An Efficient Electron Transport Material of Tin Oxide for Planar Structure Perovskite Solar Cells

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Abstract

The photovoltaic performance of a perovskite solar cell based on a new electron conducting SnO₂ film prepared at low temperature using different solvents was investigated. SnO₂ was selected as an electron conducting medium due to its superior properties over TiO₂, such as better antireflective properties, higher electron mobility, more suitable band edges and a wider band gap. A SnO₂ layer was developed by spin-coating SnCl₂ solution followed by annealing at 200°C in air. The low-temperature (200 °C) annealed SnO₂ layer exhibits enhanced crystallization, high transmittance, and uniform surface morphology using ethanol as a solvent rather than water. Solid state CuSCN hole conductor was used as HTM for reducing the device cost. A planar solar cell fabricated with CH₃NH₃PbI₃ perovskite infiltrated SnO₂ showed a power conversion efficiency of 8.38% with short-circuit current density of 18.99 mA/cm², an open-circuit voltage of 0.96 mV and a fill factor of 45%. The devices were fabricated at >60% humidity level at room temperature. The results suggest that SnO₂ is an effective charge collection system for CH₃NH₃PbI₃ based planar perovskite solar cells. In addition, these results

provide a new direction for the future improvement of perovskite solar cells using new electron conducting layers.

Keywords: SnO₂; CuSCN; Perovskite; Planar structure; Two-step process

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1. Introduction

Organometallic halide perovskites (ABX₃) have drawn much attention over the last several years and are currently under intense investigation [1-5]. The outstanding absorption properties, such as a high absorption coefficient and suitable band gap, make this material very appropriate for light harvesting applications in photovoltaics. The power conversion efficiency (PCE) of the first perovskite-based solar cell device reported in 2009 was 3.8% [6], but the certified efficiency has recently reached 20.1%. Development and improvement of the perovskite devices have been attained using different approaches, such as modifying the nature of the halide, the metal, or the cation group of the materials, as well as the development and optimization of novel fabrication techniques [7-11]. However, selective electron transporting materials (ETMs) and hole transporting materials (HTMs) were used for the high efficiency device.

TiO₂ exhibits electrical conductivity only after the formation of nanocrystallites. Therefore, the formation of TiO₂ crystallites at a low temperature is necessary for the preparation of TiO₂ ETMs. However, the preparation of low-temperature TiO₂ ETMs is relatively complicated because crystallization of TiO₂ is difficult. Although ZnO possesses high electron mobility and can be also used as an ETM for photovoltaic solar cells [12-14], it is chemically unstable and reacts easily with weak acids or bases. Efficient electron mobility of ZnO, TiO₂ and SnO₂ nanostructures has been recently reported [15]. A high electron mobility was observed for SnO₂ ($0.8 \pm 0.14 \text{ cm}^2/\text{V.s}$), ZnO ($0.08 \pm 0.01 \text{ cm}^2/\text{V.s}$) and TiO₂ ($0.1 \pm 0.03 \text{ cm}^2/\text{V.s}$). Thus, the development of new technology or new functional materials is required for

the preparation of ETMs at low temperature with simple processes. 2,2,7,7-Tetrakis-(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (Spiro-OMeTAD) is typically used as an HTM in conventional-architecture perovskite cells. However, Spiro-OMeTAD is relatively expensive, which may limit the future development and application of this type of solar cells. Recently, doctor-bladed CuSCN has also been used in a conventional-architecture perovskite cell (i.e., CuSCN deposited on the perovskite) and a high efficiency was reported [16]. In the present work, doctor-bladed CuSCN film was selected as the HTM layer due to its excellent transparency in the visible light spectrum range, high hole mobility, relatively good chemical stability and simple preparation process [17-20].

Here we report a fabrication procedure and device performance on low temperature processed SnO₂ ETM materials for perovskite solar cells using CH₃NH₃PbI₃. SnO₂ nanoparticles have good antireflective properties, wide band gap, less photocatalytic activity, high electron mobility and thermal stability. SnO₂ has been used in polymer-based solar cells and dye-sensitized solar cells with good performance [21, 22]. More recently, SnO₂ used as ETM in perovskite solar cells prepared at high annealing temperature and organic hole conductor [23-26]. However, there is no report on efficient perovskite solar cells using low-temperature processing SnO₂ ETM with high stable solid state hole conductor. In addition, this work focuses on the use of different solvents for the preparation of SnO₂ layer for planar perovskite solar cells by solution processed method. Perovskite was deposited on SnO₂ ETM layer by both one step and two step methods for comparison. It has been reported that morphological control is very important for solution-processing planar heterojunction perovskite solar cells [27]. For mesostructure perovskite solar cells, the morphology of the perovskite and crystal structure of the perovskite films also play important roles in determining the photovoltaic performance [28, 29]. To fabricate an efficient perovskite planar SnO₂/CH₃NH₃PbI₃/CuSCN/Au solar cells, a new SnO₂ electrode used as electron-blocking as well as electron-conducting layer using different

solvents, while dimethyl formamide (DMF) and 2-propanol were used to prepare PbI_2 and methylammonium iodide (MAI) solutions, respectively.

2. Experimental

2.1 Preparation of MAI

MAI powder was synthesized according to the method described by Wang et al., [30] 15.0 mL of concentrated aqueous hydroiodic acid (HI; 57 wt% in water, Alfa Aesar) was reacted with 13.5 mL of methylamine (CH_3NH_2 ; 40 wt% in aqueous solution) in a beaker at 0 °C (ice bath) for 2 h with constant stirring under air atmosphere. MAI was crystallized by rotary evaporation of the solvent. The white powder product was collected after washing three times with diethyl ether and ethanol, and then drying under vacuum at 60 °C overnight. The dried MAI powder was stored in a dark room until use.

2.2 Device Fabrication and Characterization

The solar cell devices were prepared on clean FTO coated glass (FTO, TEC-15 ($t=2$ mm), NSG-Pilkington). A blocking layer of compact SnO_2 was formed by spin-coating a precursor solution of 0.1M tin chloride in 5 mL of ethanol at 2000 rpm for 30 s. The film was then gradually heated to 200 °C and sintered at that temperature for 1 h. The deposition of tin chloride was repeated to ensure full coverage of the FTO with SnO_2 . After cooling down the film at room temperature, 1M solution of lead iodide in DMF was spin-coated onto the SnO_2 at 4000 rpm for 30 s, and dried at 70 °C for 30 min. The perovskite layer was formed using a two-step method; after drop-casting 0.1mL of $\text{CH}_3\text{NH}_3\text{I}$ solution in isopropanol (10 mg mL^{-1}) onto the substrate, and after waiting for 30 s, spin-coating for 30 s at 4000 rpm. The substrates were then dried at 100 °C for 30 min. The CuSCN HTM layer was then deposited by doctor blading at 80 °C. The HTM solution was prepared by dissolving 6 mg CuSCN (Kishida Chemical Co. Ltd.) in 1 mL of propyl sulfide. The device architecture was completed with a 50 nm gold counter electrode, which was thermally evaporated onto the top of the device. The active area of the device was 0.25 cm^2 .

2.3 Characterization

The crystal structure was characterized using X-ray diffraction (XRD; Miniflex II, Rigaku) with Cu K α radiation. The surface morphology and cross sections of the samples were investigated using high-resolution scanning electron microscopy (SEM; JSM-7400F, Jeol, accelerating voltage: 15 kV). UV/vis absorption spectroscopy (Lambda 750, Perkin Elmer) was measured in the range from 400 to 800 nm. Current density-voltage (J - V) curves were measured for samples with a cell area of 0.25 cm² by application of an external bias to the cell from the 0 to 1 V (forward bias scan) and measuring the generated photocurrent with a DC voltage current source (6240, ADCMT, Japan) under a solar simulator (AM1.5 irradiation, 100 mW cm⁻², calibrated with a standard photodetector (Bunkou Keiki, Japan)) equipped with a 500 W Xe lamp (YSS-100A, Yamashita Denso, Japan). To consider the photovoltaic effects of the solar cells, the results of reverse bias voltage scans were eliminated because these can lead to overestimation of the results [31]. Thus, all results presented here were obtained from the forward-bias voltage scans. The differential hole-transport resistance and recombination resistance (R_{rec}) were determined by electrical impedance spectroscopy (EIS) measurements in the dark at various bias voltages between 0.55 and 0.70 V. The EIS spectra were measured using a potentiostat (SP-150, Bio-Logic) and Zview2 software was used for the fitting. The differential resistances given represent the average for three different cells.

3. Results and discussion

To make a systematic comparison of the effect of solvent on the performance of planar photovoltaic device with a compact SnO₂ layer, thin film SnO₂ was spin-coated onto patterned FTO on a glass substrate. A two-step spin-coating method was used to fabricate the CH₃NH₃PbI₃ perovskite layer for the planar devices. Figure 1 shows evidence for the tetragonal structure perovskite with peaks at 2θ of 14.08° (1 1 0), 28.5° (2 2 0), and 31.7° (3 1 0) [32]. The peak at $2\theta = 12.8^\circ$ attributing to the PbI₂ phase just displays a weak intensity [33], indicating that the CH₃NH₃PbI₃ perovskites with high purity were successfully prepared on SnO₂ film by

two-step method. In the two-step method, the conversion of PbI_2 to $\text{CH}_3\text{NH}_3\text{PbI}_3$ was incomplete after depositing, with the (0 0 1) peak of PbI_2 still remaining, as shown in Fig. 1. It was speculated that $\text{CH}_3\text{NH}_3\text{I}$ in the solution could not penetrate into PbI_2 thin film so that some PbI_2 further away from the surface remained unreacted. The relative intensity of the PbI_2 peak (12.8°) was notably reduced when ethanol was used as the solvent for SnO_2 preparation. **The more conversion of the perovskite indicated good smoothness of the under layer (SnO_2) film using ethanol as solvent than the water.**

Figure 2a shows comparison of UV/vis absorption spectra for the FTO/ SnO_2 /perovskite film where the SnO_2 layer was prepared using water or ethanol as the solvent. The absorbance of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film deposited on the SnO_2 layer was significantly increased in the range of 450-800 nm, which was attributed to the more complete conversion of PbI_2 into $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite, as evidenced by the XRD patterns (Fig. 1). Near the (1 1 0) peak for the perovskite film, a diffraction peak at 12.8° appeared, which was attributed to (0 0 1) diffraction from PbI_2 crystals [34] as discussed elsewhere. **Hence, a strong peak appeared in the absorption band around 440 nm related to the characteristic of the PbI_2 .** On the other hand, it was generated by release of $\text{CH}_3\text{NH}_3\text{I}$ component from the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. An excess amount of PbI_2 in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite is expected to be detrimental to the device performance because of its electrical insulating properties [35]. **Fig. 2b shows a accompanied UV/vis absorption spectra of the bare FTO, FTO/ SnO_2 (ethanol) and FTO/ SnO_2 (water) films. Compared to the absorption spectrum of the bare FTO, FTO/ SnO_2 (ethanol) was significantly blue shifted with high intensity and FTO/ SnO_2 (water) was red shifted. The blue and red shifting of the absorption spectra is due size variation of the SnO_2 nanoparticles [36].**

The morphology of perovskite is closely related to optical and electrical properties of the device, and thus was important for enhancement of device performance. SEM images showed for bare SnO_2 (Fig. 3a, b) film on the FTO using water and ethanol, respectively. Top-view ($\text{SnO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$) and cross-sectional SEM images show the $\text{SnO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{CuSCN}/\text{Au}$

device, with ca. 50 nm thick SnO₂ films spin-coated using water (Fig. 4a-c) and ethanol (Fig. 5a-c). Due to very small film thickness (ca. 50 nm), the SnO₂ surface morphology basically replicates the homogeneous morphology of the underlying FTO layer. The surface image in Fig. 3a shows that the SnO₂ layer does not completely cover the FTO surface. Thus, inhomogeneous growth of SnO₂ particles may occur when using water as a solvent. When SnCl₂ dissolved in the water solvent, uncontrolled Sn(OH)₂ nanoparticles may grow in solution. That Sn(OH)₂ containing solution was deposited on FTO and then annealed in air at 200°C for 2h, resulting in formation of inhomogeneous SnO₂ nanoparticles by rapid oxidation, as shown in Fig. 3a. Consequently, the perovskite film showed rough surface due to the inhomogeneous SnO₂ film (Fig. 4a-b). However, when ethanol was used as the solvent for the SnO₂ film, highly uniform SnO₂ nanoparticles were grown directly from SnCl₂ (Fig. 3b) during annealing process. Uncontrolled Sn(OH)₂ was prevented in solution due to lack of (OH) molecules in ethanol. Therefore the top-view of the perovskite (SnO₂/CH₃NH₃PbI₃) film showed highly uniform structure with smooth surface (Fig. 5a-b).

Fig. 6 shows the performance of SnO₂/CH₃NH₃PbI₃/CuSCN/Au device prepared by a two-step process with different solvents used for the SnO₂ film. The detailed photovoltaic parameters are summarized in Table 1. The surface of electron-selective layer is very important for obtaining high-performance devices. The inhomogeneous SnO₂ layer promoted the recombination at FTO/CH₃NH₃PbI₃ interface and caused the fill factor to be reduced, as shown in Table 1. Therefore, the photovoltaic performance only reached 6.59% when the SnO₂ layer was prepared using water as solvent. However, a smooth SnO₂ layer that completely covered the rough FTO surface was formed using ethanol as solvent (Figs. 4a and b) and the photovoltaic performance exhibited a distinct increase to 8.38%.

Some preliminary photovoltaic experiments were conducted to evaluate the performance of devices prepared by a one-step method (Supplementary data). The contact between the SnO₂ and perovskite layers was determined to play an important role in the device performance. The

perovskite layer was in direct contact with the SnO₂ layer using a one-step perovskite coating method, and as a result the photovoltaic performance was reduced (Table S1, Supplementary Information). In contrast to one-step coating method, the two-step coating procedure used in this study resulted in significant increases in the open circuit voltage (V_{oc}), fill factor (FF), short circuit current density (J_{sc}), and efficiency, as shown in Table 1. There may be suitable band gap alignment between the compact SnO₂ and PbI₂ layers. Therefore, the two-step method was adopted to coat the perovskite on the SnO₂ layer for photovoltaic investigations. Figure 6 shows the J-V characteristics for a planar structure under standard AM 1.5 G illuminations at 100 mW cm⁻², and the photovoltaic parameters are given in Table 1. The SnO₂/CH₃NH₃PbI₃/CuSCN/Au device exhibited a PCE of 6.59% with a J_{sc} of 18.19 mA cm⁻², a V_{oc} of 0.95 V, and a FF of 0.38 when water used as solvent for SnO₂ preparation. The replacement of water with ethanol as the solvent resulted in a significant increase in V_{oc}, J_{sc}, and FF, achieving a PCE of 8.38% for device. The full coverage of SnO₂ on the FTO layer may block direct contact between the cathode and HTM, and thus minimize current leakage. The IPCE spectrum shown in Fig. 7 indicates that photocurrent was generated up to ca. 800 nm for the CH₃NH₃PbI₃ layer on the SnO₂ film. From integration of the measured IPCE spectrum over the solar spectrum, a short-circuit current density of 18.99 mA cm⁻² was estimated, which is similar to the average photocurrent generated from a typical cell [37]. It should be noted that this IPCE spectrum is taken from a representative device from the batch, not the most optimal device. It was also confirmed that the perovskite solar cell could operate well, even without a mesoporous TiO₂ film, where a thin, continuous CH₃NH₃PbI₃ layer formed on the SnO₂ surface exhibited good photovoltaic performance. The excellent device performance demonstrates the efficient charge collection properties of SnO₂ layer in the planar device.

To investigate the internal charge carrier transport and recombination, EIS was performed from 1 Hz to 10 MHz under illuminated conditions [38, 39]. Nyquist plots show various voltages from 0 to 400 mV for water (Fig. 8a-b) and ethanol (Fig. 8c-d) used as solvents for SnO₂

preparation. For both devices, two clear arcs in the high and lower frequency regions were observed. The high-frequency arc was assigned to the process of hole transport in solid CuSCN, and the low-frequency arc was attributed to recombination resistance and the chemical capacitance of the perovskite film. The charge-transport resistance at the $\text{CH}_3\text{NH}_3\text{PbI}_3$ (SnO_2 /ethanol)/selective contacts interface is presumably lower than that at the $\text{CH}_3\text{NH}_3\text{PbI}_3$ (SnO_2 /water)/selective contacts interface, leading to a lower series resistance of the device using SnO_2 /ethanol. The lower charge-transport resistance (and consequently lower series resistance) of SnO_2 /ethanol film is caused by the high smoothness of the surface, as shown in the SEM images. (Fig. 3a). This result may be attributed to the difference between the $\text{CH}_3\text{NH}_3\text{PbI}_3$ (SnO_2 /ethanol) film and the $\text{CH}_3\text{NH}_3\text{PbI}_3$ (SnO_2 /water) film. As shown in Fig. 4(a–b), the $\text{CH}_3\text{NH}_3\text{PbI}_3$ (SnO_2 /water) film exhibits more and larger cracks than that of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (SnO_2 /ethanol) film, which may reduce the carrier transport efficiency. The equivalent circuit use for fitting shown in Fig. 8e consists of one series resistance R_s , and two parallel resistance-constant phase elements ($R//\text{CPE}$). R_s is mainly the contribution from the conducting wires, contacts, and the sheet resistance of the collecting electrodes [40], and CPE is used to describe a non-ideal capacitor with a capacitive contribution and quality factor. Both devices have similar R_s , which is reasonable because of similar configurations of the solar cells. $R_a//\text{CPE}_a$ and $R_b//\text{CPE}_b$ correspond to semicircles at high and low frequencies, respectively. R_{rec} that is inversely related to the recombination rate and dependent on the applied bias voltage is plotted in Fig. 8f [41].

4. Conclusions

A high-efficiency perovskite solar cell was fabricated with new and efficient SnO_2 ETM layer using solid state CuSCN as HTM. The average efficiency for 3 cells using ethanol solvent with low-temperature processed SnO_2 ETM was 8.29%, whereas it was only 6.09% when water was used as solvent. The excellent surface smoothness of the thin film (SnO_2) using ethanol as solvent rather than water resulted in high efficiency of the device. Two-step spin-coating of PbI_2

and $\text{CH}_3\text{NH}_3\text{I}$ solutions led to a suitable contact between the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite and the SnO_2 film. The SnO_2 -based perovskite solar cell exhibited a good IPCE from 400 to 750 nm. The robust and abundant SnO_2 material promises the realization of commercial applications of $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells for low-temperature technology. The best performing planar perovskite solar cell was that with a nanocrystalline SnO_2 ETM layer prepared using ethanol as a solvent, which achieved a PCE of 8.38% with a J_{sc} of 18.99 mA cm^{-2} , a V_{oc} of 0.96 V, and a FF of 0.45 under forward scanning. This was much higher than that for the best cell where the SnO_2 ETM layer was prepared using water as solvent under the same conditions. Therefore, it was concluded that a solution method for the preparation of the SnO_2 film for perovskite-based solar cells using ethanol instead of water as a solvent resulted in good photovoltaic performance. In addition, the good performance of the planar SnO_2 based device showed fast saturation in charge collection, which indicates that the SnO_2 nanoparticles are an effective charge collection system for $\text{CH}_3\text{NH}_3\text{PbI}_3$ based perovskite solar cells. SnO_2 electron conducting materials could thus provide a future contribution to the industrial fabrication of low cost planar perovskite solar cells using roll-to-roll processing on a flexible substrate at low temperature.

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Table 1. Average photovoltaic performance of perovskite solar cells using 3 cells. The perovskite film prepared on SnO₂ by two step method. The values in the brackets show the results for the cells with the best efficiencies.

Sample details	Current density (mA cm ⁻²)	Voltage / (V)	Fill Factor	Efficiency (%)
SnO ₂ /Ethanol	18.98 (18.99)	0.96 (0.96)	45 (45)	8.29 (8.38)
SnO ₂ /Water	17.54 (18.19)	0.90 (0.95)	0.38 (0.38)	6.09 (6.59)

Fig. 1

Fig. 2 (a, b)

Fig. 3(a, b)

Fig. 4(a-c)

Fig. 5(a-c)

Fig. 6

Fig. 7

Fig. 8(a-f)