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In₂O₃ based perovskite solar cells

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ABSTRACT

Hybrid organic-inorganic perovskite solar cells have attracted lots of attention in recent years. Growth and properties of perovskite layer and its relationship to photovoltaic performance have been extensively studied. Comparably less attention was devoted to the research of the influence of electron transporting layer (ETL). Conventionally, TiO₂ is selected as ETL. However, photocatalytic property of this transparent conductive metal oxide reduces the stability of perovskite solar cells under illumination. To realize the commercialization, the stability of perovskite solar cell must be improved. In this study, we replace TiO₂ by In₂O₃, which is not only transparent and conductive, but also has little photocatalytic effect and it has higher electron mobility than TiO₂. Investigation on different solution process methods of In₂O₃ as ETL is demonstrated.

Keywords: Perovskite, In₂O₃, electron transport layer

1. INTRODUCTION

There has been a rapid development of organic-inorganic hybrid perovskite solar cells (PSCs) in the past few years.¹ By introducing an organometal halide perovskite layer as the light absorber, this new generation of solid-state photovoltaic devices has achieved remarkably high efficiency at a relatively low cost. By 2015, the world record power converting efficiency (PCE) at 21.02% has been established.² The conventional device structure consists of a perovskite absorber either synthesized in a planar form or infiltrated into a mesoporous scaffold structure, an electron transport layer and a hole transport layer which extract photogenerated electrons and holes respectively, as well as the electrodes.¹ Despite that the organometal halide perovskite layers play the determining role in the solar cell efficiency, the electron transport layer (ETL) is also critical in overall device performance. An ETL with desirable electronic and optical properties is necessary to allow efficient charge transport and decreased recombination rate, which contributes to high PSC efficiency.³

Similar to other photovoltaic devices, the successive processes of photogeneration of charge carriers and charge separation are critical to the photovoltaic performance of perovskite solar cells.^{1, 3-5} Upon light absorption, charge carriers are generated in the perovskite absorber layers within a few picoseconds.⁴ These photogenerated charge carriers are reported to exhibit considerably high mobility at the order of 10 cm² V⁻¹ s⁻¹, long diffusion lengths exceeding 1 micron in the perovskite layer, as well as slow recombination at microsecond time scale.^{4, 5} All these properties in combination provide a fundamental basis of high efficiency in charge collection and thus solar cell performances. Following charge generation, the separation and extraction of photogenerated charges are facilitated by electron and hole

transporting layers respectively. TiO₂ is the most prevalent choice of electron transporting materials for both planar and mesoporous structured perovskite solar cells, due to its favorable band structure, long electron lifetimes, as well as low fabrication costs.^{1,3} A power converting efficiency (PCE) exceeding 20% has been achieved in the devices using TiO₂ as the electron transporting layer.⁶

Nevertheless, there are particular properties of TiO₂ which lead to drawbacks in efficient and stable photovoltaic devices. First, TiO₂ has a relatively low intrinsic electron mobility of $< 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, compared to the electron mobility of $\sim 12.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ of the perovskite.⁴ Regarding the electron transport process, electron injection occurs at the interface of the perovskite absorber and the ETL, which is demonstrated to be a very efficient process. Nevertheless, the low electron mobility of TiO₂ results in unbalanced charge transport, and lowered overall mobility. The lower Fermi level of TiO₂ leads to decreased open circuit voltage, which is unfavorable for high efficiency photovoltaic devices.⁴

Another potential disadvantage of employing TiO₂ in perovskite solar cells is linked to the defect chemistry of TiO₂.⁷ The surface and bulk defects of TiO₂ serve as electronic trap sites below conduction band edge upon UV illumination, which can lead to decrease in device performance and even irreversible degradation of perovskite layers. It has been reported that TiO₂ based PSCs are inherently unstable under UV illumination even upon encapsulation, leading to a rapid decay of device performance within short time period.^{7,34} Such an inferior long-term stability is definitely detrimental to commercialization of perovskite solar cells. As pointed out in several reports,^{4,7} these properties make TiO₂ not an optimal choice of electron transporting materials in perovskite solar cells.

To overcome the drawbacks in long-term stability, research efforts have been devoted following two different strategies: further optimization of TiO₂ compact layers based on existing device structure,⁸⁻¹³ and replacing TiO₂ with alternative materials. With regard to the former option, investigation has been focused on passivating TiO₂ surface states to reduce undesired charge recombination and photocatalytic effect.⁸⁻¹¹ For instance, Y-doping is reported to increase the conductivity and electron mobility of TiO₂ which is beneficial to the solar cell efficiency.^{8,9} Doping with Al¹⁰ and Nd¹¹ are also demonstrated to enhance both the efficiency and stability of perovskite solar cells by effectively passivating bulk and surface defects in TiO₂. On the other hand, a surface blocking layer upon TiO₂ ETL has been utilized for passivation of photocatalytic effect of TiO₂ as well as undesired charge recombination. For example, significant enhancement of solar cell stability against light exposure has been achieved using a Sb₂S₃ blocking layer,¹² whereas an Nb₂O₅ blocking layer can result in an increased open circuit voltage.¹³ Through considerable progress has been achieved, the intrinsic drawback of low electron mobility and instability upon light exposure in TiO₂ based perovskite solar cells could not be eliminated, which consequently lead to increasing research interests on alternative electron transporting materials.

Possibilities of using alternative metal oxides as electron-transporting materials have been assessed since the development of dye-sensitized solar cells (DSSCs).^{14,15} For example, Al₂O₃ mesoporous scaffolds have been applied in replacement of TiO₂, and the resultant devices exhibit good stability under light exposure over 1000 h.⁷ However, Al₂O₃ could not be used in planar devices since it is an insulating material. Therefore, a step further regarding the alternative ETL materials that are viable for highly efficient and stable photovoltaic devices is necessary and well worthy of investigation. Potential candidates include ZnO, In₂O₃, SnO₂, Nb₂O₅, and WO₃. In addition to the similar electrical and optical properties, these alternative metal oxide semiconductors exhibit higher electron mobility compared to TiO₂, which is advantageous in enhancing the device efficiency.¹⁴ Recent progress has been achieved in fabricating ZnO^{16,17}, SnO₂¹⁸⁻²², as well as ZnO-SnO₂ nanocomposite²³ based perovskite solar cells with remarkably high efficiency. However, due to the well-known photocatalytic activity of ZnO, issues regarding long-term stability of ZnO based devices should be taken into consideration. On the other hand, enhanced stability of SnO₂ based devices are expected due to higher UV stability of SnO₂ compared to TiO₂ and ZnO.¹⁹

Similar to SnO₂, In₂O₃ has been widely applied as a functional material in optoelectronic devices.²⁴ In₂O₃ has a direct band gap of 2.8 eV ²⁴⁻²⁷ with electron mobility at the order of $10 \text{ to } 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,²⁸⁻³⁰ and is more robust under UV illumination compared to TiO₂. These properties make In₂O₃ promising as an electron transporting material. However, much less attention has been paid on In₂O₃ based perovskite solar cells compared to the SnO₂ based devices in the literature. In this study, we have fabricated planar perovskite solar cells with solution processed In₂O₃ ETL. The potential of In₂O₃ as alternative ETM for efficient PSCs has been demonstrated.

2. EXPERIMENTAL DETAILS

2.1 Materials

Indium chloride (99.995%, trace metal basis) was purchased from Acros Organics. Lead iodide (PbI_2 , 99%), Lead chloride (PbCl_2 , 98%), bis (trifluoromethane) sulfonimide lithium salt (Li-TFSI, 99.95%), chlorobenzene ($\geq 99.5\%$), acetonitrile (anhydrous, 99.8%), 4-tert butylpyridine (96%) were obtained from Sigma Aldrich. Methylammonium iodide (MAI) was purchased from Dyesol. Isopropanol (anhydrous, 99.5+%) was obtained from Alfa Aesar. N, N-Dimethyl formamide (DMF, HPLC grade) and acetic acid glacial (GR grade) were purchased from Duksan Pure Chemical. 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) was purchased from Shenzhen Feiming Co., Ltd. MoO_3 and Al pellets were purchased from Kurt J. Lesker.

2.2 Device fabrication and characterization

All perovskite solar cells were fabricated on patterned fluorine doped tin oxide (FTO) glass substrates. The substrates were cleaned by toluene, acetone, ethanol, and deionized water in sequence in ultrasonic bath, then dried by nitrogen flow. Two methods were utilized for fabricating indium oxide thin film as ETL. For the first method, indium chloride was dissolved in deionized water, then 10% of HCl water solution (1.2 M) is added. The precursor solution was spin coated on cleaned substrates at 3000 rpm, followed by pre-annealing at 120 °C for 5 min on hotplate, then annealing at 500 °C for 1 hour in furnace. For the second method, indium chloride is dissolved in acetonitrile and ethylene glycol (v: v = 50:1).³¹ The precursor was stirred at 50 °C for 2 hours then spin coated on cleaned substrates at 5000 rpm followed by pre-annealing at 100 °C for 5 min on hotplate, then annealing at 500 °C for 1 hour in furnace.

Both iodide only and iodide/chloride mixed perovskite films were fabricated. For perovskite containing only iodide, films were fabricated by two-step solution process³² in glove box filled by argon. Firstly, PbI_2 precursor solution (1 M PbI_2 in DMF stirred at 70 °C for two hours) was spin coated on ETL at 2500 rpm followed by annealing at 70 °C for 30 min. Secondly, solution of MAI in isopropanol (30 mg/mL) was placed on PbI_2 film for 1 min, then spin coated at 2500 rpm to remove the residual. After this, the samples were immediately annealed at 100 °C for 2 hours on hotplate. For iodide/chloride mixed perovskite, films were fabricated by one step solution process. The precursor solution containing MAI and lead chloride (molar ratio, 3:1) in DMF was spin coated on ETL, followed by drying at 65 °C for 15 min, then annealing at 105 °C for 45 min. transporting layer (HTL) precursor solution was made by dissolving 72.3 mg spiro-OMeTAD in 1 mL chlorobenzene. Then 28.8 μL 4-tert-butylpyridine and 17.5 μL Li-TFSI solution (520 mg/mL in acetonitrile) were added in the precursor. The HTLs were fabricated by spin coating the precursor solution on perovskite films at 4000 rpm in glove box, then transporting to oven filled by dry oxygen at 40 °C for 2 hours.³³ Finally, MoO_3 (15 nm)/Al (100 nm) as electrode was deposited on the top of HTL by thermal evaporation with masks to defined the active area (0.1 cm^2).

For IV curve measurement, perovskite solar cells were exposed to AM 1.5 illumination (one sun) generated by solar simulator. Because of hysteresis effect, constant bias of 1.2 V was applied for 15 seconds before scanning from 1.2 V to -0.2 V with scan rate at 1 V/s.

3. RESULTS AND DISCUSSION

Table 1 shows the performance of perovskite solar cells whose indium oxide thin films were fabricated by using deionized water. According to average PCE and variation, it is found that 0.08 M is the optimized concentration. However, this performance is still too low compared to titanium oxide based perovskite solar cells in literature.³⁴ To figure out the reasons, SEM images of cross section of indium oxide on FTO were taken, which are shown in Figure 1. For concentration of 0.05 M, the indium oxide is too thin, which means that part of FTO is not covered by ETL. This can explain the phenomenon of significant variation in cell performance when using precursor at low concentration. However, although the FTO is fully covered by indium oxide when concentration is increased to 0.1 M, the cell performance still reveals considerable variation. This can be attributed to the possible fact that the morphology of indium oxide fabricated by this method is not uniform. Besides, the roughness of FTO also affects the uniformity of indium oxide as we can see from the SEM image.

Despite of the relatively low average PCE and large variation, the highest PCE of indium oxide based perovskite cells by this method reaches 9.9%. Figure 2 shows the IV curve for this individual champion cell. This result shows the potential

of indium oxide as ETL. With better control on the morphology and the thickness of indium oxide thin film on FTO, it is expected that performance comparable to titanium oxide based perovskite solar cells can be reached. To realize this expectation, another method for fabricating indium oxide thin film is utilized, which is to dissolve indium chloride into acetonitrile and ethylene glycol. The performance of perovskite solar cells through this method is summarized in Table 2. The optimized concentration for using acetonitrile is 0.2 M, whose average PCE is even lower than by using deionized water. However, when 2% (atomic ratio) zinc is doped in indium oxide, the average cell performance is obviously improved and the variation is reduced. From this result, it is indicated that zinc helps indium oxide to form more uniform films. The SEM images of indium oxide and perovskite film which grown on it are shown in Figure 3. Although the indium oxide film is relatively rough, perovskite films on it demonstrates good morphology. Besides, the roughness of indium oxide leads to defects on the indium oxide surface. Therefore, the low average efficiency and its large variation are likely due to the interface between ETL and perovskite layer.

Iodide/chloride mixed perovskite solar cells were also fabricated based on indium oxide through this method. The results are summarized in Table 3. The average efficiencies for both concentrations are still low compared to titanium oxide based perovskite cells. Therefore, more work should be done on the optimization of indium oxide fabrication procedure.

4. CONCLUSION

Indium oxide based perovskite solar cell shows potential in achieving high efficiency. However, more research needs to be conducted on the control of indium oxide thin film morphology, as well as the interface modification between ETL and perovskite layer to realize reproducibility and consistency. Understanding the growth of indium oxide on FTO and the development of better fabrication techniques are the key issues in replacing TiO₂ ETL by other transparent conductive metal oxides.

InCl₃ concentration	J_{sc} (mA/cm²)	V_{oc} (V)	FF	PCE (%)
0.05 M	11.4 ± 9.0	0.77 ± 0.21	0.41 ± 0.11	4.8 ± 4.8
0.08 M	13.3 ± 2.8	0.88 ± 0.04	0.44 ± 0.03	5.2 ± 1.7
0.1 M	11.1 ± 6.9	0.62 ± 0.36	0.35 ± 0.10	3.5 ± 4.3

Table 1. Performance of perovskite solar cells using deionized water as a solvent for indium chloride

InCl₃ concentration	J_{sc} (mA/cm²)	V_{oc} (V)	FF	PCE (%)
0.1 M	13.0 ± 2.9	0.71 ± 0.08	0.37 ± 0.04	3.3 ± 0.8
0.2 M	15.1 ± 3.6	0.68 ± 0.15	0.37 ± 0.09	4.2 ± 2.6
0.5 M	16.1 ± 1.5	0.44 ± 0.14	0.31 ± 0.03	2.5 ± 0.9
0.2 M (zinc doped)	15.7 ± 1.1	0.92 ± 0.02	0.42 ± 0.05	6.1 ± 1.2

Table 2. Performance of perovskite solar cells using acetonitrile as a solvent for indium chloride

InCl ₃ concentration	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	PCE (%)
0.1 M	14.7 ± 6.8	0.59 ± 0.29	0.37 ± 0.1	4.3 ± 3.4
0.2 M	13.5 ± 9.3	0.59 ± 0.28	0.35 ± 0.1	4.3 ± 4.5

Table 3. Performance of iodide/chloride mixed perovskite solar cells on indium oxide prepared from acetonitrile solvent

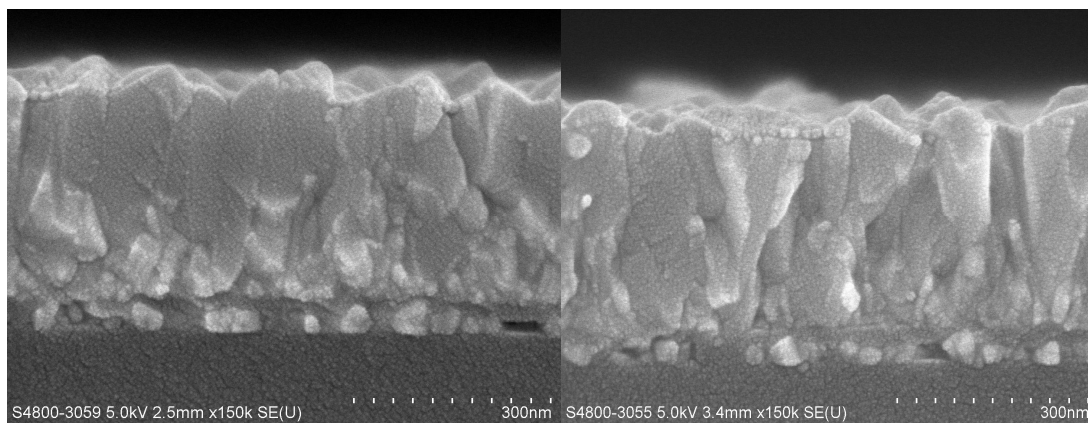


Figure 1. Indium oxide fabricated by dissolving indium chloride in deionized water; the left is 0.05 M; the right is 0.1 M

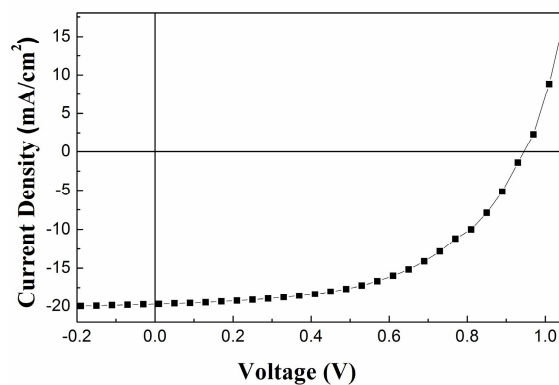


Figure 2. IV curve of best indium oxide based perovskite solar cell when using deionized water (J_{sc} 19.7 mA/cm², V_{oc} 0.95 V, FF 53%, PCE 9.9%)

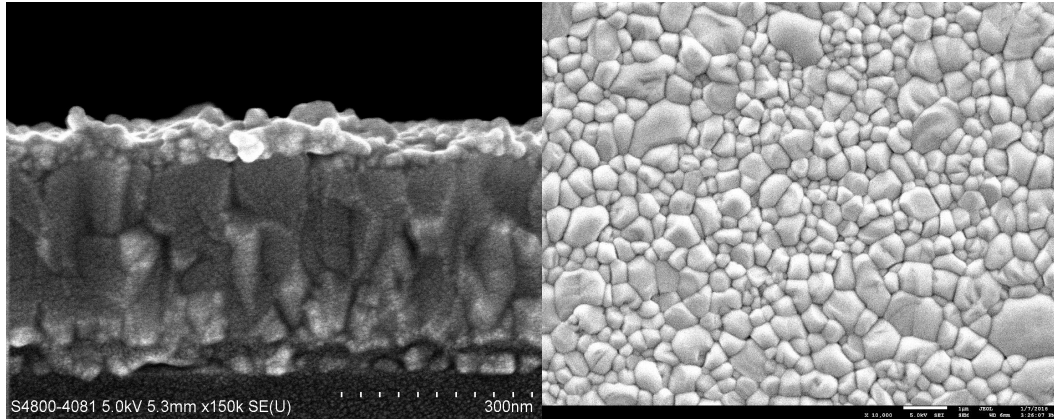


Figure 3. Left: cross section of indium oxide fabricated by using acetonitrile; Right: top view of perovskite on indium oxide

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