Development of Tin Oxide Materials as a Highly Efficient Electron Transport Layer for Perovskite Solar Cells

Peerathat Pinpithak, Ikegami Masashi and Miyasaka Tsutomu

Graduate School of Engineering, Toin University of Yokohama

（2017 年 3 月 18 日　受理）

***Abstract* — Over past few years, great achievements in high performance of organic-inorganic hybrid structured perovskite solar cell (PSC) has been witnessed with power conversion efficiency (PCE) up to 22%.[1–3] Improvement in charge collection property for solar cell materials is a potential strategy which can efficiently boost up the performance. Electron transport layer (ETL) is a prerequisite component for increasing electron extraction and simultaneously minimizing the charge recombination in solid-state type solar cells. Widely, TiO_2 blocking layer has been employed but due to UV sensitivity of TiO_2 which can destabilize perovskite, researcher diverted their attention towards alternate ETL. Tin oxide is an alternative ETL since it has effective hole blocking property and can be deposited at low-temperature. Herein, we focus on recent progress of tin oxide ETL for high efficient perovskite solar cells. Additionally, fabrication method and material modification of tin oxide based ETL are discussed.**

I. Overview of electron transport materials

Basically, photovoltaic devices can be fabricated by combining n- (donor) and p- (acceptor) type semiconductor. Electrical power is generated via light absorption, charge separation, and charge transfer process. Photogenerated electrons and holes travel across semiconductor junction and are collected at their respective electrodes (***Fig. 1a***).[4] Organohalide lead perovskite ($RPbX_3$, R=organic counter ion part, X=Cl^-, Br^-, I^-), they normally behaves as ambipolar molecule (i-layer), sandwiched between p and n-layer. The charge transfer processes in device usually depend on the behavior in n-i-p structure. Nevertheless, electrical loss due to charge recombination has still hindered progress far from practical use. To minimize back transfer of carriers, tailoring of energy band structure of materials has been applied. Appropriated energy band alignment among components can efficiently facilitate charge transfer and simultaneously reduce electrical loss.

Metal oxide based material has been frequently used owing to its high stability, easy preparation and high carrier mobility. Typically, oxide semiconductor layer is usually prepared in either planar or mesoporous architecture. As well known, TiO_2 is the most common standard semiconductor which has been employed as ETL due to its

Peerathat Pinpithak, Ikegami Masashi and Miyasaka Tsutomu
Graduate School of Engineering, Toin University of Yokohama. 1614 Kurogane-cho, Aoba-ku, Yokohama 225-8503, Japan

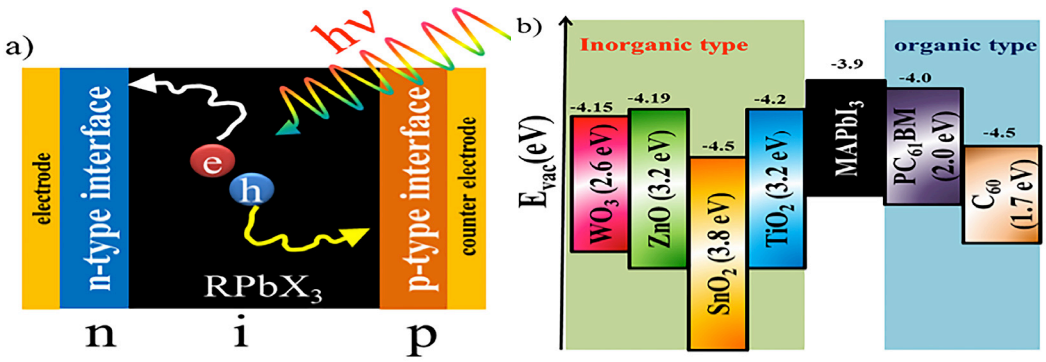

Fig. 1 Schematics showing charge transfer process in n-i-p structure a)[4] and band alignment of perovskite with in various ETL b)[5].

appropriate energy band structure and efficient electron collective property. However, electron mobility in bulk structure of titania is still low and causes charge recombination. Moreover, high temperature treatment (>450 °C) for particle sintering is still necessary for TiO_2 ETL. Attempts for low temperature process TiO_2 blocking layer and its modification have been performed[6] but perovskite degradation due to light induced photocatalytic reaction at perovskite/ TiO_2 interface limits its use.[7, 8] Hence, to overcome limitations from TiO_2 and reduce production cost, low-temperature ETL deposition processes are desired, and the ETL should have efficient electron collective properties. Various alternative n-type oxide semiconductors such as ZnO[9], Zn_2SnO_4[10], WO_x[11] *etc*. have been investigated (***Fig. 1b***). Among them, tin oxide emerged as a such kind of promising ETL due to superior properties such as appropriated band gap (~3.8 eV), large electron mobility (~240 cm^2V^{-1}), high transparency, and low temperature processed deposition.[12] Many efforts have been attempted to boost the efficiency by using SnO_2 as ETL for dye-sensitized solar cells (DSSC). Unfortunately, photovoltaic performance was not high owing to large charge recombination at SnO_2-iodide liquid electrolyte contact interface.[13, 14] However, in case of solid state perovskite solar cells, the barrier due to electrical shunting path at perovskite/oxide interface was minimized and device with tin oxide ETL showed certified PCE 20%.[15] To improve electron collection and hole blocking function, several research groups have attempted to optimize fabrication method for tin oxide material via several routes such as morphological control, energy band structure tuning (by element doping), and surface modification.

II. Fabrication method of tin oxide

As mentioned above, employing tin oxide as alternative ETL for perovskite solar cells has brought great attention due to outstanding physicochemical properties and low temperature processibility. Homogenous and ultrafine SnO_2 (as particle size less than 10 nm) deposition, which is a promising alternative method, can substantially increase photovoltaic performance and simultaneously improve stability to devices. Furthermore, ultrathin layer and pin-hole free layer can also be obtained by atomic layer deposition method (ALD).[16] As comparative studies, the strengths of these methods are discussed in further topic.

(1) Low-temperature solution process

In general, metal oxide film can be obtained by various chemical based reaction such as sol-gel,[17] hydrothermal,[18] spray pyrolysis[19] *etc*. Precursor for metal oxide can be prepared in solution form

and further converted to oxide product either by thermal and/or chemical treatment. Tin oxide layer has been prepared by low temperature solution process widely using $SnCl_2 \cdot 2H_2O$ as precursor due to its smooth coverage on substrate and low decomposition temperature (changing to oxide at temperature below 200ºC).[20]

Among many reports, Ke and co-workers proposed high efficient planar type $MAPbI_3$ perovskite solar cell with tin oxide as hole blocking layer by achieving PCE of 17.2% in backward scan direction with average curve showing 16%.[21] Our recent report revealed that at high temperature annealing, the surface coverage of low-temperature tin oxide become poor and affecting the photovoltaic performance due to effect of oxide particle sintering as shown in SEM images (***Fig. 2***).[22] To implement potential of tin oxide layer, minimization of surface trap states or improving the conductivity of pristine tin oxide are effective strategies to enhance the performance of perovskite solar cells.

Recently, Anaraki *et al*. reported comparative study of using tin oxide blocking layers which were prepared via solution processes and ALD method for triple cation mixed halide perovskite.[15] Surprisingly, surface treatment by chemical bath deposition (CBD) demonstrated superior improvement in photovoltaic properties with hysteresis less J-V curve compared with that by an ALD method. No shunting pathway was observed for compact SnO_2 crystalline film prepared via CBD which offers excellent charge transport due to which high Voc of 1214 mV with certified PCE of 20.8% was achieved. Additionally, the obtained Voc (1214 mV) is close to theoretical limit of 1320 mV. Furthermore, SnO_2 ETL with triplecation mixed halides perovskite device also showed high stability by showing PCE ca. 17% (from initial value of 20.4%) after continuous light soaking (1 sun, at 20ºC) for 60 hr and PCE completely recovered after storing in dark.

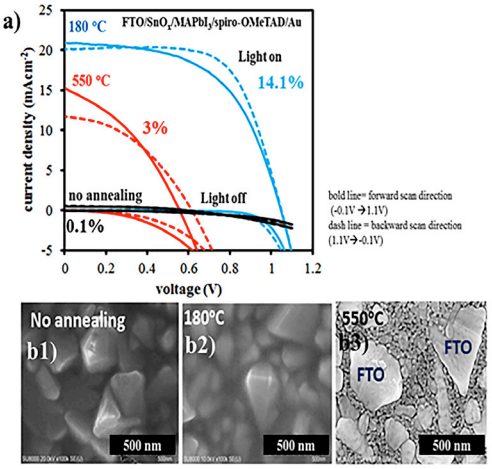

Fig. 2 Effect of annealing temperature to photovoltaic properties of tin oxide assembled $MAPbI_3$ devices a) and respective morphology of tin oxide blocking layer b) at 180ºC 2), 550ºC 3), and without annealing 1). [22]

As mentioned before, high resistivity and low free carrier concentration issue in low-temperature annealed tin oxide plays as an important role for development of photovoltaic performance. Doping with p-character elements (such as Y^{3+}, Li^{+}) is an effective method which can increase carrier concentration and conductivity of ETL and enhances the driving force for electron injection by making downward shift of conduction level in pristine structure.[19, 23, 24]

Park and co-workers modified low-temperature solution process for tin oxide by doping with Li-ion.[25] As a result of Li doping, conduction level of tin oxide showed significantly down shift of conduction level by 0.1 eV versus undoped sample, thus enhancing the conductivity of ETL. Consequently, efficiency was improved up to 18.2% by using $MAPbI_3$ as absorber. Additionally, Li-doped tin oxide also exhibited impressive performance on flexible substrate (ITO-PEN) by showing initial efficiency of ~12.2%, and ~14.8% with different active areas of 0.48, and 0.12 cm^2, respectively. For mechanical durability test, they performed cell bending test and measured its corresponding

efficiency. The deterioration of PCE was observed after bending radius was smaller than 10 mm due to deformation of ITO-PEN substrate. However, efficiency of device was maintained without any drop with bending was radius of higher than 15 mm under recycling test for 500 times.

(2) Solution processed oxide nanocrystal

Nanocrystals or sol particles have been frequently employed as as-prepared product for hole-blocking layer deposition due to ultrafine particles, scalable, robustness, and facile deposition. Typically, sol particle is dispersed with organic binder and/or in appropriated solvent, and is spin-coated directly on transparent conductive oxide glass (TCO), and annealed. Employing nanocrystal (such as ZnO, SnO_2) as ETL for perovskite solar cell also demonstrates unprecedented progress by showing high performance and simultaneous long term stability.[26)]

Jiang *et al*. demonstrated planar structured cell with $FAPbI_3$ active layer perovskite solar cells, assembled with ultrathin layer of SnO_2 nanoparticles (particle size ~ 4 nm with layer thickness ~ 25 nm) and exhibited PCE near 20% without hysteresis.[27)] Photo response edge of $FAPbI_3$ based device was extended to 820 nm and EQE yield reaches as high as 93%.

The excellent photovoltaic properties with the use of SnO_2 nanoparticle thin film not only found in case of regular structure devices but also demonstrated high potential in inverted structure devices. Recently, Zhu and co-workers found that hydrothermal method under high temperature (200ºC) and pressure in autoclave can produce highly crystalline SnO_2 with uniform grain size ~ 5–10 nm.[28)] Due to the fact that highly crystalline SnO_2 nanoparticle can demonstrate efficient electron transport in device with relative thickness ca. 120 nm, with SnO_2 nanoparticle as ETL was employed for inverted structure devices. Highly compact SnO_2 as top layer can effectively protect $MAPbI_3$ perovskite layer from oxygen and moisture as well. In addition, hysteresis issue which was accounted for large capacitance resistance in pristine structure of SnO_2, was eliminated via interface engineering of fullerene (C_{60}). SnO_2 layer assembled with C_{60} in inverted structure devices employing NiO as HTL, exhibited tremendous results with PCE of 18.8% and substantial robustness for 30 days under relative humidity over 70%.

(3) Atomic layer deposition (ALD)

In addition to thin film deposition techniques, ALD method emerged as a promising method which can produce smooth oxide film whose thickness and composition can be precisely controlled. Basically, layer-by-layer deposition in ALD is conducted via self-controlling chemical reaction of gaseous precursors with solid surface. As reported earlier, SnO_2 which is derived from oxidizing reaction of tetrakis(diamino)tin ($Sn(DMA)_4$) with hydrogenperoxide, generates highly quality SnO_2 film by yielding high transparency (over 90% on glass) without agglomeration of particle and corrosive problem due to by-products.[29, 30)]

Despite the aforementioned advantages of SnO_2 by ALD method, according to the work reported by Kavan *et al*., low-(118ºC) and high temperature (450ºC) treatment during the deposition process still plays as an important key role for electron extraction properties due to disparity of energy band alignment between amorphous and crystalline tin oxide phase.[31)] Thus, the optimal condition of tin oxide for each kinds of structure is required to further explore.

III. Conclusion and outlook

In this review article, we have given an overview of the function and importance of electron transport materials for perovskite solar cells. The

electron transport can be efficiently manipulated by charge extraction of ETL. To adequately serve electron transfer processes, a few nanometers of thickness and appropriated interfacial energy band alignment between ETL and perovskite without charge barrier and electrical shunting path are prerequisite. Apart from electronic properties, availability of low-temperature processes and/or stability enhancement also attracts attention for alternative material. Among them, an effort to utilize low temperature deposited tin oxide for perovskite solar cells has been intensively concentrated. In recent years, solution based processes (liquid solution or colloidal as-prepared) have shown great interest due to facile process and high qualities of tin oxide blocking layer. Remarkably, due to excellent properties in surface coverage and compactness, tin oxide layer can effectively hinder hole diffusion and simultaneously minimize charge recombination processes. However, high capacitance resistivity issues derived from non-stoichiometric (SnO_{2-x}) or amorphous tin oxide has still limited reaching to full potential. Interfacial engineering is an effective strategy to improve electronic properties of pristine structure and reduce hysteresis by doping with p-character element or high conductivity molecules (such as fullerene derivatives). In view of devices stability, tin oxide can well sustain photovoltaic properties without showing deterioration of performance from light induced perovskite degradation under continuous illumination compared with TiO_2. Furthermore, tin oxide also can surprisingly work as bi-functional layer (ETL and humidity-oxygen protective layer) for inverted structure devices by preserving performance under humidity for several days. As parallel studies, atomic layer deposition or ALD is a precise technique to prepare conformal oxide by layer-by-layer deposition. In spite of advantages in conformal layer forming, but the performance of devices still not go so far from the best progress in solution processes due to intrinsic capacitance resistivity in densely oxide film.[15] Moreover, this technique is costly and complicate to scalable. In future, to replace high temperature processes and open up roll-to-roll manufacturing, studies for morphological and composition control and/or effect of extrinsic doping to electronic properties for tin oxide blocking layer should be deeply investigated. Additionally, to overcome issues from inevitable surface trap state due to annealing processes and more efficiently manipulate electron transport, surface modification by self-assembly monolayer (SAM) of highly conductive molecules such as fullerene and their derivatives[32], or selective functional group bearing silane[33] on tin oxide surface will become an interesting topic.

[References]

1) Kojima A, Teshima K, Shirai Y, Miyasaka T, (2009) Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J. Am. Chem. Soc.*, 131: 6050–6051.; Miyasaka T, (2015) Perovskite photovoltaics: rare functions of organo lead halide in solar cells and optoelectronic devices. *Chem. Lett.*, 6: 720–729.; The best power conversion efficiencies record: https://www.nrel.gov/pv/assets/images/efficiency-chart.png (accessed Mar 13, 2017)
2) Yang WS, Noh JH, Jeon NJ, Kim YC, Ryu S, Seo J, Seok SIl, (2015) High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science*, 348:1234–1237
3) Saliba M, Matsui T, Seo J-Y, Domanski K, Correa-Baena JP, Nazeeruddin MK, Zakeeruddin SM, Tress W, Abate A, Hag-feldt A, Grätzel M, (2016) Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. *Energy Environ. Sci.*, 9:1989-1997.
4) Seo J, Noh JH, Seok Sil, (2016) Rational strategies for effcient perovskite solar cells. *Acc. Chem. Res.*, 49: 562–572.
5) Yang G, Tao H, Qin P, Ke W, Fang G, (2016) Recent

progress in electron transport layers for efficient perovskite solar cells. *J. Mater. Chem. A*, 4:3970–3990.

6) Liu Z, Chen Q, Hong Z, Zhou H, Xu X, Macro ND, Sun P, Zhao Z, Cheng Y-B, Yang Y, (2016) Low-temperature TiOx compact layer for planar heterojunction perovskite solar cells. *ACS Appl. Mater. Interfaces*, 8:11076–11083.
7) Li W, Li J, Niu G, Wang L, (2016) Effect of cesium chloride modification on the film morphology and UV-induced stability of planar perovskite solar cells. *J. Mater. Chem. A*, 4:11688–11695.
8) Niu G, Guo X, Wang L, (2015) Review of recent progress in chemical stability of perovskite solar cells. *J. Mater. Chem. A*, 3:8970–8980.
9) Zhang J, Pauporté T, (2015) Effects of oxide contact layer on the preparation and properties of $CH_3NH_3PbI_3$ for perovskite solar cell application. *J. Phys. Chem. C*, 119:14919–14928.
10) Shin SS, Yang WS, Noh JH, Suk JH, Jeon NJ, Park JH, Kim JS, Seong WM, Seok Sil (2015) High-performance flexible perovskite solar cells exploiting Zn_2SnO_4 prepared in solution below 100°C. *Nat. Commun.*, 6:7140–7147.
11) Wang K, Shi Y, Dong Q, Li Y, Wang S, Yu X, Wu M, Ma T, (2015) Low-temperature and solution-processed amorphous WOX as electron-selective layer for perovskite solar cells. *J. Phys. Chem. Lett.*, 6:755–759.
12) Grätzel M, (2014) Photoelectrochemical cells. *Nature*, 414:338-344.
13) Green ANM, Palomares E, Haque SA, Kroon JM, Durrant JR, (2005) Charge transport versus recombination in dyesensitized solar cells employing nanocrystalline TiO_2 and SnO_2 Films. *J. Phys. Chem. B*, 109:12525–12533.
14) Desai UV, Xu C, Wu J, Gao D, (2013) Hybrid TiO_2–SnO_2 Nanotube arrays for dyesensitized solar cells. *J. Phys. Chem. C*, 117:3232–3239.
15) Anaraki EH, Kermanpur A, Steier L, Domanski K, Matsui T, Tress W, Saliba M, Abate A, Grätzel M, Hagfeldt A, Correa-Baena JP, (2016) Highly efficient and stable planar perovskite solar cells by solution-processed tin oxide. *Energy Environ. Sci.*, 9:3128–3134.
16) Correa Baena JP, Steier L, Tress W, Saliba M, Neutzner S, Matsui T, Giordano F, Jacobsson TJ, Kandada ARS, Zakee-ruddin SM, Petrozza A, Abate A, Nazee-ruddin MK, Grätzel M, Hagfeldt A, (2015) Highly effcient planar perovskite solar cells through band alignment engineering. *Energy Environ. Sci.*, 8:2928–2934.
17) Dong Q, Shi Y, Wang K, Li Y, Wang S, Zhang H, Xing Y, Du Y, Bai X, Ma T, (2015) Insight into Perovskite Solar Cells Based on SnO_2 Compact Electron-Selective Layer. *J. Phys. Chem. C*, 119:10212–10217.
18) Liu Q, Qin M-C, Ke WJ, Zheng X-L, Chen Z, Qin P-L, Xiong L-B, Lei H-W, Wan J-W, Wen J, Yang G, Ma J-J, Zhang Z-Y, Fang G-J, (2016) Enhanced Stability of Perovskite Solar Cells with Low-Temperature Hydrothermally Grown SnO_2 Electron Transport Layers. *Adv. Funct. Mater.*, 26:6069–6075.
19) Bagheri-Mohaghegi M-M, Shokooh-Saremi M, (2004) Electrical, optical and structural properties of Li-doped SnO_2 transparent conducting films deposited by the spray pyrolysis technique: a carrier-type conversion study. *Semicond. Sci. Technol.*, 19:764–769.
20) Al-Gaashani R, Radiman S, Tabet N, Daud AR, (2012) Optical properties of SnO_2 nanostructures prepared via one-step thermal decomposition of tin (II) chloride dehydrate. *Mater. Sci. Eng. B*, 177:462–470.
21) Ke W, Fang G, Liu Q, Xiong L, Qin P, Tao H, Wang J, Lei H, Li B, Wan J, Yang G, Yan Y, (2015) Low-temperature solution-processed tin oxide as an alternative electron transporting layer for efficient perovskite solar cells, *J. Am. Chem. Soc.*, 137:6730–6733.
22) Pinpithak P, Chen H-W, Kulkarni A, Sanehira Y, Ikegami M, Miyasaka T, (2017) Low-temperature and ambient air processes of amorphous SnO_x-based mixed halide perovskite planar solar cell. *Chem. Lett.*, 46:382–384.

23) Yang G, Lei H, Tao H, Zheng X, Ma J, Liu Q, Ke W, Chen Z, Xiong L, Qin P, Chen Z, Qin M, Lu X, Yan Y, Fang G., Reducing hysteresis and enhancing performance of perovskite solar cells using low-temperature processed Y-Doped SnO_2 nanosheets as electron selective layers (2017). *Small*, 13:1601769.

24) Zhou H, Chen Q, Li G, Luo S, Song T-B, Duan H-S, Hong-Z, You J, Liu Y, Yang Y, (2014) Interface engineering of highly efficient perovskite solar cells. *Science*, 345:542–546.

25) Park M, Kim J-Y, Son HJ, Lee C-H, Jang S-S, (2016) Low-temperature solution-processed Li-doped SnO_2 as an effective electron transporting layer for high-performance flexible and wearable perovskite solar cells. *Nano Energy,* 26:208–215.

26) You J, Meng L, Song T-B, Guo T-F, Yang Y(M), Chang W-H, Hong Z, Chen H, Zhou H, Chen Q, Liu Y, Macro ND, Yang Y, (2016) Improved air stability of perovskite solar cells via solution-processed metal oxide transport layers. *Nat. Nanotechnol.*, 11:75–81.

27) Jiang Q, Zhang L, Wang H, Yang X, Meng J, Liu H, Yin Z, Wu J, Zhang X, You J, (2016) Enhanced electron extraction using SnO_2 for high-efficiency planar-structure $HC(NH_2)_2PbI_3$-based perovskite solar cells. *Nat. Energy*. 2:16177

28) Zhu Z, Bai Y, Liu X, Chueh C-C, Yang S, Jen AK.-Y., (2016) Enhanced efficiency and stability of inverted perovskite solar cells using highly crystalline SnO_2 nano-crystals as the robust electron-transporting layer. *Adv. Mater.*, 28:6478–6484.

29) Elam JW, Baker DA, Hryn AJ, Martison ABF, Pellin MJ, Hupp JT, (2008) Atomic layer deposition of tin oxide films using tetrakis(dimethylamino)tin. *J. Vac. Sci. Technol.*, 26:244–252.

30) Heo J, Hock AS, Gordon RG, (2010) Low temperature atomic layer deposition of tin oxide. *Chem. Mater.*, 22:4964–4973.

31) Kavan L, Steier L, Grätzel M, (2017) Ul-trathin buffer layers of SnO_2 by atomic layer deposition: perfect blocking function and thermal stability. *J. Phys. Chem. C*, 121:342–350.

32) Wojciechowski K, Stranks SD, Abate A, Sadoughi G, Sadhanala A, Kopidakis N, Rumbles G, Li C-Z, Friend R-H, Y. Jen AK, Snaith HJ, (2014) Heterojunction modification for highly effcient organic-inorganic perovskite solar cells. *ACS Nano*, 8:12701–12709.

33) Liu L, Mei A, Liu T, Jiang P, Sheng Y, Zhang L, Han H, (2015) Fully printable mesoscopic perovskite solar cells with organic silane self-assembled monolayer. *J. Am. Chem. Soc.*, 137:1790–1793.