Current Advances in the Preparation of SnO₂ Electron Transport Materials for Perovskite Solar Cells

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ABSTRACT

Design of semiconductor SnO_2 nanomaterials have gained considerable attention owing to their intriguing performance of electron transport in halide perovskite solar cells (PSC). The purpose of this paper is to investigate the different preparation methods of semiconductor SnO_2 films as electron transport layers for PSC. Particular focus is paid to the preparation and characteristics of the SnO_2 particles/films in order to understand the relationship between the quality of nanostructured SnO_2 films and performance of solar cells. One of the major approaches to obtain SnO_2 layers has been the spin-coating deposition of SnO_2 nanofluids, made by the surface modification of SnO_2 nano-colloids. The preparation of SnO_2 nanoparticles using Tin(IV) salts has also been reported to produce a smooth SnO_2 film. Light-to-electricity conversion efficiency of near 20% has been reported in several reports on PSC. The advantage of using SnO_2 materials includes its superior conductivity, which is much higher than TiO_2. This paper also presents the creation of SnO_2 nanoparticles, an alternative process of obtaining SnO_2 electron transport materials, that can be achieved through a freeze-drying process of Tin(IV) precursors. Crystal growth of SnO_2 can be controlled at significantly low temperatures at less than 40 °C.

KEY WORDS: SnO_2 Nanoparticles, Nanofluids, Electron Transport, Perovskite Solar Cells

1. INTRODUCTION

In the past few decades, there has been a decline in the availability of fossil fuels and increase in energy consumption globally leading to rise in pollution to the environment. This has led to a rapid hike in the development of renewable energy sources with solar power being one of the major candidates due to the sun being able to provide the ultimate solution to the challenge of sustainable energy supply. There two general methods to generate solar power via solar cells and passive/active solar thermal systems. Focusing on the solar cells for electric power generation there are different ways to harvest the solar energy of which the conventional solid-state solar panels are the most common. The cons of these silicon based solar panels are their productions cost and their negative environmental impact. In recent years different variations of solar cells have emerged promising low productions cost and low environmental impact, and also high efficiency such as perovskite solar cells (PSC) [1] and dye-sensitized solar cells (DSSC) [2]. In these types of solar cells, one of the electrodes is composed of nano-crystalline material such as TiO_2 and/or SnO_2, forming the semiconductor layer for the photon-electron transfer process. The nano-crystalline material is often

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placed on a transparent conducting glass in order to achieve a high surface coverage of light-absorbing materials, essential for high-performance devices.

Recently, tin(IV) oxide (SnO_2) has been explored as potential electron transport material as an alternative to TiO_2. SnO_2 has been well studied for example in connection with perovskite solar cells (PSCs) mostly due to its favorable attributes such as high electron mobility ~100-200 cm^2 V^{-1} s^{-1}) and wide bandgap of 3.6 eV compared to 3.2 eV for TiO_2 [3]. The high mobility can promote faster electron transport and thereby reducing the recombination probability of photoinduced electrons. In addition, SnO_2 forms a homo-junction with the FTO substrate and thus solves the high contact resistance issue as observed in hetero-junctions formed with other oxides like TiO_2. Despite the apparent advantages over TiO_2 there are some concerns using SnO_2 as electron transport layer and the main concern is that it suffers from degradation at higher temperature processes. Much research has been done to show that the efficiency of solar cells can be increased further using SnO_2 rather than TiO_2. In this paper, notable achievements in the preparation of SnO_2 thin-filmsas well as the unique attributes of SnO_2 as electron transport layers in PSCs (Tables 1 and 2) are described.

2. PREPARATION OF TIN OXIDE LAYERS AND APPLICATIONS FOR PEROVSKITE SOLAR CELLS

Table 1 Overview of the typical deposition technique of SnO_2 films and PSC performance. MA and FA denote methylammonium and formamidinium ions, respectively.

Deposition technique of SnO_2	Perovskite	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	η (%)	Ref.
Sol-gel process (Spin-coating of Tin salt, Anealing)	$CH_3NH_3PbI_3$	22.83	1110	0.640	16.02	4
Deposition of SnO_2 colloidal solution (Spin-coating)+ Anealing	$(FAPbI_3)_{0.97}(MAPbBr_3)_{0.03}$	24.87	1090	0.748	20.27	5
Deposition of SnO_2 colloidal solution (Spin-coating)+ Anealing	$FA_{0.95}Cs_{0.05}PbI_3$	24.57	1110	0.792	21.60	6
Deposition of SnO_2 colloidal solution (Spin-coating)+ Anealing	$(FAPbI_3)_x(MAPbBr_3)_{1-x}$	24.1	1120	0.789	21.30	7
Sol-gel process (Spin-coating of Tin salt, Anealing)	$MAPbI_3$	22.66	1070	0.727	17.61	8
Deposition of SnO_2 colloidal solution (Spin-coating)+ Anealing	$MAPbI_3$	24.28	1150	0.768	21.38	9

Electrodeposition (Tin sailts)+Anealing	$MAPbI_{3-x}Cl_x$	18.65	1020	0.791	14.97	10
Deposition of SnO_2 colloidal solution (Spin-coating)+ Anealing	$CH_3NH_3PbI_3$	20.11	1110	0.643	14.36	11
Magnetron sputtering	$CH_3NH_3PbI_3$	21.94	994.98	0.670	14.63	12
Atomic layer deposition	$Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{2.7}Br_{0.3})$	22.1	1078	0.750	17.80	13

High-performance lead halide perovskite solar cells typically used high-temperature processed TiO_2 as the electron transport layers. One of the early studies on SnO_2-based perovskite solar cells was reported by Ke et al. [4], demonstrating that low-temperature solution-processed nano-crystalline SnO_2 could be an excellent alternative to TiO_2. In this study, the SnO_2 were synthesized by a solution process i.e. spin-coating of $SnCl_2$ precursor that can be prepared at a room temperature. This was followed by thermal annealing in air at 180 °C for 1 h. The obtained thin films were treated with UV-ozone for 15 min. before perovskite deposition. SEM and TEM analysis indicated that the film consisted of nanoscale grains and the SnO_2 was crystallized. Atomic force microscopy images showed that the surface became smoother when the FTO substrate was covered with the SnO_2 nano-crystalline film. The best performing perovskite cell using a 60 nm-thick SnO_2, $CH_3NH_3PbI_3$(600 nm), and Spiro-OMeTAD achieved a PCE of 17.21% (V_{oc}: 1.11 V, Jsc: 23.27 mA cm^{-2}, and FF: 0.67) when it was measured under a reverse voltage scan. For a forward voltage scan of the same cell, the PCE was 14.82%, an V_{oc} of 1.11 V, a J_{sc} of 22.39 mA cm^{-2}, and a FF of 0.60. The perovskite solar cells using the SnO_2 layer had a low hysteresis. They concluded that the better charge transport (a fast electron injection process) at the SnO_2/ perovskite interface could be partially responsible for the low hysteresis observed in the PSC. This study paved a new way to push the performance of lead halide perovskite solar cells to a higher level.

Improved electron extraction of SnO_2 for high-efficiency planar-structure $HC(NH_2)_2PbI_3$-based PSC have been demonstrated by Jiang et al. [5]. The commercial SnO_2 colloid precursor (tin(IV) oxide, 15% in H_2O colloidal dispersion) was spin coated onto ITO substrates and then baked on a hot plate in ambient air at 150°C for 30 min. The mobility of the SnO_2 film was calculated to be 1.9 x 10^{-3} $cm^2V^{-1}s^{-1}$. After depositing the SnO_2 electron transport layer, the perovskite layer was deposited by a two-step spin coating method as following. First, PbI_2 in dimethylformamide (DMF) was spin-coated and then annealed at 70°C for 30 min. Secondly, the mixture solution of FAI:MABr:MACl in isopropanol was spin-coated onto the PbI_2. The best performing device using SnO_2 nanoparticles produced an V_{OC} of 1.09V, J_{sc} of 24.87mAcm^{-2}, FF of 74.77% and PCE of 20.27% under reverse scan (Spiro-OMeTAD was used as a hole-conductor.). Under forward scan, the same device showed a V_{OC} of 1.09V, a J_{SC} of 24.88mAcm^{-2}, a FF of 75.73%, and a PCE of 20.54%. The photo response edge has been extended to 820 nm, when it was compared to 780nm from $CH_3NH_3PbI_3$. The authors also demonstrated that the SnO_2-based devices had better photostability than the TiO_2-based devices, although the mechanism was not clear.

Use of surface modified tin oxide (SnO_2) has also been shown to be an effective approach for high-efficiency PSC. Yang et al. have recently reported planar-type perovskite solar cell (PSC) using a chelating agent, EDTA, for the SnO_2 modification [6]. The EDTA was dissolved in deionized water,

and the SnO_2 aqueous colloidal dispersion were separately prepared to remove residual solvent. The EDTA and SnO_2 solution were mixed with a volume ratio of 1:1, using a hot plate at 80 °C the milky-white 'E-SnO_2' colloidal solution i.e. SnO_2 nanofluid was obtained. Finally, the E-SnO_2 films were obtained by spin-coating via drying with a vacuum oven at 60 °C for 30 min. Atomic force microscopy (AFM) images of the SnO_2-coated ITO substrates revealed that the E-SnO_2 film showed the smallest roughness of 2.88 nm. Energy band alignment between perovskites and SnO_2 was also determined. It was found that the Fermi level of E-SnO_2 was very close to the conduction band of perovskite. The authors showed that SnO_2 films displayed high average transmittance in the visible region. In addition, the electron mobility of E-SnO_2 was 2.27×10^{-3} $cm^2V^{-1}s^{-1}$, which was significantly higher than that of the unmodified SnO_2 (9.92×10^{-4} $cm^2V^{-1}s^{-1}$). $FAPbI_3$ was used as the active light-absorber for its proper band gap, with the addition of a small amount of Cs to improve its phase stability. Regarding the perovskite film deposited on the SnO_2 substrates, it was observed that continuous pinhole-free films were obtained. Notably, the average perovskite grain size was enhanced to be as much as about 828 nm for the E-SnO_2 substrates. The device based on EDTA produced a PCE of 16.42% with J_{sc} =22.10 $mAcm^{-2}$, V_{oc}=1.08 V, and FF=0.687. The device employing unmodified SnO_2 substrate showed a PCE of 18.93% with J_{sc}=22.79 $mAcm^{-2}$, V_{oc}=1.10V, and FF=0.755. When the E-SnO_2 was employed as ETL, the PCE was increased to up to 21.60% (the J_{sc}, FF, and V_{oc} were increased to 24.55 $mA\ cm^{-2}$, 0.792, and 1.11V). The higher J_{sc} and FF were ascribed to the high electron mobility of the SnO_2 that can effectively extract electrons. The larger V_{oc} could be explained as being due to the closer energy level between E-SnO_2 and perovskite.

Liu et al. have reported on the passivation effect of a fullerene derivative with 2-hydroxyl anchoring groups on the performance of SnO_2 electron transport layer in PSC [7]. The hydroxyl groups at the end of the long alkyl chain in C9 were introduced to passivate the oxygen vacancies on the surface of SnO_2 through the coordination to Sn. In other words, the fullerene-modifying layer could efficiently passivate the defects on the surface of the SnO_2 layer. A thin layer of SnO_2 nanoparticles was spin-coated on the ITO substrate using a water-based SnO_2 colloidal solution and annealed at 150 °C for 30 min. C9- fullerene derivative was dissolved in chloroform and integrated onto the SnO_2 by spin-coating. The perovskite film was further spin-coated in an N_2 atmosphere. The perovskite precursor solution was dropped onto SnO_2 and spin-coated, and annealed at 150 °C for 10 min. With Spiro-OMeTAD as a hole-transport layer, a configuration of ITO/SnO_2/C9- fullerene /$(FAPbI_3)_x(MAPbBr_3)_{1-x}$/spiro-OMeTAD/Au were tested. The C9-fullerene modified devices yielded a maximum PCE of 21.3% with negligible hysteresis, which was higher than that of the control devices of bare SnO_2 (PCE: 20.0%). This work indicated that fullerene derivatives with anchoring hydroxyl groups were beneficial in the materials interface engineering of SnO_2-based PSCs.

Bilayer SnO_2 has also been demonstrated to show an effective electron transport layer for PSC [8]. Yi et al. used SnO_2 nanoparticles to fill the pin-holes of sol−gel SnO_2 layer to form a bilayer structure. For ETL, sol−gel SnO_2 precursor solution using Tin(IV) chloride pentahydrate was spin-coated on ITO inside the N_2 filled glovebox and annealed at 200 °C for 60 min. at ambient condition.. SnO_2 colloid dispersion was spin-coated on UVO-treated substrate and then annealed at 150 °C for 30 min. The methylammonium lead iodide perovskite films ($CH_3NH_3PbI_3$) were prepared by one-step method. The surface of SnO_2 top layer (bilayer structure) showed an amorphous-like morphology and pin-holes on the surface have not been observed, whereas only sol−gel SnO_2 exhibited visible pin-holes in the film. The AFM measurement revealed that the surface roughness of double layered SnO_2 ETL was 1.69 nm. With the help of thin-layer SnO_2 nanoparticles, the average PCE of bilayer SnO_2-based PSC has been increased from 12.97% to 16.84%. The main factor was the 23.7% enhancement of FF. The reported bilayer SnO_2 ETL is expected to open up new perspectives towards developing highly efficient PSC.

Hysteresis of I-V curves for SnO_2-based PSC was suppressed by the method of Liu et al. [9]. To the aqueous SnO_2 colloidal dispersion was mixed with NH_4Cl to obtain NH_4Cl-SnO_2 precursor, by stirring at room temperature. The NH_4Cl-SnO_2 layers were formed by spin-coating onto the clean ITO substrates, and then annealed to remove solvent. The $MAPbI_3$ perovskite film was deposited on top of SnO_2. The devices consisted of ITO/SnO_2/perovskite/Spiro-OMeTAD/Ag. The perovskite solar cells with NH_4Cl -induced coagulated SnO_2 colloids produced PCE of 21.38 % with negligible hysteresis, whereas the PCE was 18.71 % with hysteresis for the reference solar cell. They also mentioned that the device stability can be significantly improved.

Ko et al., have shown that electrodeposition of SnO_2 on FTO can be used for application in planar heterojunction perovskite aolar cells [10]. A chronovoltammetry technique was adapted for the electrodeposition of Sn nanospheres on FTO substrate using a three-electrode system (working electrode: FTO, counter electrode: platinum plate, reference electrode: Ag/AgCl electrode) using the water-based solution of $SnCl_2 \cdot 2H_2O$ and nitric acid. The nanospheres were heated in air at 400 °C for 30 min to convert to SnO_2. $TiCl_4$ treatment was also applied by using a $TiCl_4$ solution at 70 °C for 30 min. and drying the substrates at 150 °C in air. For perovskite layer, a mixture of PbI_2 and $PbCl_2$ dissolved in N, N-dimethylformamide was spin-coated on the SnO_2-coated FTO in a glove box and dried at 70 °C. A methylammonium iodide solution was spin-coated and then annealed at 105 °C for 75 min in the ambient environment. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] solution was used as the HTM. When a deposition time of 150 s, the PCE of the device was 9.11% with short-circuit current density, open-circuit voltage, fill factor of 17.84 mA/cm^2, 1.03V, 0.496, respectively. Whereas the deposition time was increased to 180 s, a higher PCE of 10.0% was obtained because of the improved Jsc. The use of a deposition time of 210 s lower the PCE (8.22%).

Besides the solution-processed SnO_2 film deposition as mentioned above, Li et al. showed the effects of UV treatment of low-temperature processed SnO_2 on the performance of PSCs [11]. They prepared a compact layer by spin-coating water-based SnO_2 precursor and then treated with ultraviolet ozone. The SnO_2 thin films were prepared by spin-coating the SnO_2 precursor solution (changing the concentration: 10, 15, 20, and 30%) on the ITO substrates and dried at 50 °C. The substrates were then treated by ultraviolet ozone cleaner for 60 min. at 60 °C. Each layer in solar cells were processed at low temperatures less than 90 °C. The device structures were planar hetero-junction PSC; ITO/SnO_2/$MAPbI_3$/Spiro-OMeTAD/Au. When the concentration of SnO_2 was 20%, the performance was optimized with J_{sc} of 20.11 mA/cm^2, V_{oc} of 1.11 V, FF of 0.643, PCE of 14.36%.

A vacuum processed SnO_2 film was also reported by Sun et al. [12]. They successfully prepared the film with radio frequency reactive magnetron sputtering under room temperature. The obtained SnO_2 thin films exhibited lower surface roughness than FTO substrate, leading to the improvement of the interface morphology with perovskite layers. The FTO glass without sputtering had a roughness of 31.8 nm and the roughness of the sputtering sample was 30.2 nm. The sputtering process made the perovskite film smoother and more uniform, reducing defects in interfacial contact. Planar perovskite cells based on bare FTO had a PCE of only 5.08% due to a poor Jsc and FF. When the reactive sputtering was applied to deposit an electron transport layer, PCE of the device produced 12.02% (Jsc: 20.20 mA/cm^{-2} , Voc: 0.95, and FF: 0.62).

Kuang et al. have reported on plasma-assisted atomic-layer-deposition of SnO_2 for PSC [13]. SnO_2 film with a low electrical resistivity of 1.8×10^{-3} Ω cm, a carrier density of 9.6×10^{19} cm^{-3} , and a high mobility of 36.0 cm^2 /V s was deposited at 200 °C, using tetrakis(dimethylamino)tin (TDMASn) as a precursor. ITO layers were used as substrates and SnO_2 layers with a thickness of 15

nm were deposited at a temperature of either 50 or 200 °C. The SnO_2 layers were pretreated with an O_2 plasma at room temperature prior to perovskite deposition. Planar $Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{2.7}Br_{0.3})$ PSCs were fabricated. PCEs of 17.5 and 17.8% have been achieved for the best performing devices using 50 and 200 °C-processed SnO_2.

Recently, the authors have for the first time demonstrated that crystallized SnO_2 nanoparticles can be obtained via low-temperature process using a dry-freezing method. $SnCl_2$ was adapted for the dry-freezing as a starting material to form the precursor solution of water and methanol mixture at less than 30 ºC. This method enabled to effectively dehydrate from the amorphous Sn(II)-containing precursor, leading to the formation of crystallized SnO_2 nanoparticles [14]. Nanoparticles in the size of around 5 nm were clearly observed on Transmission Electron Microscope. XRD pattern indicated that SnO_2 nanocrystals formed in the dry freezing process. The device applications using the SnO_2 as an electron transport layer in PSC are now in progress.

3. TIN OXIDE/TITANIUM OXIDE HYBRID LAYERS FOR PEROVSKITE SOLAR CELLS

Table 2 Examples of the deposition technique of SnO_2/TiO_2 films and PSC performance.

Deposition technique of SnO_2/TiO_2	Perovskite	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	η (%)	Ref.
TiO_2 nanoparticles coated by an amorphous SnO_2 (Spin-coating)	CsI + $(FAPbI_3)_{0.87}(MAPbBr_3)_{0.13}$	22.51	1168	0.776	20.40	15
Three-step chemical bath	$(FAPbI_3)_{0.3}(MAPbI_3)_{0.7}$	23.38	1122	0.778	20.40	16
Magnetron sputtering (TiO_2)/Deposition of SnO_2 colloidal solution (Spin-coating)+ Anealing (SnO_2)	$Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	23.28	980	0.670	15.39	17

Tavakoli et al. have reported on a mesoscopic oxide double layer (SnO_2/TiO_2) as an electron selective contact for PSC [15]. This electron selective layer consisted of TiO_2 nanoparticles coated by an amorphous SnO_2. The surface of mesoporous-TiO_2 was modified with SnO_2 precursor solution ($SnCl_2$ dissolved in ethanol). This solution was spin-coated on top of mesoporous-TiO_2, followed by annealing films at 180 °C. From SEM measurements, the grain size of perovskite film formed on amorphous SnO_2 was found to be slightly larger than that of perovskite film on top of the bare mesoporous-TiO_2 layer. This indicated that the number of nucleation cites for amorphous SnO_2 was reduced, resulting in the larger grain size of perovskite. The XRD data showed that the spin-coated SnO_2 film treated at 180 °C to be amorphous and it was converted to crystalline SnO_2 upon annealing at 450 °C. The device consisted of FTO glass coated by a compact TiO_2 layer, a 150 nm-thick mesoporous-TiO_2, a thin layer of SnO_2, a 300 nm-thick perovskite film, a 150 nm-thick spiro-OMeTAD, and gold contact. The hysteresis in the I-V curves of devices was suppressed and carrier recombination was also retarded. As results, the PSC of mesoporous-TiO_2/amorphous SnO_2 produced the highest PCE of 20.4% (J_{sc}: 22.51mA/cm^2, V_{oc}: 1.168 V, and FF: 77.6%). The reference cell using a bare mesoporous-TiO_2 gave a PCE of 19.14% (J_{sc}: 22.21 mA/cm^2, V_{oc}: 1.098 V, FF: 78.5%). They

also found that the amorphous SnO_2 prevented UV degradation of the PSC, retaining 97% of the initial PCE under 60 h. irradiation of UV light

SnO_2 nanoparticle-modified TiO_2 as the ETL in PSC have been reported by Ding et al. [16]. The $SnO_2@TiO_2$ film was fabricated using the following chemical bath. $SnCl_2$ ethanol solution was first prepared and stored in the freezer at 5 °C. The aqueous $TiCl_4$ solution was prepared by mixing $TiCl_4$ with water at 0 °C and then stored in a freezer at 5 °C. The FTO substrate was soaked in the dilute 2M aqueous $TiCl_4$ solution. The glass container was dried at 70 °C. The FTO substrate was rinsed using ethanol and water, and dried at 120 °C. The substrate was then treated at 70 °C with the solution prepared by 2M aqueous $TiCl_4$ solution and water (the molar ratio was 1:100). The FTO substrate coated with TiO_2 nanoparticles by the chemical bath was soaked in the solution that was obtained by mixing 2M $SnCl_2$ ethanol with water (the molar ratio was 1:50). The glass was dried at 70 °C. Finally the substrate was annealed at 140 °C. Regarding the performance of perovskite solar cells, they achieved average PCE of 21.27%, 19.79%, 17.21%, and 16.31% for the active areas of 0.10 cm^2 , 1.13 cm^2 , 5.25 cm^2 , and 10.56 cm^2, respectively. Their results indicated that the $SnO_2@TiO_2$ ETL can significantly facilitate electron extraction and decrease the trap states. They also mentioned that their low-temperature processability and absence of spin-coating process will provide a promising way for the commercialization of PSC.

Liu et al. have demonstrated a TiO_2/SnO_2 bilayer as electron transport layer for carbon counter electrode based planar-heterojunction PSC [17]. TiO_2 film was fabricated with radio frequency magnetron sputtering. The sputtering could fully cover the surface of the FTO substrate, passivating the FTO surface defects and thus reducing the recombination. The SnO_2 layer was integrated by spin-coating a $SnCl_2$ ethanol solution, followed by heating at 195°C. The TiO_2/SnO_2 bilayer gave a lowest root-mean-square (RMS) roughness of 9.3 nm, which was beneficial for the deposition of high-quality perovskite films. Their devices used a Cs/MA/FA perovskite film combined with Cu-Phthalocyanine (CuPc) as a hole transport layer. The device produced a PCE of 15.39% and an excellent stability over 1200 h.

4. CONCLUSIONS

Progress in fundamental science of SnO_2 nanomaterials has been made towards developing renewable energy technologies, especially as the key material in PSC. In this paper, recent advances on preparation and characteristics of the SnO_2 particles/films were described in order to understand the relationship between the quality of nanostructured SnO_2 films and performance of PSC. One of the major approaches in forming SnO_2 layers has been the spin-coating deposition of SnO_2 nanofluids that were prepared by the surface modification of SnO_2 nano-colloid precursors. Remarkably, light-to-electricity conversion efficiency of near 20% for PSC has been reported in several reports. The advantage for realizing high efficiency includes superior conductivity of SnO_2, which is much higher than TiO_2. In addition, the fast electron injection at the perovskite/SnO_2 interface can reduce hysteresis phenomena. Compared to those of TiO_2 nano-crystalline systems for PSC, the design strategies of SnO_2 nanoparticles including the chemical synthesis and thin-film formation have not been well established so far. For further improvement, one research direction would be a greater understanding of the relation of microstructures of SnO_2 nanoparticles and device performance. As a new approach towards the development of semiconductor nanoparticles, our dry-freezing method can provide versatile metal oxides at low temperatures. In parallel to the advancement of SnO_2 nanoparticles synthesis, it is also crucial to optimize materials interfaces of SnO_2 layers in the PSC. Controlling SnO_2 crystal growth will explore avenues in the low cost production of high-efficiency perovskite solar cell modules.

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