Photocurrent enhancement by incorporation of air-stable Cs$_2$SnI$_6$ Perovskite in dye-sensitized solar cell

H Pujiarti$^1$, P Wulandari$^{1,*}$ and R Hidayat$^1$

$^1$Physics of Magnetism and Photonics Research Division, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jl.Ganesha 10, 40132, West Java, Indonesia

E-mail: *wulan@fi.itb.ac.id

Abstract

Cs$_2$SnI$_6$ is an inorganic lead-free perovskite variant which is air and thermal stable and its application in the third generation of photovoltaic devices is undergoing rapid expansion over the past few years. This paper presents a fabrication of dye-sensitized solar cell (DSSC) with the incorporation of Cs$_2$SnI$_6$ perovskite in the active layer of N-719 dye. The absorbance spectra of N-719 dye on TiO$_2$ mesoporous layer is found to increase by the addition of 2 wt% and 3 wt% of Cs$_2$SnI$_6$ in N719 dye in comparison to the reference of N-719 dye leading the role of Cs$_2$SnI$_6$ as photon absorber in the devices. Our fabricated DSSC device reveals a photocurrent enhancement from 6.36 mA/cm$^2$ to 12.87 mA/cm$^2$ by the addition of 3 wt% of Cs$_2$SnI$_6$, along with the enhancement of power conversion efficiency from 1.71% to 3.94%.

1. Introduction

Over the past few years, metal halide perovskites with superior advantages in optical and electrical properties have been considered as a promising material for applications in photovoltaic devices. These perovskite solar cells have been much improved with high power conversion efficiencies (PCE) over 20%. Spiro-OMeTAD derivatives have been much used as the hole transporting material (HTM), for instance, in perovskite solar cells with the TiO$_2$/CH$_3$NH$_3$PbI$_3$/HTM/Au structure configurations. The PCE increased from 15% to 16.7% for conventional p-OMe substituents [1]. Zhou et al. have reported a controlled formation of the perovskite layer, which can suppress carrier recombination in the absorber, facilitate carrier injection into the carrier transport layer and maintain good carrier extraction at the electrodes. In addition, PCE of these perovskite solar cells can be improved from 16.5% on average to the highest efficiency of ~19.3% in a planar geometry without anti-reflective coating [2].

Dye-Sensitized Solar Cells (DSSCs) are organic solar cells with monolayer dye molecules as active material. Since the first fabrication in 1991 by O’Regan and Gratzel [3], DSSCs have received much attention because of their environmentally friendly, using non-toxic materials, easy fabrication, and low-cost production [4,5]. Generally, the structure of DSSC consists of photoelectrode, electrolyte and cathode or counter electrode. Photoelectrode is the key factor which is responsible for light harvesting production and the existence of active material inside photoelectrode to absorb incident light. There are so many improvements and modification which have been done for the optimization purpose of the
active material. The ruthenium-based dye was commonly used because of their favorable photoelectrochemical properties and high stability in the oxidized state, making practical applications feasible [6]. In recent years, the perovskite materials become popular materials as an electron transporting materials [7] or as a photoanode [8]. Shin et al. have modified the perovskite BaSnO₃ (BSO) nanoparticles with the treatment of TiCl₄. TiCl₄ treatment was found to form an ultrathin TiO₂ layer on the BSO surface. The doctor blade method was used to deposit of the perovskite paste. They obtained the highest PCE of 5.5% after a TiCl₄ treatment in 3 min (cf. 4.5% for bare BSO). Increasing BSO film thickness led to an increase in PCE up to 6.2%. Lung-Chie and co-workers used (CH₃NH₃)PbI₃ perovskite that was deposited on the TiO₂ layers via spin coating. In this work, they introduced 20% and 40% perovskite materials into the DSSC and obtained PCE up to 33% and 59% higher than the traditional DSSC.

In this research work, we synthesized an air-stable metal halide perovskite Cs₂SnI₆ by using a simple chemical reaction in solution. We introduced this type of perovskite into the conventional DSSC, by mixing this perovskite into the dye N719, and then investigated the J-V characteristics.

2. Experiments

2.1. Synthesis of Cs₂SnI₆

Hydriodic acid (HI), cesium carbonate (Cs₂CO₃), and stannic iodide (SnI₂) were purchased from Sigma-Aldrich and used without any further purification. The acidic cesium iodide (CsI) solution was prepared by solving 325 mg of Cs₂CO₃ into 2 mL of HI in a beaker glass and stirred at room temperature to form a homogenous solution. A 313 mg of SnI₂ was dissolved in 1 mL of warm ethanol and stirred to form a homogenous orange solution. Next, the SnI₂ solution was then added into the acidic CsI solution and stirred vigorously for 10 min to yield black powder precipitate. The final solution was purified for 3 times by using ethanol (C₂H₅OH, Merck). The top solution was taken out and the black precipitate was re-dispersed and then dried at room temperature. Our synthesized result of black powder Cs₂SnI₆ is quite stable at room temperature.

2.2. Fabrication of Photoelectrode

Fabrication of DSSC refers to our previous works [9,11], except for the dye preparation. In this work, we use N719 dye with the addition of Cs₂SnI₆ perovskite. The photoelectrodes were prepared as followings. FTO glass (15Ω/sq, Solaronix) was firstly washed with detergent. Then it was cleaned by using an ultrasonic bath with acetone and isopropanol (1:1) for 15 min and drying. Afterward, a compact blocking layer of TiO₂ (Blocking Layer, Dyesol) was deposited onto FTO by spin coating method with 5000 rpm for 30 min and heated at 500 °C for 30 min. The next layer was a porous TiO₂ (TiO₂ DSL, Dyesol) layer deposited by a screen-printing technique with ~14 μm thickness. Then the screen printed films were heated at 100 °C for 15 min, at 300 °C for 15 min, and at last at 500 °C for 30 min. Finally, the films were treated in a 40 mM Ti-isopropanoxide solution in isopropanol and sintered at 500 °C for 30 min. After cooling down naturally to 80 °C, these TiO₂ electrodes were immersed into 0.7 mM Ruthenium (N719, Solaronix) dye solution in GBL mixed with Acetonitrile 1:8 volume ratio, respectively.

In this work, we used three different dye compositions, which were referred as Ref for the DSSC using N719 dye only, Sample 1 for DSSC using the N719 dye with 2 wt% of Cs₂SnI₆ perovskite and Sample 2 for the DSSC using N719 dye with 3 wt% of Cs₂SnI₆ perovskite.

2.3. DSSC assembly and characterization

The photoanode and the Pt drilled counter electrode (Solaronix) were sealed together with a 25 μm Surlyn (Solaronix) spacer using hot press equipment. Then the ionic liquid electrolyte (Mosalyte TDE 250, Solaronix) was injected into the cell using a vacuum pump. The morphology of TiO₂ nanoparticles and the thickness of the layer were observed by SEM, and its porosity analyzed by the PoreDizM70 Matlab program [11]. The characterization of these spectra of N-719 dye incorporated with Cs₂SnI₆ in
the TiO$_2$ mesoporous layer was done by UV-Vis spectroscopy. The photocurrent-voltage characteristics were measured using a digital electrometer under light illumination of 100 mW/cm$^2$.

3. Results and Discussion

3.1. Synthesis result of Cs$_2$SnI$_6$
Cs$_2$SnI$_6$ perovskite has been successfully synthesized by a simple chemical reaction in solution by mixed an acidic solution of CsI and a stannic iodide (SnI$_4$) solution and revealed black precipitate powder of Cs$_2$SnI$_6$ (data shown in previous work). The grain size of Cs$_2$SnI$_6$ powder is found in the range of 0.5 – 4 µm.

3.2. Porosity of TiO$_2$
Figure 1 shows a Scanning Electron Micrograph (SEM) image of mesoporous TiO$_2$ film fabricated by screen printing method from TiO$_2$ paste. From the porosity analyzed using the PoreDizM70 Matlab program, we found that the mean pore diameters are estimated to be about 60 nm while the particle sizes are about 30-40 nm.

![Figure 1. SEM image of TiO$_2$ mesoporous film](image)

3.3. UV Vis Spectra
The absorption spectra of TiO$_2$ layers containing dye and Cs$_2$SnI$_6$ are shown in Figure 2. It has been well-known that the N-719 dye has a broad absorption peak in the visible light region (400 – 700 nm). It shows the enhancement of absorbance peaks for the sample with the addition of Cs$_2$SnI$_6$ perovskite in N719 dye solution which indicates the play role of Cs$_2$SnI$_6$ to participate in light absorption.

3.4. Photovoltaic Characteristics
Incorporation of Cs$_2$SnI$_6$ perovskite inside DSSC device can be investigated from photovoltaic characteristics of DSSC as shown in Figure 3. The current density-voltage (J-V) characteristics curve of the fabricated device was obtained from the J-V measurements. The parameter performances of DSSC including PCE and FF are summarized in Table 1. It shows that the PSC of DSSC using N719 dye only,
or the Ref cell, is 1.71%. In the case of Sample 1, namely DSSC using 2 wt% Cs$_2$SnI$_6$ perovskite, the PCE increases up to 3.08%. The short-circuit photocurrent density also increases further for Sample 3, namely the DSSC using 3 wt% Cs$_2$SnI$_6$ perovskite. The PCE of this Sample 3 increases up to 3.94%. Therefore, the addition of Cs$_2$SnI$_6$ perovskite into the N719 dye active material increases the DSSC PCE up to 80% and 130% of the reference cell based on N719 dye only.

![Figure 2](image2.png)

**Figure 2.** The absorption spectra of N-719 dye incorporated with Cs$_2$SnI$_6$ in the TiO$_2$ mesoporous layer.

![Figure 3](image3.png)

**Figure 3.** The photocurrent density-voltage ($J$-$V$) characteristics of the fabricated DSSCs incorporating Cs$_2$SnI$_6$ perovskite.
Table 1. The parameter photovoltaic performances of DSSC incorporation of Cs$_2$SnI$_6$ perovskite

| Sample  | $J_{sc}$ (mA/cm$^2$) | Voc (V) | FF (%) | Eff. (%) | Enhanced Efficiency |
|---------|----------------------|---------|--------|----------|--------------------|
| Ref     | 6.36                 | 0.65    | 41.3   | 1.71     | -                  |
| Sample 1| 11.01                | 0.67    | 41.7   | 3.08     | 80%                |
| Sample 2| 12.87                | 0.67    | 45.8   | 3.94     | 130 %              |

Figure 4 shows the relationship between the short-circuit photocurrent density and the open circuit voltage of the fabricated DSSCs. The increasing of $J_{sc}$ is the result of photon absorption enhancement due to the incorporation of Cs$_2$SnI$_6$ perovskite.

4. Conclusions

The solar cell characteristics of DSSCs with the addition of Cs$_2$SnI$_6$ perovskite in N719 dye have been investigated. The addition of Cs$_2$SnI$_6$ perovskite into N719 sensitizing dye enhanced the light absorption as evident from their absorption spectra. It also led to the increase in their solar cell performances, where $J_{sc}$ increased from 6.36 mA/cm$^2$ to 12.87 mA/cm$^2$ by addition of 3 wt% Cs$_2$SnI$_6$, along with the PCE improvement from 1.71% to 3.94%.

References
[1] Jeon N J, Lee H G, Kim Y C, Seo J, Noh J H, Lee J and Seok S I L 2014 J Am Chem Soc 136 7837-7840
[2] Zhou H P, Chen Q, Li G, Luo S, Song T, Duan H S, Hong Z, You J B, Liu Y S, Yang Y 2014 Science 345 542-546
[3] O’Regan and Gratzel M 1991 Nature 353 737-740
[4] Sarker S, Ahammad A J S, Seo H W and Kim D M 2014 Int. J. of Photoenergy ID 851705 1-17
Acknowledgments
The authors acknowledge the financial support from P3MI ITB 2018.

[5] Lung-Chie, C and Yi-He, C 2015 Science of Advane Materials 7 (8) 1636-1639
[6] Qin Y and Peng Q 2012 Int. J. of Photoenergy ID 291579 1-21
[7] Shin S S, Kim J S, Suk J H, Lee K D, Kim D W, Park J H, Cho I S, Hong K S and kim J Y 2013 ACS Nano 7 (2) 1027-1035
[8] Okamoto Y and Suzuki Y 2014 Journal of the Ceramic Society of Japan 122 (8) 728-731
[9] Arsyad W S, Bahar H, Prijamboedi B and Hidayat R 2018 Ionics 24 901–914
[10] Lee B, Stoumpos. C C, Zhou N, Hao F, Malliakas C, Yeh C Y, Marks T J, Kanatzidis M G and Chang R P H 2014 J. Am. Chem. Soc 136 15379
[11] Pujiarti H, Arsyad W S, Shobih, Muliani L and Hidayat R 2018 J. Phys.: Conf. Ser. 1011 012020