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RESEARCH PAPER

Application of an Amino Acid as an Efficient Additive in Fabrication of Sn-perovskite Solar Cell

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ABSTRACT

Herein, a famous amino acid, cysteine (LC), apply as an available and low cost additive to construct perovskite solar cells based on Sn (Sn-PSCs). A carbon cell configuration is used to decrease the costs. In this study, we try to solve one of the most important issues in Sn-PSCs, the tin oxidation phenomenon. Because, oxidation phenomenon results in p-type doping and severe device deterioration and low performance in Sn-PSCs. Our results reveal that the adding of LC improves the photovoltaic parameters as a result of an effective decrease in Sn^{+2} oxidation. LC is a proper alternative for expensive additives to decrease tin oxidation. It is found that this strategy will open up a promising direction to application of these kinds of additives in the fabrication of Sn-PSCs.

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INTRODUCTION

During a long time, Pb-PSCs have been known as high-performance solar cells. Nevertheless, the lead toxicity problem has been a significant issue in environmental pathologies, large-scale applications and commercialization. Lead can caused detrimental effects to health that are not obvious with some clinical examinations. Some of these effects are impairment of haem biosynthesis, neurological function, hypertension, and fetal damage [1]. It is a good idea to utilize lead free-PSCs which involve metals with lower toxicity such as Bi, Sn, Cu [2–4]. Among them, only Sn^{2+} has exceedingly used due to similar coordination geometry and electron configuration to lead. Nevertheless, the stability for the (2+) oxidation states reduces in the periodic table group 14 when going up toward Sn. Also, the stability and efficiency amounts in lead-free PSC will get much worse in comparison to Pb-PSC [5]. Sn-PSCs, with the formula of $ASnX_3$, have some advantages in comparison to Pb-PSCs such as better bandgaps (1.2-1.4 eV), higher carrier mobility, and lower exciton binding energies, higher short-circuit current densities (J_{SC}). However, Sn-PSCs shows lower efficiency. It is attributed to Sn^{2+} oxidization in Sn-PSCs after exposing them to air in a low level of O_2. The lack of inert pair effects in Sn^{2+} leads to p-doping. It provides Sn vacancies in perovskite lattice and results in an intensive cell deterioration in the ambient therefore, performance reproducibility is poor Besides, some rapid reactions that occur between organic ammonium salts and tin iodide is a serious problem

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in the controlling of morphology [6]. Different suggestions have been presented to address these problems. For example SnF_2 [7] and $SnCl_2$ [8] applied as some proper additives to reduce oxidation of Sn. Some researchers optimized the Sn-PSC morphology, utilized a reducing agent, and modified the cell structure. In addition, the 2D/3D Sn-PSC indicated better stability because of the boosted robustness in the perovskite films [9]. The influence of organic cations replacing on the crystallinity, morphology, performance and Sn-PSCs stability were investigated [10]. The quality of Sn-perovskite films has also critical effect on the device performance by producing trapping states because of dangling bonds at grain boundaries [11]. Hao et al [12] used Dimethyl sulfoxide (DMSO) solvent to reduce the rate of crystallization in Sn-PSCs. It cussed a monotonous and pinhole-free Sn-PSC films. Hydrazine as a reducing atmosphere showed two important effects on decrease tin oxidation and improvement of Sn-PSCs quality [13]. Application of other additives such as piperazine, triethylphosphine and hypophosphorous acid were reported [14]. Some two dimensional (2D) perovskites films were suggested that presented better stability than the common 3D films, nevertheless, their performance was low [15]. Some researchers utilized antioxidant additives as a proper idea with various effects on reduction of tin oxidation and, improvement of the morphology and efficiency [16]. Because of larger Lewis acid ability for Sn in comparison to Pb spices, the crystallization process in tin-perovskite is much faster than that of lead-perovskites, thus, providing of a compact and homogenous perovskite films is so difficult. It is so valuable to introduce new ideas that can suppress tin oxidation and also obtain perovskite films with proper quality [17].

Herein, cysteine (LC) is added as an additive in perovskite precursor. LC as a “biogenic” amino acid, belongs sulfur-containing amino acids (Fig. 1). Amino acids are the most important bio ligands which can form chelate complexes with various metal ions such as Vanadium [18], cu [19], Co [20], Pb [21] and Sn(IV) Also, cysteine molecule ,as three-dentate chelating ligand, can be coordinated to Sn(II). The Sn (II) is connected to O, N, and the S atoms as carboxyl, amino and thiol groups, respectively [22].

Herein, a low-cost Sn-PSCs based on carbon cathode and HTM-free layer was used by this structure (FTO/ TiO_2 compact/ TiO_2 mesoporous/ Al_2O_3/ Carbon). The effect of using LC additive was investigated by different methods, ultraviolet–visible spectroscopy (UV), X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), photoluminescence (PL), I-V curve measurement, and X-ray photoelectron spectroscopy (XPS). Characterization section can be found in the supplementary.

MATERIALS AND METHODS

Materials

Formamidine iodide (99%, Dyesol), SnI_2 (99%, Alfa Aesar), SnF_2 (99.9%), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), titanium diisopropoxide bis acetylacetonate (75% in iso-propanol) and cysteine (≥ 97%), all from Sigma-Aldrich and TiO_2 paste (Dyesole 18NR-T) were used without more purification.

Device fabrication

Al_2O_3 and carbon pastes were prepared in our lab [16]. To assemble of the device, after washing step, a compact layer (TiO_2~50 nm) was deposited on FTO and annealed. Other layers were deposited by screen printed method and sintered for 30

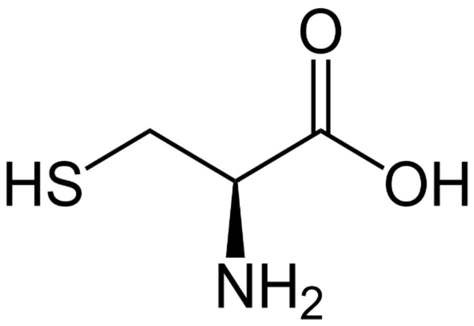


Fig. 1. L-cysteine structure

minutes. A $FASnI_3$ solution was fabricated with the similar ratio of FAI and SnI_2 in the same ratio of solvents (DMF: DMSO) and SnF_2 as an additive. At the final step, perovskite solution was casted on the cell, evaporated and annealed.

RESULTS AND DISCUSSION

Herein, a simple and low-cost Sn-PSC structure was used to investigate the effect of adding an amino acid, LC, on the tin oxidation and thus device performance and stability. To investigate the antioxidant function of LC, different $FASnI_3$ solutions were fabricated by utilization of LC and exposed to the ambient for 50 minutes (Fig. S1). The $FASnI_3$ solution changed from yellow to dark red totally, indicating Sn^{2+} oxidation [23]. Nevertheless, other solutions involving LC did not show rapid and severe dark red. Remarkably, change of color in solutions involving 10% and 15% LC was lower than that of 5% LC. These results obviously reveal the effective behavior of LC to decrease tin oxidation. To study the effect of LC additive, different measurements were carried out. UV-vis spectrum of control ($FASnI_3$) film and the $FASnI_3$ by various LC additive percent was compared in Fig. S2. As can be seen, absorbance intensities intensified after adding LC, indicating additive could improve the crystallinity and film quality which led to larger light harvesting [24, 25]. In comparison to control film, the absorption at the band region was increased after adding LC with different percentages, however, absorption wavelengths decreased for 5% and 15% LC additive. The 10 percent of LC was utilized as the optimized amount in further investigations. Fig. 2 investigates the XRD plots for control film and $FASnI_3$ with 10 percent of LC (named it LC). The XRD includes peaks at 14.0°, 24.4°, 28.22°, 31.65°, and 40.37°, exhibiting an orthorhombic phase in control film [26]. The LC film exhibited intensive patterns, proving enhanced crystallinity in accordance with the UV spectra results.

Fig. 3a and 2b illustrates the SEM cross-section for control device and LC device. It clearly shows a lot of holes in the filling and unsuitable penetration of the perovskite solution in the porous layers. However, after adding LC additive the filling happens more completely with a few holes and thus provides compact films which are important to improve device performance. To better understand the influences of LC on film morphology, SEM images of control film with LC film were compared. Many pinholes can be seen in the control film due to rapid and uncontrollable crystallization process, however, LC film provided a better film quality with compact and pinhole free morphology (Fig. S3). Improvement of film quality can be attributed to decreased crystallization rate and homogenous distribution of SnF_2 in perovskite films because of formation of Lewis acid–base

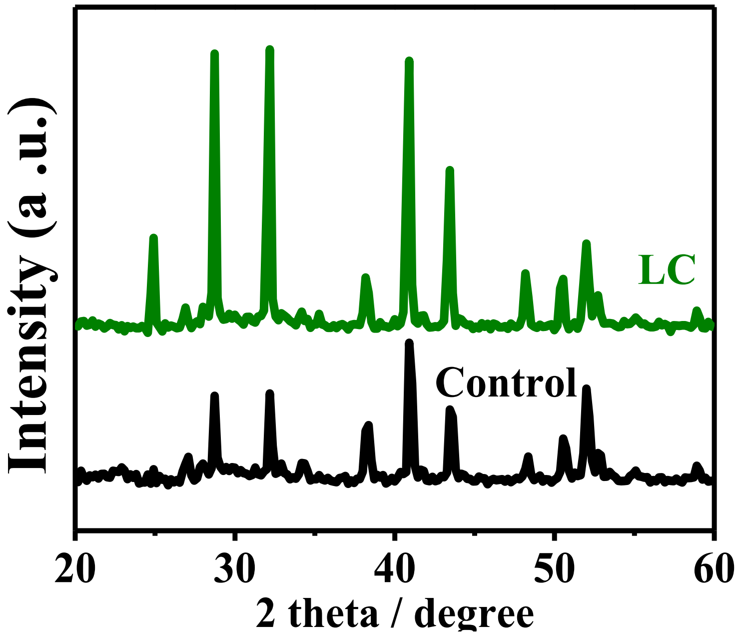


Fig. 2. XRD plot of control film and LC film ($FASnI_3$ +LC 10%)

spices [27]. Fig. S4 compares the XRD patterns for SnI_2+SnF_2 and SnI_2 +SnF_2+LC compounds. It is important to note that the peak intensity for SnI_2 +SnF_2+LC decreased, confirming the creation of SnY_2-LC complexes (Y= F, I, Cl) in result of Lewis acid –base adducts [28, 29].

To investigate the influence of LC on tin oxidation, the XPS result for control film and LC film was compared (Fig. 3c and 3d). The XPS plot shows the binding energy of 486.6 eV for Sn^{4+} and the binding energy of 486.0 eV for Sn^{2+} species. It can be seen lower Sn^{4+} peak for LC film than that of the control film, indicating LC can noticeably prevent tin oxidation. Steady-state photoluminescence (PL) of control film and LC was displayed in Fig. 3e to reveal the charge transfer

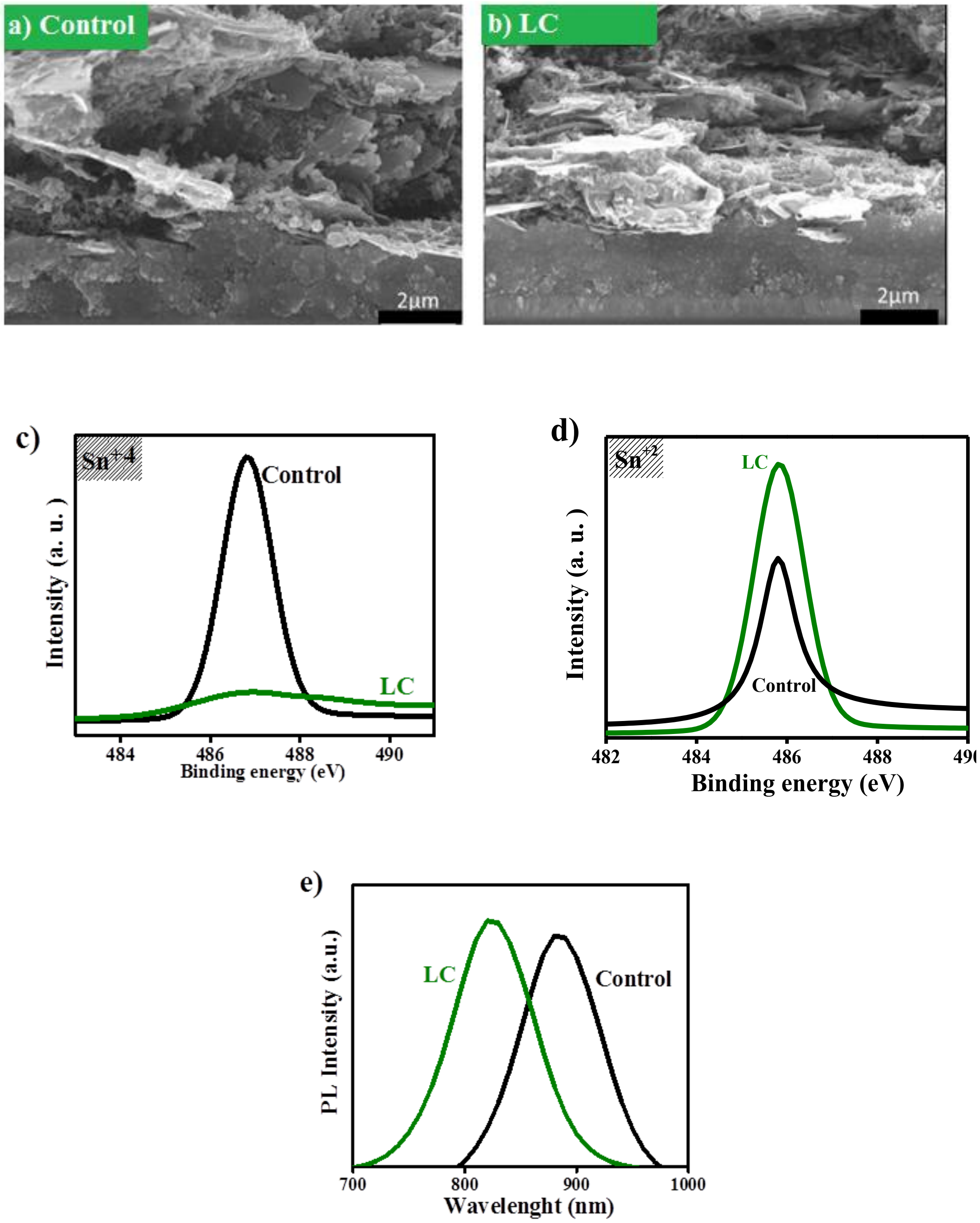


Fig. 3. SEM cross-section of a) the control cell and b) LC cell. XPS patterns to show distribution of c) Sn^{+4} in the control and LC, d) Sn^{+2} in control and LC. e) Photoluminescence of control and LC film.

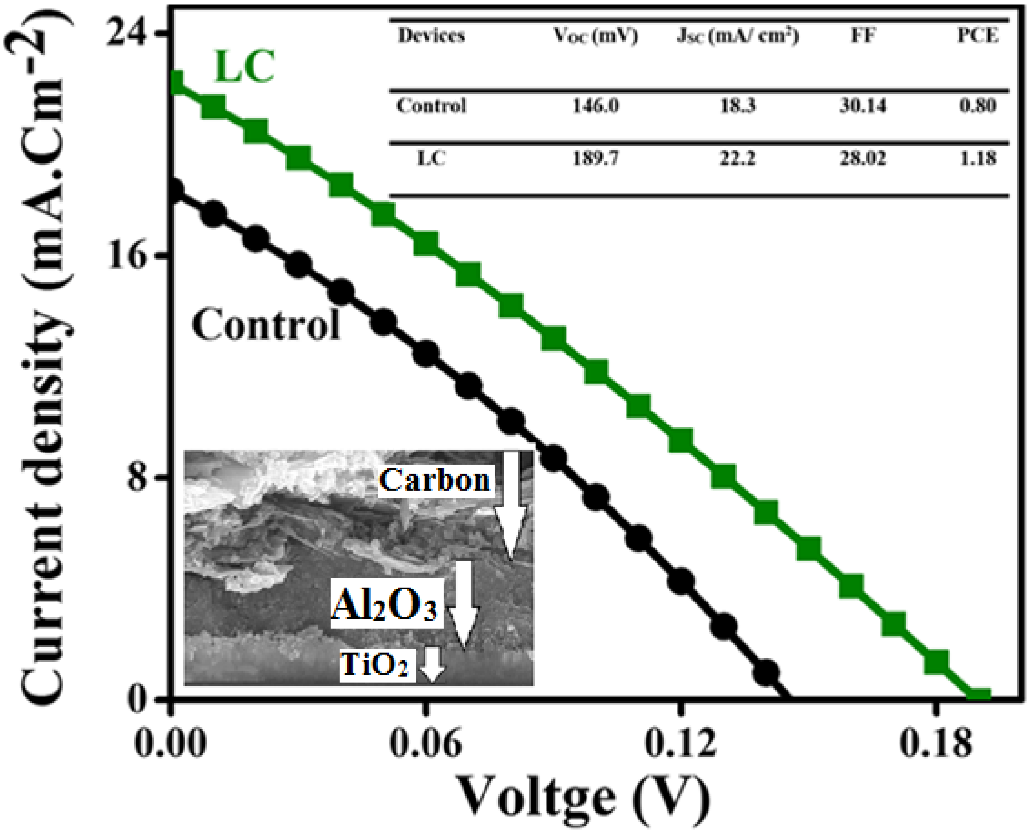
behavior of fabricated films. The PL spectrum demonstrated a blue shift for LC film which can be attributed to alteration of nanocrystal structure at the superficies [30] and reduction of spontaneous radiative recombination among trap states which is likely the reason of increased V_{OC} [32, 33].

A mesoscopic carbon-electrode tin-based perovskite was prepared to examine the influence of LC additive on the photovoltaic performance. In this purpose, photocurrent-voltage curves (I-V) were recorded for control cells and LC cells (Sn-PSCs prepared with perovskite solution and additive). Fig. 4 demonstrates the I-V curves along with calculated photovoltaic parameters for two kinds of cells. The control cell exhibited a small amount of PCE (0.80%), however, in the LC cell, it can see an improved PCE of 1.18%. The improvement of PCE can be ascribed to enhance V_{OC} and J_{SC} parameters because of suppressing tin oxidation, improvement of crystallinity and film quality according to XPS, XRD and SEM results, respectively.

The stability is one of the most important factors to investigate the PSC functions. Fig. 5a displayed the UV-vis spectra for control and LC film after leaving them in the ambient with 30% humidity at different hours. In addition, long-term stability was examined after leaving LC samples on 1 week, 2 weeks, and 1 month in GB, (Fig. 5b). UV-vis results indicated that the fabricated films by LC additive show better stability than that of control. Fig. 5c illustrates XRD patterns for fresh and old prepared LC films. The control film was quickly decompose to SnI_4 [15], but those with LC were stable around two weeks. These results reveal that using LC not only can reduce Sn^{2+} oxidation, but also can improve stability.

CONCLUSION

In this study, we applied a carbon perovskite solar cell free of expensive organic HTM layer and rare metal electrodes; this is thus hopeful as all-screen printable photovoltaic cells. This study introduced a low cost and available amino acid additive, LC, to fabricate efficient Sn-PSCs. LC additive indicated an effective function to



Devices	Voc (mV)	Jsc (mA/ cm²)	FF	PCE
Control	146.0	18.3	30.14	0.80
LC	189.7	22.2	28.02	1.18

Fig .4. J–V curves for two kinds of devices, control and LC devices, photovoltaic parameters and device structure

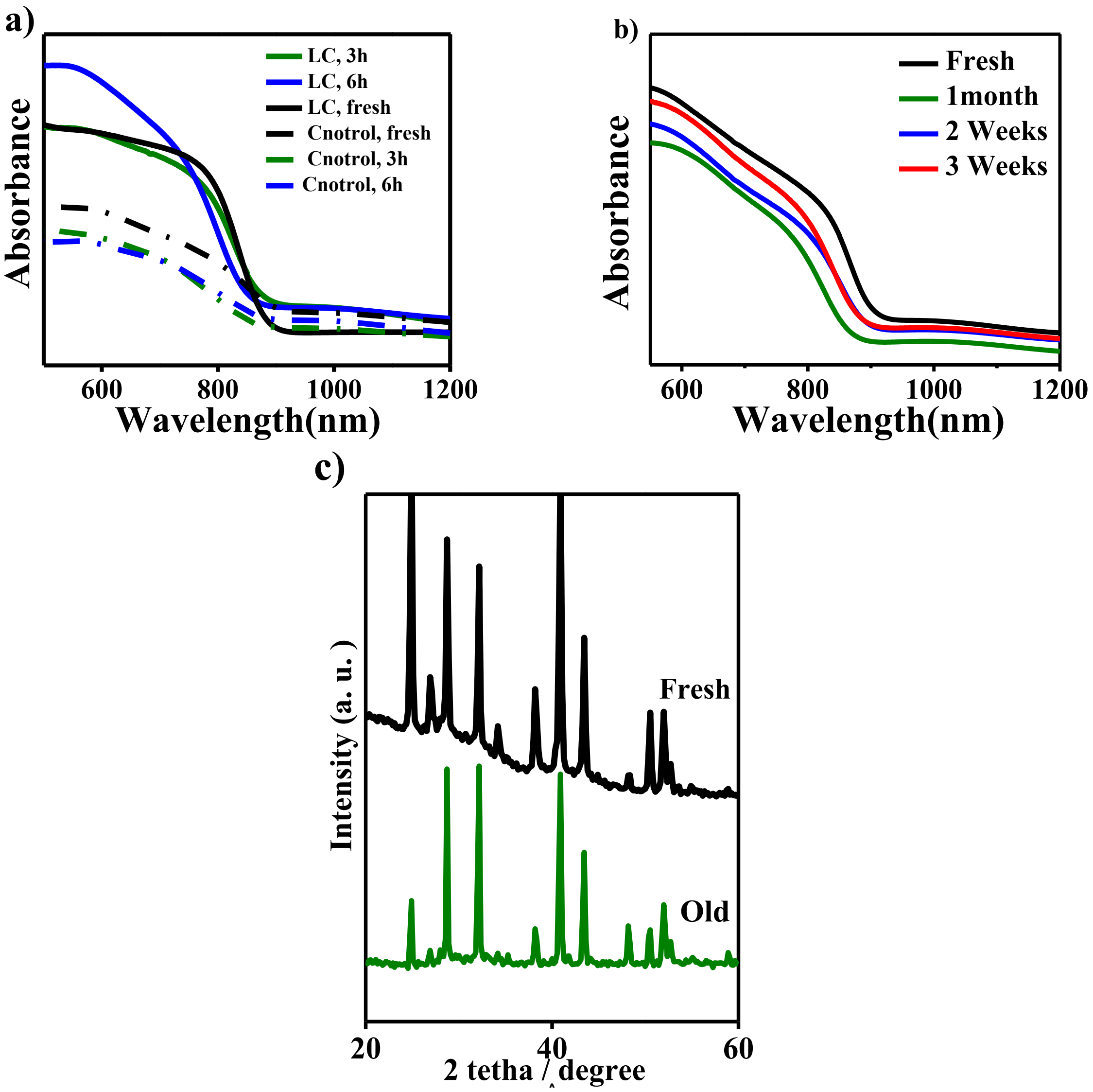


Fig. 5. a) Comparing of stability for LC and control films after exposing of ambient (30% humidity) for 0, 3 and 6 hours, b) Long term stability for LC film after 1week, 2 weeks, 1 month in GB, and C) Comparing of XRD for fresh and old (2 weeks in GB) LC.

decrease Sn^{2+} oxidation. The results reveal that LC is a good idea to improve performance and stability in Sn-PSCs. It is ascribed to the decrement of tin oxidation, and improvement of crystallinity. Utilization of amino acids to solve tin oxidation problem and enhancement of efficiency and stability Sn based PSCs is a good idea to replace some expensive additives.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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