J-V characteristic of perovskite solar cells using lead(II) thiocyanate doped-methylammonium lead iodide (MAPbI₃) as active material

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Abstract. Perovskite solar cells based on methylammonium iodide (MAPbI₃) as active material have been intensively investigated for low cost and high power conversion efficiency (PCE). Today's, the PCE beyond 20% have been obtained using different structures of solar cells. However, there are still many problems needed to be solved prior to mass production and commercialization, in particular the stability of solar cells. The PCE decreases significantly in high humidity due to the decomposition of organic methylammonium iodide with water vapor from air-humid into lead iodide. Many researchers are now paying a lot of attentions to improve the stability of perovskite solar cells, including device structures, interfaces engineering and materials engineering. Recently, perovskite solar cell based on methylammonium lead(II) thiocyanate [MA(PbSCN)₂] improved the humidity-stability of solar cells, due to higher binding energy of thiocyanate (SCN) ions to Pb ions as than that of iodide (I) ions to Pb ions. However, the PCE is lower than that of commonly used MAPbI₃ solar cells, because the large bandgap leads to low light absorption. In this work, we present our recent study on J-V characteristic of solar cells using lead(II) thiocyanate Pb(SCN)₂ doped lead(II) iodide as active materials of perovskite solar cells. We prepared perovskite films using two-step spin-coating method. We used two different structures of solar cells, mesoporous device and inverted planar structure. The best PCE of solar cells is 7% obtained with inverted planar structure. The mesoporous device structure shows lower performance than that of inverted planar structure, which is due to poor quality of electron transport layer, both titanium dioxide (TiO₂) both blocking and mesoporous layers.

1. Introduction
Perovskite solar cells have much great research interest in the last decade, due to their highly potential as high performance and low-cost solar cells [1]. Perovskite materials have crystal structure ABX₃, where the A is the organic cation, the B is the metal cation and the X is the halogen anion. This perovskite crystals have superior optoelectronic properties, including optimal band-gap (~1.5 eV) [2], high absorption coefficient [3], long carrier diffusion length (~1 μm) [4] and high carrier mobility (~25 cm² V⁻¹ s⁻¹) [5]. Perovskite properties also can be widely tuned by various elements positioned at A, B and X, such as methyl ammonium iodide (MAI), formamidinium iodide (FAI), lead(II) iodide,
lead(II) chloride, etc. [6–8]. Perovskite materials can be used not only as light absorber in solar cells but also as charge transport materials both for hole and electron. Power conversion efficiency (PCE) of perovskite solar cells is increased dramatically only less than a decade from the first report by Miyasaka with 3.9% in 2009 [9] to beyond 20% reported by several groups [10–16]. However, stability in particular to humidity or moisture is a main drawback for mass production being used as electricity generating devices. Perovskites based lead is easily to react with water and oxygen, which leads to degradation of perovskite solar cells. Recently, many researches are focussing on fabricating high stability of perovskite solar cells, in particular to humidity, including new stable perovskite materials, device structure optimization and interface engineering [17]. Moreover, morphology of perovskite layer is very crucial for obtaining high performance and high stability solar cells. The perovskite film has to possess homogeneous grains with size larger than 500 nm and pinhole free [12, 18–19]. Pin-holes in the perovskite layer cause direct contact between hole- and electron-transport layers and thus lead to high resistance value of device and low performance of solar cells.

Recently, Tai et al. [20] fabricated perovskite solar cell using methylammonium lead(II) thiocyanate [MA(Pb SCN)2] instead of methylammonium lead(II) iodide (MAPbI3) as active material. The solar cell showed stable high stability, irrespective to the relative humidity-stability. The high stability of MA(Pb SCN)2 of solar cells is due to higher binding energy of thiocyanate (SCN) ions to Pb ions than that of iodide (I) ions to Pb ions [21]. However, the maximum PCE (15%) is lower than that of MAPbI3 solar cells, due to higher bandgap (> 1.5 eV) [21]. Moreover, MA(Pb SCN)2 has different crystal structure, therefore its optoelectronic properties are also different as MAPbI3 [21].

In this paper, we report our recent study of Pb(SCN)2 doped MAPbI3 to form new perovskite MAPbI3X(SCN)X with the aim to improve moisture stability of perovskite while maintain the superior optoelectronic properties of MAPbI3. We fabricated two different perovskite solar cells structure, namely mesoporous and inverted planar solar cells.

2. Materials and Experimental Methods
2.1 Materials
Titanium dioxide (TiO2) blocking layer (BL-1) and mesoporous (18NR-T) were purchased from Dyesol. Methylammonium iodide (MAI) and spiro-OMeTAD were purchased from Luminescence Technology Inc. and used as received without further purification. Lead (II) iodide (PbI2), lead(II) tyocyanate [Pb(SCN)2], poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), methanol, isopropanol (IPA), N-N’-dimethylformamide (DMF) were purchased from Sigma Aldrich.

2.2 Characterization
UV-Vis spectroscopy (T70+ PG Instrument) was applied to measure optical absorption of thin films of PbI2, Pb(SCN)2 precursor and perovskite MAPbI3X(SCN)X. Crystal structures of films were measured by use of X-Ray diffractometer. Cross section images of perovskite solar cells were measured by scanning electron microscope (SEM) SU3500 (Hitachi).

2.3 Fabrication of Perovskite Solar Cells
We fabricated two different solar cells structures, namely mesoporous and inverted planar structures. The mesoporous structure consists of glass/FTO/TiO2/perovskite/spiro-OMeTAD/Au, while inverted structure comprises of Glass/ITO/PEDOT:PSS/perovskite/C60/BCP/Ag.

2.3.1. Mesoporous Solar Cells Structure
Titanium oxide (TiO2) layers consist of solid film as blocking layer (bl) and mesoporous layer (mp). TiO2 blocking layer was prepared by screen printing of TiO2 solution in methanol using mesh T71 at room temperature. The film was then annealed at 450°C with two-step process. First, the film was heated to 250°C for 15 minutes and then at 450°C for another 15 minutes. The increasing temperature from room temperature to 250°C and from 250°C to 450°C was adjusted to have slow increased temperature gradient in order to have good quality of TiO2 layer. The mesoporous TiO2 layer was
prepared by spin-coated of TiO$_2$ mesoporous paste at 1500 rpm for 30 s. The film was then annealed at 450\(^{\circ}\)C using the same procedure as TiO$_2$ blocking layer.

Perovskite film was prepared from mixture of PbI$_2$ and 5\% wt Pb(SCN)$_2$ precursor in DMF solvent. The solution was previously prepared by mixing 461 mg PbI$_2$ and 23 mg Pb(SCN)$_2$ in 1 ml DMF to form PbI$_2$(SCN)$_2$ solution. The mixed solution was then stirred for 3 hours at 60\(^{\circ}\)C to obtain yellow transparent solution. The perovskite film was spin-coated on TiO$_2$ layer at spinning speed 3000 rpm for 40 s, using two-step process, i.e. 500 rpm for 5 s and 3000 rpm for 40 s. The MAI solution (10 mg MAI in 1 ml IPA) was then spin-coated with 3000 rpm for 40 s on top perovskite precursor film to convert the precursor film into perovskite film and followed by annealing it at 80\(^{\circ}\)C for 5 minutes.

Hole transport layer was prepared by spin-coated Spiro-OMeTAD solution at 3000 rpm for 40 s using two-step process, first 500 rpm for 5 s and 3000 rpm for 40 s. The spiro-OMeTAD solutions were prepared dissolving 90 mg spiro-OMeTAD in 1 ml chlorobenzene and stirred at 70\(^{\circ}\)C for 60 minutes. Finally, 100 nm of metal electrode consisting nickel and gold (5 nm Ni/95 nm Au) was deposited by thermal evaporation using a shadow mask to pattern the electrodes.

2.3.2. Inverted Solar Cells Structure

Devices structure of inverted planar perovskite solar cells comprises p-i-n structure, where PEDOT:PSS was used as p-type or hole transport material. Hole transport layer was prepared by spin-coated of PEDOT:PSS solution at 2500 rpm for 60 s. The film was then annealed at 140\(^{\circ}\)C for 10 minutes, forming a PEDOT:PSS layer of 45 nm. Perovskite solution was prepared similar way as in mesoporous structure. The perovskite film was spin-coated on PEDOT:PSS layer at spinning speed 3000 rpm for 40 s, using two-step process, i.e. 500 rpm for 5 s and 3000 rpm for 40 s. The MAI solution (40 mg MAI in 1 ml IPA) was then spin-coated on top perovskite precursor film to convert into perovskite film and followed by annealing it at 100\(^{\circ}\)C for 5 minutes.

Electron transport layer was prepared by highly vacuum thermal evaporation of fullerene C60 layer. The thickness of C60 was set 40 nm. The buffer layer bathocuproine (BCP) with thickness 8 nm was evaporated onto C60 layer by vacuum evaporation. Finally, 100 nm silver (Ag) was thermally evaporated on top of the device to form the cell’s back contact using a shadow mask to pattern the electrodes.

2.4. J-V Characteristic Measurement

The current density-voltage (J-V) curves of the photovoltaic devices were obtained by a Keithley 4200 source-measure unit with a scanning forward direction from −0.2 to 1.0 V and reverse direction from 1.0 to −0.2 V with a sweep rate of 0.2 V/s. The photocurrent was measured under simulated 100 mW/cm$^2$ AM 1.5 G irradiation using a Xe-lamp-based solar simulator [Oriel 300 W solar simulator (Thermo Oriel 91160–1000)]. The simulated irradiance was calibrated using a certified silicon diode, as determined by a standard silicon solar cell. The effective area of the cell was defined as approximately 0.10 cm$^2$ using a non-reflective photo mask.

3. Results and Discussion

Figure 1 shows UV-Vis spectra of thin precursor films of PbI$_2$, Pb(SCN)$_2$ and perovskite MAPbI$_3$.x(SCN)$_x$. Thin film Pb(SCN)$_2$ absorbs light at wavelength shorter than 400 nm, while PbI$_2$ absorbs light at wavelength shorter than 500 nm. Absorption of perovskite MAPbI$_{3-x}$(SCN)$_x$ cover wide range of wavelength ranging from 780 nm to UV light. This wide range absorption of light is expected to generate large number of excitons in active material of solar cells, thus to obtain the high PCE of solar cells.
Figure 1. UV-Vis spectra of thin films of PbI$_2$, Pb(SCN)$_2$ and perovskite MAPbI$_{3-X}$(SCN)$_X$.

Figure 2. XRD pattern of PbI$_2$, Pb(SCN)$_2$ and perovskite MAPbI$_{3-X}$(SCN)$_X$ films.

XRD pattern of PbI$_2$, Pb(SCN)$_2$ and perovskite MAPbI$_{3-X}$(SCN)$_X$ films are shown in figure 2. Lead(II) iodide has four distinguished peaks at 12.76°, 26.00°, 38.74° and 52.46° corresponding to the crystal plane of (001), (002), (003) and (004), respectively. All crystal planes are oriented in z-axis similar to the hexagonal 2H polytype [22]. PbI$_2$ film deposited by spin-coating from DMF solution crystallizes in the form of the hexagonal 2H polytype [22]. The XRD pattern of lead(II) thiocyanate shows similar peaks reported in literature [23]. Lead(II) thiocyanate has monoclinic crystal structure with $a = 9.661\, \text{Å}$, $b = 6.544\, \text{Å}$, $c = 8.253\, \text{Å}$, $\alpha = \gamma = 90^\circ$ and $\beta = 92.37^\circ$, belonging to the space group C2/c [24]. We calculated the XRD pattern of Pb(SCN)$_2$ powder using its crystal structure to identify the crystal plane. The peaks at 16.47°, 19.91°, 21.64°, 27.58°, 29.14°, 37.08°, and 43.03° correspond to the crystal plane of (110), (111), (002), (112), (113) and (023), respectively. No XRD peak is observed in perovskite film MAPbI$_{3-X}$(SCN)$_X$ originated both from PbI$_2$ and Pb(SCN)$_2$ peaks. It shows that both precursors are fully converted into perovskite crystal. The XRD pattern of perovskite shows tetragonal crystal structure [25-26]. The peaks at 14.25°, 20.12°, 23.60°, 24.63°, 28.57°, 31.98°, 35.07°, 37.88°, 40.67° and 43.26° correspond to the crystal plane of (110), (200), (211), (202), (220), (310), (312), (321), (224) and (314), respectively [25-26]. No significant PbI$_2$ peak
at around 12° is observed, which shows that the perovskite MAPbI$_3$(SCN)$_x$ film is stable to high humidity as compared to the common perovskite material MAPbI$_3$ [19-20]. In the case of MAPbI$_3$, the perovskite is easily degraded into lead iodide PbI$_2$, even less than one hour during annealing of the film in ambient air with high relative humidity [27].

Figure 3 shows J-V curves of mesoporous and inverted planar perovskite solar cells in dark and illuminated conditions both forward and reverse measurements. The solar cell's parameters are displayed in table 1. In dark condition, the mesoporous solar cell shows very good diode characteristic with voltage threshold’s value of 0.48 V. It shows that p-i-n junction is well formed. However, in illuminated condition, the current in the device is very low that causes low value of short-circuit current ($J_{SC}$). Moreover, the open-circuit voltage ($V_{OC}$) is lower than that of in dark condition. The fill-factor (FF) value is also very low that resulted PCE less than 1%. On the other hand, the PCE of inverted planar structure is 6.56%. This PCE and also the value of $V_{OC}$, $J_{SC}$ and FF are higher than that of mesoporous solar cells.

![Figure 3. J-V Curve of perovskite solar cells (a) Mesoporous structure and (b) Inverted planar structure.](image)

| Table 1. Measured parameters of perovskite solar cells. |
|---------------------------------------------------------|
| V$_{OC}$ (V) | J$_{SC}$ (mA/cm$^2$) | FF  | PCE (%) |
| Mesoporous    | Forward: 0.38 | 0.35 | 0.38 | 0.05 |
|              | Backward: 0.38| 0.52 | 0.37 | 0.07 |
| Inverted planar| Forward: 0.70 | 15.21| 0.62 | 6.56 |
|              | Backward: 0.60 | 14.97| 0.56 | 5.00 |

The low values of solar cell’s parameters of mesoporous structure are strongly related to the quality of TiO$_2$ layer as electron transport layer. Figure 4 shows the SEM images of solar cells cross section both mesoporous and inverted planar structure. It is clearly seen that the thickness of mesoporous TiO$_2$ layer, perovskite film and hole-transport spiro-OMeTAD layer is more than 2 μm which is too thick for optimum perovskite solar cells. The thickness of TiO$_2$ blocking layer must be less than 100 nm [28-29]. The layers in inverted planar structure, on the other hand, show homogeneous layer. The thicknesses of hole transport layer PEDOT:PSS (300 nm), electron transport layer C60/buffer layer BCP (60 nm) and electrode Ag (100 nm) are the optimum thickness of each layer in high reported PCE perovskite solar cells. The thickness of C60 needs to be carefully controlled. It needs to be thick enough to form a compact layer over the perovskite film, but a too thick C60 layer will increase the series resistance of the device. The thickness of perovskite film is around 800 nm which is two-times thicker than that the optimum layer for high PCE perovskite MAPbI$_3$ (300 – 400 nm) [30]. Liu et.al. [30] reported that for the devices with perovskite film thicknesses larger than 400 nm, the PCE decreases significantly. As the film thickness continues to increase, the series resistance of device is
increased. The series resistance of the cells with the thickness of perovskite layers more than 500 nm is over an order of magnitude higher than for optimized devices.

Hysteresis in J-V curves of mesoporous and inverted planar solar cells might be caused by poor quality of perovskite film, in particular related to the “pin-holes” which lead to high series resistance [17]. However, mesoporous structure shows less hysteresis than inverted planar which might be due to a better p-i-n junction formation. Morphological control is highly needed to obtain high quality perovskite film, i.e. pin-hole free and homogeneous perovskite grains with average size larger than 500 nm [16-18]. The large hysteresis of J-V curve in inverted planar structure might be caused by poor contact between perovskite and PEDOT:PSS layer due to nature hydrophilic property of PEDOT:PSS.

Figure 4. Cross section SEM images of (a) Mesoporous structure and (b) Inverted planar structure.

4. Conclusion
We have fabricated perovskite solar cells using lead(II) thiocyanate-doped lead(II) iodide as precursor materials to form perovskite MAPbI$_{3-x}$(SCN)$_x$ as active material both in mesoporous and inverted planar structures. The best PCE 6.56% is obtained with inverted planar solar cells. All parameters of mesoporous solar cells show lower values than that of inverted planar structure, which is caused by poor quality and too thick of electron transport layer, titanium dioxide (TiO$_2$) both blocking and mesoporous layers. However, mesoporous structure shows less hysteresis of J-V curve than that of inverted planar structure.

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