Controlled synthesis of lead-free perovskite Cs$_2$SnI$_6$ as hole transport layer in dye sensitized solar cells

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Abstract. Hybrid organic-inorganic perovskite material is undergoing rapid expansion over the past few years due to their application in solar cells. In particular, tin (Sn)-based perovskite has been considered to replace lead (Pb)-based perovskite because of toxic issues and it can cause adverse environmental impact. Cesium tin halide based perovskite (Cs$_2$SnI$_6$) material appears promising for large scale module fabrication and also oxygen and moisture stable because of high oxidation state of tin. In this study, we successfully synthesized Cs$_2$SnI$_6$ perovskite by mixing process of cesium carbonate (Cs$_2$CO$_3$) in hydriodic acid (HI) solvent and stannic iodide (SnI$_4$) in ethanol solvent to form precipitate and all the processes was done in air and room temperature. Cubic crystal structure of perovskite was confirmed by X-ray Diffraction (XRD) measurement in comparison to the crystal structure of Pb-based perovskite. Scanning Electron Microscope (SEM) revealed morphology of Cs$_2$SnI$_6$ with the size of 0.4 – 5 mm. We controlled the solutions of Cs$_2$SnI$_6$ by mixing two kinds of solvent (gamma-butyrolactone and acetonitrile) with different volume ratio and the Cs$_2$SnI$_6$ thin films were confirmed by used of UV-vis spectrometer. The absorbance spectra give a characteristic two humps feature due to the specific band structure of Cs$_2$SnI$_6$ and it indicates the direct band gap about 2.8 eV.

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. Development of metal halide perovskites as solar cell absorber has been increased significantly and demonstrated high power conversion efficiencies over 20%. Three spiro-OMeTAD derivatives were synthesized and employed as hole transporting material (HTM) in the structure of solar cell of TiO$_2$/CH$_3$NH$_3$PbI$_3$/HTM/Au. Highly improved performance of power conversion efficiency (PCE) increase to 16.7% from 15% for conventional p-OMe substituents [1]. Zhou et.al. controlled formation of perovskite layer, suppressed carrier recombination in the absorber, facilitated carrier injection into the carrier transport layer and maintained good carrier extraction at the electrodes. Cell PCE is typically boosted to 16.5% on average with the highest efficiency of ~19.3% in a planar geometry without antireflective coating [2].

In general, metal halide perovskites have a crystal structure with ABX$_3$ formula. The A, B and X are the organic or inorganic cation (CH$_3$NH$_3^+$, Cs$^+$), the metal cation (Pb$^{2+}$, Sn$^{2+}$, or Cu$^{2+}$), and the halide anion (Cl, Br, or I), respectively. The A and B cations have very different ionic radii and the X anions bond to both cations. The A cations coordinate with 12 anions X forming cuboctahedral...
geometry (AX$_{12}$ polyhedron) and the B cations coordinate with six anions X forming octahedral geometry (BX$_6$ configuration) [3]. Development of metal halide perovskite have to face the problem regarding to instability and toxicity issues especially for perovskite material based on lead (Pb). Peedikakkandy et al. reported synthesis and stability analysis of cesium tin iodide (CsSnI$_3$) prepared through solid state and solution route methods for its application as HTM in dye sensitized solar cell (DSSC) [4]. Lead-free hybrid tin halide perovskites (MASnI$_3$Br$_{1.5}$) were prepared and investigated by a rapid screening technique and it exhibits enhanced performance and stability in liquid-junction PEC solar cells, with PCE of 1.51% (an increase of 20.8%) in comparison to MASnI$_3$ perovskites [5]. Wang et al. developed a facile solution-phase hot injection approach for shape-controlled synthesis of lead-free and stable single crystalline perovskite derivative Cs$_2$SnI$_6$ nanocrystals [6]. Cs$_2$SnI$_6$ perovskite as a hole transporter has been demonstrated in solid-state DSSC with a mesoporous TiO$_2$ film, where doping of this perovskite with additives helps to reduce the internal device resistance and improving cell efficiency about 4.7% [7].

In this research work, we attempt to synthesize a lead-free metal halide perovskite based on Sn (Cs$_2$SnI$_6$) by used of simple chemical reaction in solution. We also control the homogenous formation this type of perovskite by used of organic solvents engineering for application in dye-sensitized solar cells (DSSC). It has been known that Cs$_2$SnI$_6$ exhibits air and moisture stability because it contains Sn$^{4+}$ ion which is air stable and also has high hole effective masses. Based on this fact, Cs$_2$SnI$_6$ can be applied as potential hole transport layer (HTL) in dye sensitized solar cell (DSSC).

2. Experiments

2.1. Synthesis of Cs$_2$SnI$_6$

Hydriodic acid (HI), cesium carbonate (Cs$_2$CO$_3$), and stannic iodide (SnI$_4$) were purchased from Sigma-Aldrich and used without any further purification. The acetic cesium iodide (CsI) solution was prepared by solved 325 mg of Cs$_2$CO$_3$ into 2 mL of HI in a beaker glass and stirred at room temperature to form homogenous solution. A 313 mg of SnI$_4$ was dissolved in 1 mL of warm ethanol and stirred to form homogenous orange solution. Next, the SnI$_4$ 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 used of ethanol (C$_2$H$_5$OH, 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 Cs$_2$SnI$_6$ is quite stable at room temperature.

2.2. Preparation of Cs$_2$SnI$_6$ Thin Film

In our case, Cs$_2$SnI$_6$ perovskite was prepared on thin film structure of glass substrate/TiO$_2$ compact layer/TiO$_2$ mesoporous because Cs$_2$SnI$_6$ is known has very poor wettability to attach directly on glass substrate. This film structure was also done to facilitate in fabrication of DSSC by used this type of perovskite as hole transporter. Glass substrate was cleaned in ultrasonic bath by de-ionized (DI) water and continued by used of mixed iso-propanol and acetone and finalized by ethanol. Glass substrate was dried by N$_2$ gas before used. Next, TiO$_2$ compact layer was spin-coated on the top of the glass substrate at 2000 rpm for 30 s and annealed at 500°C for 10 min. Layer of TiO$_2$ mesoporous was screen-printed on the top of TiO$_2$ compact layer and annealed to 500°C. In this study, we controlled the volume ratio of solvent for Cs$_2$SnI$_6$ perovskite in order to get homogenous solution and thin film. Cs$_2$SnI$_6$ solution was prepared by dissolved 0.1 mg of powder-synthesized Cs$_2$SnI$_6$ in 1 mL mixed of gamma-butyrrolactone (GBL) and acetonitrile (CH$_3$CN) solvent (GBL:CH$_3$CN) in volume ratio of 1:0; 0:1; 1:1; 1:5; 5:1; 1:10, and 10:1. Subsequently, Cs$_2$SnI$_6$ solutions were deposited over the TiO$_2$ mesoporous by drop-casting in all area of thin film and then annealed at 100°C for 10 min.

2.3. Characterizations

Optical properties of Cs$_2$SnI$_6$ in thin films were characterized by an ultraviolet-visible (UV-vis) spectrometer at room temperature by using an Agilent Technologies 8453 UV-visible spectrometer. The absorbance spectrum was then used to determine band gap of the Cs$_2$SnI$_6$ using Tauc-Plot
calculation. Scanning Electron Microscope (SEM) of SU3500 model was used to get morphology images of Cs\(_2\)SnI\(_6\) powder without additional chemical and mechanical treatment. Measurement of X-ray Diffraction (XRD) was done by Philips Analytical PW 1710 diffractometer.

3. Results and discussions

In this research work, Cs\(_2\)SnI\(_6\) perovskite has been successfully synthesized by a simple chemical reaction in solution by mixed an acidic solution of Cs\(_3\)I and a stannic iodide (SnI\(_4\)) solution and revealed black precipitate powder of Cs\(_2\)SnI\(_6\). Figure 1 shows SEM images of the powder-synthesized Cs\(_2\)SnI\(_6\) measured at different magnification. The grain size of Cs\(_2\)SnI\(_6\) powder is not homogenous in the range of 0.5 – 4 \(\mu\)m. Further study regarding to the homogenous size and shape of our synthesized Cs\(_2\)SnI\(_6\) is still under our investigation.

![SEM Images of the powder-synthesized Cs\(_2\)SnI\(_6\) at room temperature under (a) 5000 and (b) 20000 times of magnification.](image)

**Figure 1.** SEM Images of the powder-synthesized Cs\(_2\)SnI\(_6\) at room temperature under (a) 5000 and (b) 20000 times of magnification.

X-ray diffraction (XRD) pattern of the powder-synthesized Cs\(_2\)SnI\(_6\) in room temperature is shown in figure 2. Appearance peaks at 2\(\theta\) equal to 26.34°, 30.6°, 43.96°, 52.00°, 54.60°, and 63.95° correspond to (222), (400), (440), (622), (444), and (800) planes, respectively. It shows the typical crystal structure of Cs\(_2\)SnI\(_6\) perovskite which agrees well with the reference result from Lee *et al.* [7] and CH\(_3\)NH\(_3\)PbI\(_3\) perovskite in our previous work. Rietveld refinement using Match identifies that the powder-synthesized Cs\(_2\)SnI\(_6\) has a cubic structure in Fm-3m (225) space group. The lattice parameter is given by 11.6276 Å.

![XRD pattern of powder Cs\(_2\)SnI\(_6\) perovskite.](image)

**Figure 2.** XRD pattern of powder Cs\(_2\)SnI\(_6\) perovskite.
In our investigation, Cs$_2$SnI$_6$ has good solubility in mixed of GBL and CH$_3$CN as shown in figure 3(a). Thin films of Cs$_2$SnI$_6$ in GBL:CH$_3$CN solvents with volume ratio of 5:1 and 10:1 show good solubility and homogenous surface coverage compare to the other films with typical colour of bright yellow. Absorbance spectra of Cs$_2$SnI$_6$ in figure 3(b) exhibit characteristic two hump feature at 308 nm and 360 nm, which is due to the specific band structures of Cs$_2$SnI$_6$. In case of thin film with solvent ratio of 1:10, it is found that the absorbance intensity drastically enhance among to the other thin film samples eventhough the homogeneity of the thin film is less than thin film in solvent ratio of 5:1 and 10:1. In contrast, the film resulted from solvent ratio of 0:1 does not show the characteristic of Cs$_2$SnI$_6$ absorbance spectra, which indicated the CH$_3$CN affect the formation of the perovskite as shown in thin film with inhomogeneous black color (figure 3(a)).

![Figure 3.](image)

Figure 3. (a) Top view picture and (b) absorption spectra of Cs$_2$SnI$_6$ thin films in various ratio of GBL:CH$_3$CN solvent.

The band gap of our synthesized-Cs$_2$SnI$_6$ thin film was determined from the corresponding UV-visible spectra. Optical band gap calculated from the Tauc plot of the absorbance data was estimated to be 2.8 eV by assuming that Cs$_2$SnI$_6$ had a direct band gap. In previous research, Lee et al. reported that Cs$_2$SnI$_6$ had a direct band gap and gave a value of 1.3 eV [7]. In contrast, Kaltzoglou et al. determined the band gap by UV-visible diffuse reflectance spectra and they found band gap of 3.9 eV and 2.7 eV for Cs$_2$SnI$_6$ and Cs$_2$SnBr$_6$, respectively and it showed indirect band gap [8].

4. Conclusions
We successfully synthesized lead-free metal halide perovskite of Cs$_2$SnI$_6$ by used of simple chemical reaction in solution. X-ray Diffraction (XRD) measurement shows the characteristic pattern of Cs$_2$SnI$_6$ in a good agreement to the literature. Based on the UV-visible spectra, mixed of gamma-butyrolactone (GBL) and acetonitrile (CH$_3$CN) is a good solvent for Cs$_2$SnI$_6$ in order to form homogenous thin film for solar cell applications. Absorbance spectra of Cs$_2$SnI$_6$ thin films give a characteristic two hump feature due to the specific of the band structure of Cs$_2$SnI$_6$. The Tauc plot indicates that the direct band gap of Cs$_2$SnI$_6$ is resulted in 2.8 eV.

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