

SrTiO₃/TiO₂ composite electron transport layer for perovskite solar cells

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Abstract

Perovskite solar cells (PSCs) with SrTiO₃ mesoporous layer (MPL) generally show higher V_{OC} but lower J_{SC} than those with standard TiO₂-MPL. In this letter, we propose a new PSC with SrTiO₃/TiO₂ composite MPL to overcome this lower J_{SC} problem. The PSC with the SrTiO₃/TiO₂ composite MPL generated a comparable J_{SC} (19.3 mA/cm²) to that with the TiO₂-MPL, with keeping higher V_{OC} , which resulted in relatively high power conversion efficiency of 9.98 %.

Keywords: perovskite solar cells, SrTiO₃, composite mesoporous layer, electron transport layer

1. Introduction

Perovskite solar cells (PSCs) have attracted much attention due to the rapid increase of power conversion efficiency (PCE) from 3.8 % in 2009 [1] to 22.1 % in 2016 [2]. The PSCs are divided into two types by the structure of electron transport layer (ETL); one is mesoscopic type and the other is planer type. Although anatase TiO₂ is commonly used for the ETL of PSCs [3,4], other oxides, such as ZnO [5], SnO₂ [6] and Al₂O₃ [7], have also been studied as the ETL materials.

In dye-sensitized solar cells (DSCs), SrTiO₃ has recently been studied as an alternative ETL material [8–11]. Since it has a conduction band at ~ 0.2 eV higher position than that of anatase TiO₂, a band offset between SrTiO₃ and dyes is smaller than that of TiO₂, resulting in larger open circuit voltage (V_{OC}). We have reported that the SrTiO₃/TiO₂ composite mesoporous layer for the ETL of DSCs is effective to improve the performance by suppressing decrease of J_{SC} with relatively high V_{OC} [10].

In PSCs, similarly to DSCs, Bera et al. [12] reported that SrTiO₃ mesoporous layer (MPL) is effective to obtain larger V_{OC} than TiO₂-MPL, but its J_{SC} was smaller. Wang et al. [13] succeeded to increase the J_{SC} with keeping the high V_{OC} by using the SrTiO₃/conductive-graphene composite MPL, and they achieved relatively high PCE of 9.41%. **Recently, we have reported BaTiO₃/TiO₂ mesoporous double layer in the ETL with enhanced photovoltaic performances [14]. Instead of using the double layer structure,** in this letter, we propose the PSCs with SrTiO₃/TiO₂ composite

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mesoporous layer (SrTiO₃/TiO₂-MPL). The PSC with SrTiO₃/TiO₂-MPL showed larger V_{OC} than that with TiO₂-MPL without the decrease of J_{SC} .

2. Experimental

2.1 TiO₂ compact layer

On the transparent conductive oxide glass (0052, Geomatec, 10 Ω/sq.), a TiO₂ compact layer was prepared by spin coating of 0.15 M titanium diisopropoxide bis(acetylacetonate) solution (Ti(acac)₂OⁱPr₂, 75 wt.% in isopropanol, Sigma Aldrich) in 1-butanol for 20 s at 2000 rpm, followed by annealing at 125°C for 5 min. Then, this process was repeated twice with 0.3 M Ti(acac)₂OⁱPr₂ solution. The coated substrates were annealed at 500°C for 30 min in air.

2.2 SrTiO₃/TiO₂-MPL and device preparation

TiO₂-dispersed SrTiO₃ sol (TDSTS, ST-B, prototype product, Denka Co.) was used for the preparation of SrTiO₃/TiO₂-MPL. Figure 1 shows the SEM image and XRD pattern of the dried powder from the TiO₂-dispersed SrTiO₃ sol. The SrTiO₃/TiO₂ composite powder (particle size of ~50–100 nm) was mainly composed of cubic SrTiO₃ with some anatase TiO₂ (~5 vol.%).

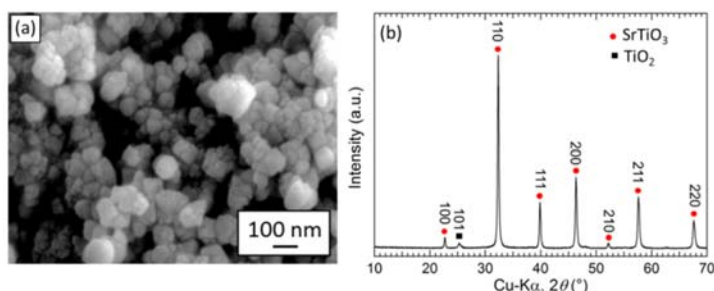


Fig. 1

The SrTiO₃/TiO₂ composite paste was prepared by mixing the TDSTS, ethyl cellulose (80 ~ 120 cps, Nacalai tesque) and ethanol with a hot stirrer at 120°C for 30 min, followed by an ultrasonication for 1 h. The SrTiO₃/TiO₂-MPL was prepared by spin-coating the prepared SrTiO₃/TiO₂ composite paste on the TiO₂ compact layer for 25 s at 4000 rpm and annealing at 500°C for 15 min. We controlled the thickness of SrTiO₃/TiO₂-MPL by changing the concentration of the paste. Then, the glass was placed in 40 mM of TiCl₄ solution in distilled water at 70°C for 30 min, rinsed with ethanol, and annealed at 500°C for 1 h. As a comparison, TiO₂-only MPL was also prepared with a commercial TiO₂ powder (particle size: ~30 nm, P-25, AEROSIL[®]), ethyl cellulose, α-terpineol (96.0 %, Alfa Aesar), lauric acid (>98.0 %, Tokyo chemical industry), and ethanol in the same manner as the SrTiO₃/TiO₂ composite paste.

The CH₃NH₃PbI₃ layer was prepared by a standard two-step method. A hole transport layer was

prepared by spin-coating a Spiro-OMeTAD-based solution, and finally, the Ag electrode was thermally evaporated. The details of preparation conditions are described in our previous study [14].

2.3 Characterization

The morphology of particles and cross sections of the prepared films were observed by scanning electron microscopy (SEM, SU-70, Hitachi and JSM-5600LV, JEOL). The SrTiO₃/TiO₂ composite powder was characterized by X-ray diffraction analysis (XRD, Multiflex, Cu-K α , 40 kV and 40 mA, Rigaku). Optical transmittance of the CH₃NH₃PbI₃/mesoporous layer was measured by UV-Vis (UV3100PC, Shimadzu). Current density–voltage (J – V) characteristics were measured with a solar simulator (XES-40S1, SAN-EI Electric) calibrated to AM 1.5, 100 mW/cm² with a standard silicon photodiode (BS-520BK, Bunkokeiki). A black mask was used during the J – V measurement and the active area was 8.7 mm².

3. Results and discussion

Figures 2(a)–(c) show the cross sectional SEM images of prepared mesoporous layers. The thickness of TiO₂-MPL, SrTiO₃/TiO₂-MPL (thinner), SrTiO₃/TiO₂-MPL (thicker) were ~250 nm, ~200 nm, and ~300 nm, respectively. Compared with the TiO₂-MPL, the SrTiO₃/TiO₂-MPLs had somewhat rough surface, which is attributable to some aggregated particles. Figures 2(d)–(f) show the cross sectional SEM images of prepared CH₃NH₃PbI₃ layers on (a)–(c). Although the total thickness of the CH₃NH₃PbI₃/MPL was almost same (~500 nm) for (d)–(f), the transmittance of (f) was much smaller than that of (d) and (e), as shown in Fig. 2(g), due to its thicker mesoporous layer.

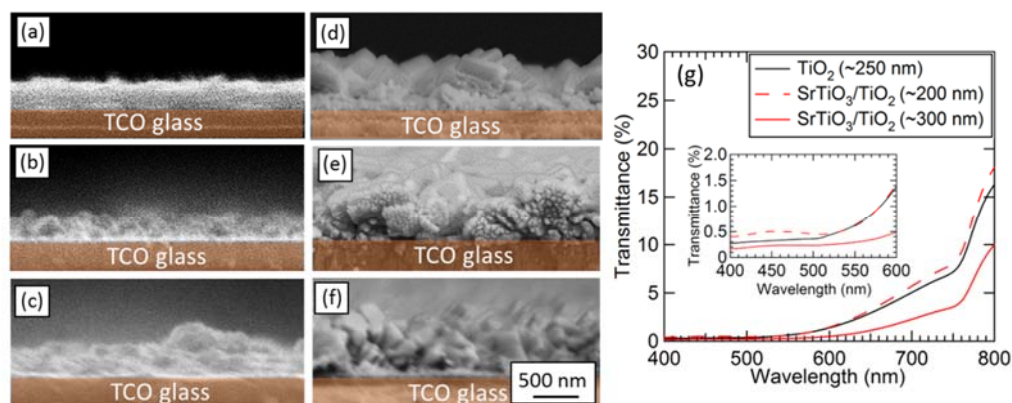


Fig. 2

Current density versus voltage (J – V) curves of back scan are shown in Fig. 3, and their parameters are listed in Table 1. These data are average of 3 batches of the solar cells. Here, we denote the solar cells with TiO₂-MPL (~250 nm), SrTiO₃/TiO₂-MPL (~200 nm) and

SrTiO₃/TiO₂-MPL (~300 nm) as "TiO₂ (~250 nm)", "SrTiO₃/TiO₂ (~200 nm)", and "SrTiO₃/TiO₂ (~300 nm)", respectively. The TiO₂ (~250 nm) and SrTiO₃/TiO₂ (~200 nm) showed similar J_{SC} , FF and conversion efficiency. The V_{OC} of SrTiO₃/TiO₂ (~200 nm) was higher than that of TiO₂ (~250 nm), which is attributable to a better band alignment of SrTiO₃ and CH₃NH₃PbI₃. The best performance of SrTiO₃/TiO₂ (~200 nm) was $J_{SC} = 18.9 \text{ mA/cm}^2$, $V_{OC} = 0.97 \text{ V}$, $FF = 0.58$ and $\eta = 10.6 \%$ as shown in Fig. S1 and Table S1.

When the thickness of the SrTiO₃/TiO₂-MPL increased from ~200 nm to ~300 nm, J_{SC} decreased from 19.3 mA/cm² for SrTiO₃/TiO₂ (~200 nm) to 18.5 mA/cm² for SrTiO₃/TiO₂ (~300 nm) in spite of its lower transmittance (Fig. 2(g)). Other parameters also decreased to $V_{OC} = 0.87 \text{ V}$, $FF = 0.49$ and $\eta = 7.96 \%$ compared with the SrTiO₃/TiO₂ (~200 nm). Thicker mesoporous layer increases the distance of electron transportation, resulting in an increase of charge recombination. Moreover, the series resistances (R_s), which were calculated from inverse of the J - V curves around V_{OC} , significantly increased from 15.8 Ω for SrTiO₃/TiO₂ (~200 nm) to 28.8 Ω for SrTiO₃/TiO₂ (~300 nm). These factors must cause the lower performance with thicker mesoporous layer in SrTiO₃-MPL based PSCs.

The SrTiO₃-MPL based perovskite solar cells generally show lower J_{SC} (12~14 mA/cm²) than TiO₂-MPL due to its inefficient electron collection [12,13]. Furthermore, Bera et al. [12] reported that J_{SC} dramatically decreased by increasing the thickness of SrTiO₃-MPL from 13.37 mA/cm² for 200 nm to 7.95 mA/cm² for 350 nm. On the other hand, the solar cells in this study, a J_{SC} of SrTiO₃/TiO₂ (~200 nm) was comparable to that for TiO₂ and a decrease of J_{SC} by increasing the SrTiO₃/TiO₂-MPL thickness was much smaller in spite of using the similar particle size and MPL thickness to the reported study. These results indicate that the decrease of J_{SC} by using SrTiO₃ was suppressed in the SrTiO₃/TiO₂ composite cells.

Compared to the reported studies, we carried out dipping the solar cells in a TiCl₄ solution after preparation of SrTiO₃/TiO₂-MPL. We also prepared the solar cells which were dipped in the TiCl₄ solution before the preparation of SrTiO₃/TiO₂-MPL, and its average J_{SC} was 18.9 mA/cm². Therefore, the TiCl₄ treatment cannot be the main reason of the high J_{SC} for the SrTiO₃/TiO₂ (~200 nm). We have recently reported that a SrTiO₃/TiO₂-MPL showed higher J_{SC} than SrTiO₃ pure MPL in DSCs [11]. Considering these results, anatase TiO₂ included in the SrTiO₃/TiO₂ composite powder must be a key factor to improve the electron collection in SrTiO₃-MPL and to achieve high J_{SC} . Further improvement can be realized by optimizing the TiO₂ ratio and film thickness.

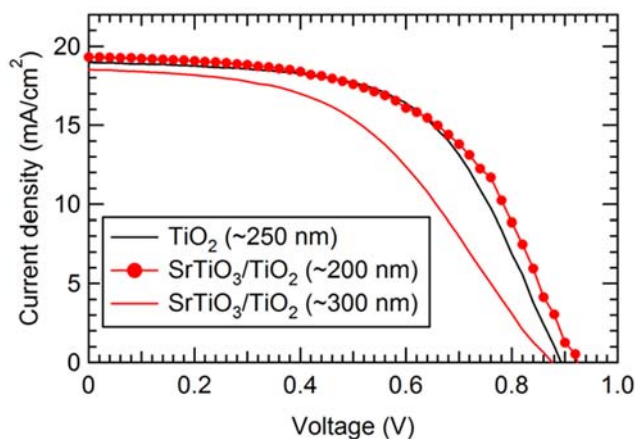


Fig. 3

Table 1 The average $J-V$ characteristics of back scan for TiO_2 (~250 nm), $\text{SrTiO}_3/\text{TiO}_2$ (~200 nm) and $\text{SrTiO}_3/\text{TiO}_2$ (~300 nm). The data are averages of the 3 batches.

Samples	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	η (%)	R_s (Ω)
TiO_2 (~250 nm)	19.0	0.89	0.59	9.98	12.7
$\text{SrTiO}_3/\text{TiO}_2$ (~200 nm)	19.3	0.93	0.56	9.98	15.8
$\text{SrTiO}_3/\text{TiO}_2$ (~300 nm)	18.5	0.87	0.49	7.96	28.8

4. Conclusions

In this letter, we demonstrated the improvement of photovoltaic performances for the SrTiO_3 -MPL based perovskite solar cells by using $\text{SrTiO}_3/\text{TiO}_2$ composite powder included ~5 vol% of anatase TiO_2 . The solar cells with the $\text{SrTiO}_3/\text{TiO}_2$ -MPL showed a higher J_{SC} of 19.3 mA/cm² than that of reported SrTiO_3 -MPL based solar cells with keeping a high V_{OC} . It is attributable to an improvement of electron collection in SrTiO_3 -MPL by the included anatase TiO_2 . As a result, we obtained a high PCE of 9.98 % as the SrTiO_3 -MPL based perovskite solar cells.

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Figure Captions

Fig. 1 Dried powder from the TiO₂-dispersed SrTiO₃ sol: (a) SEM image and (b) XRD pattern.

Fig. 2 Cross sectional SEM images of (a) TiO₂-MPL (~250 nm), (b) SrTiO₃/TiO₂-MPL (~200 nm) from the composite paste (thinner concentration), (c) SrTiO₃/TiO₂-MPL (~300 nm) from the composite paste (thicker concentration), (d) CH₃NH₃PbI₃ layer on TiO₂-MPL (~250 nm), (e) CH₃NH₃PbI₃ layer on SrTiO₃/TiO₂-MPL (~200 nm), (f) CH₃NH₃PbI₃ layer on SrTiO₃/TiO₂-MPL (~300 nm); (g) Optical transmittance of the prepared CH₃NH₃PbI₃/mesoporous layers for (d)–(f).

Fig. 3 The average $J-V$ curves of back scan for TiO₂ (~250 nm), SrTiO₃/TiO₂ (~200 nm) and SrTiO₃/TiO₂ (~300 nm). The data are average of the 3 batches.