after 12 h has not been checked. After using a very stable device, the light stability after over 1000 h shall be checked in the further research. Further investigation is necessary to understand the inside of the degradation mechanism.

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**Notes**

The authors declare no competing financial interest.

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### REFERENCES


