Environmentally stable perovskite film for active material of high stability solid state solar cells

A Bahtiar1*, M Putri1, E S Nurazizah1, Risdiana1 and Y Furukawa2

1 Department of Physics, Universitas Padjadjaran, Jatinangor, Indonesia
2 Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, Shinjuku-ku, Tokyo, Japan

*Corresponding author’s e-mail: ayi.bahtiar@phys.unpad.ac.id

Abstract. We studied new perovskite material lead (II) thiocyanate \([\text{Pb(SCN)}_2]\) in ambient air with humidity above 90%. We prepared perovskite film by use of two-step method combination of spin-coating and dip-coating technique. The \(\text{Pb(SCN)}_2\) film was first spin-coated either on bare glass or \(\text{TiO}_2\) coated glass and then followed by dipping it into methylammonium iodide (MAI) solution. The UV-Vis spectrum of \(\text{Pb(SCN)}_2\) film shows absorption at wavelength shorter than 400 nm. Meanwhile, perovskite \(\text{MAPb(SCN)}_x\text{I}_3-x\) film absorbs light ranging from 300 nm to 760 nm, which shows that the perovskite film can absorb more light to be converted into free charge carrier for generating electricity in solar cells. The XRD patterns shows that perovskite peaks are clearly observed which confirms that perovskite is already well formed. We also observe no significant changes in XRD pattern of perovskite films after stored for five days at ambient air with humidity exceed 90%. This result shows that perovskite \(\text{MAPb(SCN)}_x\text{I}_3-x\) film is environmentally stable, therefore high stability perovskite solar cells is expected to be produced in ambient air with high humidity. This is in accordance with the SEM images of surface morphology that shows no “pin-hole”.

1. Introduction
Perovskite solar cells have been great interest to be studied due to their superior optoelectronic properties lead to high power conversion efficiency (PCE). Recently, PCE beyond 20% is already achieved \([1,2]\) and therefore perovskite solar cells are expected to be mass fabricated and commercialized. Moreover, large size area of solar cell is already fabricated with PCE larger than 10% which is the commercial barrier for competing with current commercially available semiconductor solar cells \([3,4]\).

Stability and degradation of solar cells, however are still remain serious problem to be overcome prior to mass production, in particular to ambient air and humidity. Perovskite that consist of lead (Pb) react easily with humidity (\(\text{H}_2\text{O}\) and \(\text{O}_2\)) forming insulating material \(\text{PbO}\) or \(\text{PbO}_2\). In case of common perovskite \(\text{CH}_3\text{NH}_3\text{PbI}_3\) material, organic part of methylammonium iodide (MAI) reacts with humidity and therefore the perovskite changes into insulating \(\text{PbI}_2\) causes low PCE of solar cells. Many efforts are intensively investigated to improve the stability of perovskite material, such as finding more environmentally stable perovskite materials, encapsulation of solar cells and processing of solar cells in controlled humidity atmosphere \([5,6]\).
Lead (II) tycyanate or Pb(SCN)$_2$ material is a perovskite material which more stable to the humidity due to less reactive of SCN$^-$ ions. It is currently used by many researchers as additive material in MAPbI$_3$ for improving the stability and high quality morphology of perovskite films [7,8,9]. The high quality perovskite films must have no “pin-hole” to improve the electron mobility and therefore will increase the PCE solar cells [10]. Moreover, the PCE of perovskite solar cells is significantly affected by grains size of perovskite crystal [11].

In this paper, we report for the first time the optical, structural and morphological properties of perovskite MAPb(SCN)$_{X}$I$_{3-X}$ film prepared by use of two-step method combining spin-coating and dip-coating techniques in ambient air with high relative humidity above 90%. Our study can be used as guideline for preparation perovskite solar cells in air with high relative humidity.

2. Methods

2.1. Materials
All chemical substances are used as received without further purification. Lead (II) tyocyanate Pb(SCN)$_2$, isopronal (IPA), N-N’-dimetylformamide (DMF) were purchased from Sigma Aldrich. Titanium dioxide blocking layer was purchased from Dyesol, meanwhile methyammonium iodide (MAI) was purchased from Luminescence Technology Inc.

2.2. Solutions preparation
Metylammonium iodide (MAI) solution was prepared by dissolving 50 mg of MAI into 5 ml IPA and stirred for 30 minutes at room temperature forming transparent solution. 325 mg lead (II) thiocyanate Pb(SCN)$_2$ was dissolved in 1 ml DMF and stirred for 3 hours at 60°C to form transparent yellow solution.

2.3. Thin film preparation
Figure 1 shows schematic steps for preparation of perovskite MAPb(SCN)$_{X}$I$_{3-X}$ film using two-step method. The Pb(SCN)$_2$ precursor film was spin-coated Pb(SCN)$_2$/DMF solution on bare or TiO$_2$ coated glass substrate. The spinning speed was varied from 700 to 1500 rpm for 30 seconds. The precursor film was then dipped into MAI solution for 5 or 10 minutes. Finally, the perovskite MAPb(SCN)$_{X}$I$_{3-X}$ film is formed and then thermally annealed at 90°C for 10 minutes on temperature controlled hot plate.

![Figure 1. Schematic illustration of perovskite film preparation using two-step method.](image)

2.4. Characterizations
UV-Vis spectroscopy (T70+ PG Instrument) was applied to measure optical absorption of thin Pb(SCN)$_2$ precursor film and perovskite film. X-Ray Diffraction (XRD) measurement was carried out by use of X-pert Pro, PW3050/60 X-Ray Diffractometer. Surface morphology of Pb(SCN)$_2$ and MAPb(SCN)$_{X}$I$_{3-X}$ films were measured by Scanning Electron Microscopy (JEOL JSM-6510A).
3. Results and Discussion

UV-Vis absorption spectra of Pb(SCN)$_2$ film and perovskite MAPb(SCN)$_{x}$I$_{3-x}$ are shown in figure 2. The lead (II) thiocyanate absorbs light at shorter wavelength with an absorption edge at 380 nm. Meanwhile, the perovskite has wide absorption spectrum ranging from 300 nm to 760 nm. It shows that more light will be absorbed and more free charge carrier will be generated in perovskite films when used as active material of solar cells. The change of absorption spectrum also confirms that perovskite material is already formed.

Figure 2. UV-Vis absorption spectra of thin films Pb(SCN)$_2$ and perovskite MAPb(SCN)$_{x}$I$_{3-x}$ films.

Figure 3 shows XRD patterns of Pb(SCN)$_2$ and perovskite MAPb(SCN)$_{x}$I$_{3-x}$ films as prepared and after stored for 5 (five) days in ambient air with humidity exceed 90%. All films are deposited on TiO$_2$ layer. The formation of perovskite is confirmed by clear appearance in the XRD peaks at 14.18°, 28.54°, 31.90°, 40.60° and 43.16° corresponding to the crystal plane of (110), (202), (310), (224) and (330), respectively. Two peaks are clearly observed at 11.54° and 12.68° which are originated from PbI$_2$ due to incomplete conversion into perovskite. The unconverted PbI$_2$ causes low performance of perovskite solar cells [12]. Several additional perovskite peaks are clearly observed in the film after stored for five days in ambient air with humidity above 90% at 23.60°, 24.58°, 34.94° which are related to the peaks of (211), (220) and (312) planes, respectively. Moreover, no PbI$_2$ peak is observed in the film, which confirm that the precursor is completely converted into perovskite. These results show that the perovskite MAPb(SCN)$_{x}$I$_{3-x}$ film is stable to high humidity as compared to the common studied perovskite material MAPbI$_3$ [8]. In the case of MAPbI$_3$, the perovskite is easily degraded into lead iodide PbI$_2$, even less than one hour after spin coating if the films are prepared in high humidity atmosphere [5-6]. Several efforts have been developed to improve the stability of perovskite film, including preparation in low humidity and less oxygen atmosphere [13]. Our recent study showed that the stability of perovskite MAPbI$_3$ film can be improved by deposition it onto reduced graphene oxide (rGO) capped zinc oxide (ZnO) layer, even when prepared in ambient air with humidity above 90%. However, the preparation of rGO/ZnO layer is not straightforward for mass production of perovskite solar cells. Many parameters are needed to be controlled to produce homogeneous and well capped ZnO with rGO layer.
Figure 3. XRD patterns of Pb(SCN)$_2$ film and perovskite MAPb(SCN)$_{3-X}$ films as prepared and five days after stored in ambient air with humidity exceed 90%.

SEM surface morphology of Pb(SCN)$_2$ film and perovskite MAPb(SCN)$_{3-X}$ film are shown in figure 4. We varied the spinning speed of spin-coated Pb(SCN)$_2$ film from 700 rpm to 1500 rpm for 30 seconds. The homogeneous surface of Pb(SCN)$_2$ is formed when spin-coated at 700 rpm. Only few white grains are observed which might be originated from large size of particles. Large and dense perovskite grains are clearly observed in perovskite MAPb(SCN)$_{3-X}$ film. The grains have average size above 500 nm which is an expected size for producing high efficiency of perovskite solar cells. In perovskite MAPbI$_3$ solar cells, the performance of solar cells is significantly affected by perovskite grains size [11]. Moreover, no “pin-hole” is observed in the film, which indicates that the perovskite is formed completely. Pin-hole in the surface must be avoided for producing high performance perovskite solar cells. The “pin-hole” will act as electron traps which causes less transported electron from perovskite as active material into electrode, therefore produces low performance of solar cells [10]. Some methods are applied to produce less “pin-hole” in perovskite films, such as solvent vapor annealing method, fast-crystallization growth method, anti-solvent drop during spin-coating and controlled spin-coating parameters in preparation of perovskite films [14]. However, all those methods are not straightforward method due to low producibility for preparing high quality perovskite films.
We also varied the dipping time of spin-coated Pb(SCN)$_2$ film into MAI solution to study the effect of dipping time into crystal growth and grains size of perovskite film. Figure 5 shows SEM images of morphology of perovskite films with different dipping time into MAI solution. The Pb(SCN)$_2$ films were spin-coated with speed of 700 rpm for 30 seconds. Both films show dense and no “pin-hole” which indicate that the high quality perovskite films are produced. Larger grain size above 1 micrometre is clearly observed when the perovskite film is was prepared from dipping Pb(SCN)$_2$ film for 10 minutes in MAI solution. Longer dipping time gives perovskite crystal to grow forming large grains size. These results show that 10 minutes dipping is the optimum time for producing high quality perovskite film with no “pin-hole” either grains size above 1 micrometre.

4. Conclusions
We have prepared perovskite MAPb(SCN)$_{3-X}$I$_X$ film prepared by two-step method combining spin-coating and dip-coating techniques in ambient air with humidity exceed 90%. The perovskite film is very stable even after stored them 5 (five) days in ambient air with high humidity which is confirmed by its XRD pattern. The films are also very dense and no “pin-hole” is observed, indicate high quality
perovskite films. The film with grains size above 1 micrometre is obtained when prepared with dipping time of Pb(SCN)₂ precursor film for 10 minutes in MAI solution. This study shows that the perovskite MAPb(SCN)ₓI₃₋ₓ material is very suitable for producing stable solar cells in high humidity atmosphere.

5. References
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