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## SrTiO<sub>3</sub>/TiO<sub>2</sub> composite electron transport layer for perovskite solar cells

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### Abstract

Perovskite solar cells (PSCs) with SrTiO<sub>3</sub> mesoporous layer (MPL) generally show higher  $V_{OC}$  but lower  $J_{SC}$  than those with standard TiO<sub>2</sub>-MPL. In this letter, we propose a new PSC with SrTiO<sub>3</sub>/TiO<sub>2</sub> composite MPL to overcome this lower  $J_{SC}$  problem. The PSC with the SrTiO<sub>3</sub>/TiO<sub>2</sub> composite MPL generated a comparable  $J_{SC}$  (19.3 mA/cm<sup>2</sup>) to that with the TiO<sub>2</sub>-MPL, with keeping higher  $V_{OC}$ , which resulted in relatively high power conversion efficiency of 9.98 %.

**Keywords:** perovskite solar cells, SrTiO<sub>3</sub>, 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 TiO<sub>2</sub> is commonly used for the ETL of PSCs [3,4], other oxides, such as ZnO [5], SnO<sub>2</sub> [6] and Al<sub>2</sub>O<sub>3</sub> [7], have also been studied as the ETL materials.

In dye-sensitized solar cells (DSCs), SrTiO<sub>3</sub> 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 TiO<sub>2</sub>, a band offset between SrTiO<sub>3</sub> and dyes is smaller than that of TiO<sub>2</sub>, resulting in larger open circuit voltage ( $V_{OC}$ ). We have reported that the SrTiO<sub>3</sub>/TiO<sub>2</sub> 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 SrTiO<sub>3</sub> mesoporous layer (MPL) is effective to obtain larger  $V_{OC}$  than TiO<sub>2</sub>-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 SrTiO<sub>3</sub>/conductive-graphene composite MPL, and they achieved relatively high PCE of 9.41%. **Recently, we have reported BaTiO<sub>3</sub>/TiO<sub>2</sub> 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 SrTiO<sub>3</sub>/TiO<sub>2</sub> composite

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mesoporous layer (SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL). The PSC with SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL showed larger  $V_{OC}$  than that with TiO<sub>2</sub>-MPL without the decrease of  $J_{SC}$ .

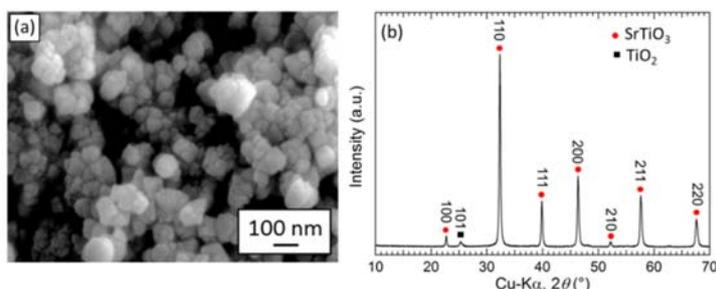
## 2. Experimental

### 2.1 TiO<sub>2</sub> compact layer

On the transparent conductive oxide glass (0052, Geomatec, 10 Ω/sq.), a TiO<sub>2</sub> compact layer was prepared by spin coating of 0.15 M titanium diisopropoxide bis(acetylacetonate) solution (Ti(acac)<sub>2</sub>O<sup>i</sup>Pr<sub>2</sub>, 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)<sub>2</sub>O<sup>i</sup>Pr<sub>2</sub> solution. The coated substrates were annealed at 500°C for 30 min in air.

### 2.2 SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL and device preparation

TiO<sub>2</sub>-dispersed SrTiO<sub>3</sub> sol (TDSTS, ST-B, prototype product, Denka Co.) was used for the preparation of SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL. Figure 1 shows the SEM image and XRD pattern of the dried powder from the TiO<sub>2</sub>-dispersed SrTiO<sub>3</sub> sol. The SrTiO<sub>3</sub>/TiO<sub>2</sub> composite powder (particle size of ~50–100 nm) was mainly composed of cubic SrTiO<sub>3</sub> with some anatase TiO<sub>2</sub> (~5 vol.%).



**Fig. 1**

The SrTiO<sub>3</sub>/TiO<sub>2</sub> 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 SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL was prepared by spin-coating the prepared SrTiO<sub>3</sub>/TiO<sub>2</sub> composite paste on the TiO<sub>2</sub> compact layer for 25 s at 4000 rpm and annealing at 500°C for 15 min. We controlled the thickness of SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL by changing the concentration of the paste. Then, the glass was placed in 40 mM of TiCl<sub>4</sub> solution in distilled water at 70°C for 30 min, rinsed with ethanol, and annealed at 500°C for 1 h. As a comparison, TiO<sub>2</sub>-only MPL was also prepared with a commercial TiO<sub>2</sub> powder (particle size: ~30 nm, P-25, AEROSIL<sup>®</sup>), ethyl cellulose, α-terpineol (96.0 %, Alfa Aesar), lauric acid (>98.0 %, Tokyo chemical industry), and ethanol in the same manner as the SrTiO<sub>3</sub>/TiO<sub>2</sub> composite paste.

The CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> 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 SrTiO<sub>3</sub>/TiO<sub>2</sub> composite powder was characterized by X-ray diffraction analysis (XRD, Multiflex, Cu-K $\alpha$ , 40 kV and 40 mA, Rigaku). Optical transmittance of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/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/cm<sup>2</sup> 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 mm<sup>2</sup>.

### 3. Results and discussion

Figures 2(a)–(c) show the cross sectional SEM images of prepared mesoporous layers. The thickness of TiO<sub>2</sub>-MPL, SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL (thinner), SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL (thicker) were ~250 nm, ~200 nm, and ~300 nm, respectively. Compared with the TiO<sub>2</sub>-MPL, the SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPLs had somewhat rough surface, which is attributable to some aggregated particles. Figures 2(d)–(f) show the cross sectional SEM images of prepared CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layers on (a)–(c). Although the total thickness of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/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.

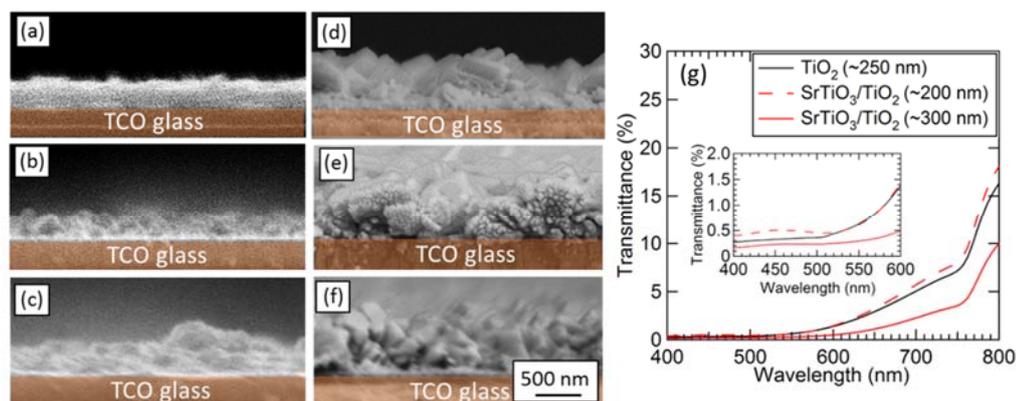


Fig. 2

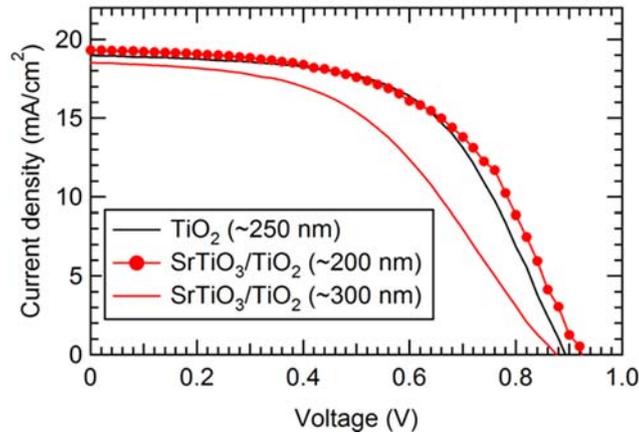
Current density versus voltage ( $J$ – $V$ ) curves of back scan are shown in Fig. 3, and their parameters are listed in Table 1. These data are average of 3 batches of the solar cells. Here, we denote the solar cells with TiO<sub>2</sub>-MPL (~250 nm), SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL (~200 nm) and

SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL (~300 nm) as "TiO<sub>2</sub> (~250 nm)", "SrTiO<sub>3</sub>/TiO<sub>2</sub> (~200 nm)", and "SrTiO<sub>3</sub>/TiO<sub>2</sub> (~300 nm)", respectively. The TiO<sub>2</sub> (~250 nm) and SrTiO<sub>3</sub>/TiO<sub>2</sub> (~200 nm) showed similar  $J_{SC}$ ,  $FF$  and conversion efficiency. The  $V_{OC}$  of SrTiO<sub>3</sub>/TiO<sub>2</sub> (~200 nm) was higher than that of TiO<sub>2</sub> (~250 nm), which is attributable to a better band alignment of SrTiO<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. The best performance of SrTiO<sub>3</sub>/TiO<sub>2</sub> (~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 SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL increased from ~200 nm to ~300 nm,  $J_{SC}$  decreased from  $19.3 \text{ mA/cm}^2$  for SrTiO<sub>3</sub>/TiO<sub>2</sub> (~200 nm) to  $18.5 \text{ mA/cm}^2$  for SrTiO<sub>3</sub>/TiO<sub>2</sub> (~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 SrTiO<sub>3</sub>/TiO<sub>2</sub> (~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  $15.8 \Omega$  for SrTiO<sub>3</sub>/TiO<sub>2</sub> (~200 nm) to  $28.8 \Omega$  for SrTiO<sub>3</sub>/TiO<sub>2</sub> (~300 nm). These factors must cause the lower performance with thicker mesoporous layer in SrTiO<sub>3</sub>-MPL based PSCs.

The SrTiO<sub>3</sub>-MPL based perovskite solar cells generally show lower  $J_{SC}$  ( $12\sim 14 \text{ mA/cm}^2$ ) than TiO<sub>2</sub>-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 SrTiO<sub>3</sub>-MPL from  $13.37 \text{ mA/cm}^2$  for 200 nm to  $7.95 \text{ mA/cm}^2$  for 350 nm. On the other hand, the solar cells in this study, a  $J_{SC}$  of SrTiO<sub>3</sub>/TiO<sub>2</sub> (~200 nm) was comparable to that for TiO<sub>2</sub> and a decrease of  $J_{SC}$  by increasing the SrTiO<sub>3</sub>/TiO<sub>2</sub>-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 SrTiO<sub>3</sub> was suppressed in the SrTiO<sub>3</sub>/TiO<sub>2</sub> composite cells.

Compared to the reported studies, we carried out dipping the solar cells in a TiCl<sub>4</sub> solution after preparation of SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL. We also prepared the solar cells which were dipped in the TiCl<sub>4</sub> solution before the preparation of SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL, and its average  $J_{SC}$  was  $18.9 \text{ mA/cm}^2$ . Therefore, the TiCl<sub>4</sub> treatment cannot be the main reason of the high  $J_{SC}$  for the SrTiO<sub>3</sub>/TiO<sub>2</sub> (~200 nm). We have recently reported that a SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL showed higher  $J_{SC}$  than SrTiO<sub>3</sub> pure MPL in DSCs [11]. Considering these results, anatase TiO<sub>2</sub> included in the SrTiO<sub>3</sub>/TiO<sub>2</sub> composite powder must be a key factor to improve the electron collection in SrTiO<sub>3</sub>-MPL and to achieve high  $J_{SC}$ . Further improvement can be realized by optimizing the TiO<sub>2</sub> ratio and film thickness.



**Fig. 3**

**Table 1** The average  $J-V$  characteristics of back scan for  $\text{TiO}_2$  (~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	$J_{\text{SC}}$ (mA/cm <sup>2</sup> )	$V_{\text{OC}}$ (V)	$FF$	$\eta$ (%)	$R_s$ ( $\Omega$ )
$\text{TiO}_2$ (~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  $\text{SrTiO}_3$ -MPL based perovskite solar cells by using  $\text{SrTiO}_3/\text{TiO}_2$  composite powder included ~5 vol% of anatase  $\text{TiO}_2$ . The solar cells with the  $\text{SrTiO}_3/\text{TiO}_2$ -MPL showed a higher  $J_{\text{SC}}$  of 19.3 mA/cm<sup>2</sup> than that of reported  $\text{SrTiO}_3$ -MPL based solar cells with keeping a high  $V_{\text{OC}}$ . It is attributable to an improvement of electron collection in  $\text{SrTiO}_3$ -MPL by the included anatase  $\text{TiO}_2$ . As a result, we obtained a high PCE of 9.98 % as the  $\text{SrTiO}_3$ -MPL based perovskite solar cells.

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## References

- [1] Kojima A, Teshima K, Shirai Y, Miyasaka T. J. Am. Chem. Soc. 2009; 131: 6050–1.
- [2] Research cell efficiency records, [http://www.nrel.gov/ncpv/images/efficiency\\_chart.jpg](http://www.nrel.gov/ncpv/images/efficiency_chart.jpg), (accessed August 2016).
- [3] Burschka J, Pellet N, Moon SJ, Humphry-Baker R, Gao P, Nazeeruddin MK, Grätzel M. Nature 2013; 499: 316–9.
- [4] Kim HS, Lee CR, Im JH, Lee KB, Moehl T, Marchioro A, Moon SJ, Humphry-Baker R, Yum JH, Moser JE, Grätzel M, Park NG. Sci. Rep. 2012; 2: 591.
- [5] Kumar MH, Yantara N, Dharani S, Grätzel M, Mhaisalkar S, Boix PP, Mathews N. Chem. Commun. 2013; 49: 11089–91.
- [6] Ke W, Fang G, Liu Q, Xiong L, Qin P, Tao H, Wang J, Lei H, Li B, Wan J, Yang G, Yan Y. J. Am. Chem. Soc. 2015; 137: 6730–3.
- [7] Lee MM, Teuscher J, Miyasaka T, Murakami N T, Snaith HJ. Science 2012; 338: 643–7.
- [8] Jayabal P, Sasirekha V, Mayandi J, Jeganathan K, Ramakrishnan V. J. Alloys Compounds 2014; 586: 456–61.
- [9] Gholamrezaei S, Niasari MS, Dadkhah M, Sarkhosh B. J Mater Sci: Mater Electron 2016; 27: 118–25.
- [10] Okamoto Y, Suzuki Y. J. Ceram. Soc. Jpn. 2014; 122: 728–31.
- [11] Okamoto Y, Suzuki Y. J. Ceram. Soc. Jpn. 2015; 123: 967–71.
- [12] Bera A, Wu K, Sheikh A, Alarousu E, Mohammed OF, Wu T. J. Phys. Chem. C 2014; 118: 28494–501.
- [13] Wang C, Tang Y, Hu Y, Huang L, Fu J, Jin J, Shi W, Wanga L, Yang W. RSC Adv. 2015; 5: 52041–7.
- [14] Okamoto Y, Suzuki Y. J. Phys. Chem. C 2016; 120: 13995–4000.

### Figure Captions

**Fig. 1** Dried powder from the TiO<sub>2</sub>-dispersed SrTiO<sub>3</sub> sol: (a) SEM image and (b) XRD pattern.

**Fig. 2** Cross sectional SEM images of (a) TiO<sub>2</sub>-MPL (~250 nm), (b) SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL (~200 nm) from the composite paste (thinner concentration), (c) SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL (~300 nm) from the composite paste (thicker concentration), (d) CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer on TiO<sub>2</sub>-MPL (~250 nm), (e) CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer on SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL (~200 nm), (f) CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer on SrTiO<sub>3</sub>/TiO<sub>2</sub>-MPL (~300 nm); (g) Optical transmittance of the prepared CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/mesoporous layers for (d)–(f).

**Fig. 3** The average  $J-V$  curves of back scan for TiO<sub>2</sub> (~250 nm), SrTiO<sub>3</sub>/TiO<sub>2</sub> (~200 nm) and SrTiO<sub>3</sub>/TiO<sub>2</sub> (~300 nm). The data are average of the 3 batches.