



Revealing and reducing the possible recombination loss within TiO₂ compact layer by incorporating MgO layer in perovskite solar cells



Ashish Kulkarni*, Ajay K. Jena*, Hsin-Wei Chen, Yoshitaka Sanehira, Masashi Ikegami, Tsutomu Miyasaka

Toin University of Yokohama, 1614 Kurogane-cho, Aoba-ku, Yokohama, Kanagawa 225-8503, Japan

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ABSTRACT

Here, we report an origin of loss in open circuit voltage (V_{oc}) in perovskite solar cells due to the possible trap-assisted recombination within the widely used TiO₂ compact layer (CL) and at its interface with FTO substrate. A thin layer (TL) of MgO was employed to investigate the recombination mechanism. MgO in place of TiO₂ CL (50–60 nm) enhances V_{oc} of the cell significantly while the MgO layer coated on TiO₂ CL (TiO₂-MgO bilayer) does not change the V_{oc} much. In combination with open-circuit voltage decay (OCVD) measurements, we reveal that recombination at FTO/TiO₂ interface is a major factor regulating the voltage and efficiency of TiO₂-based perovskite solar cells.

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1. Introduction

After our pioneering report on perovskite (CH₃NH₃PbX₃, X = I, Br) as visible light absorber in liquid junction solar cells with 3.8% efficiency (Kojima et al., 2009; Miyasaka, 2015), the drive for research on this material became tremendously fast with the use of this material in solid junction devices and a certified power conversion efficiency (PCE) of 22.1% was achieved very recently (http://www.nrel.gov/ncpv/images/efficiency_chart.jpg). Moreover, the fabrication of such high efficiency perovskite solar cells involves simple and inexpensive solution methods. Therefore, this new photovoltaic technology shows enormous potential as a cheaper alternative to existing conventional photovoltaic technologies. The intrinsic electronic properties, such as ambipolar charge mobility and long carrier diffusion length of the perovskite semiconductor are two major attributes to high PCE of the devices (Stranks et al., 2013; Sun et al., 2014; Xing et al., 2013). In addition, well-suppressed recombination of photoexcited charge carriers, which is strongly affected by the surrounding carrier collecting materials, leads to generation of large photocurrent as well as high

voltage. In other words, surrounding carrier collecting materials play equally an important role in maximizing the current and voltage by minimizing the recombination loss.

Generally, a thin compact layer (CL) or a hole blocking layer (BL) (~50–60 nm) is required to be deposited on fluorine doped tin oxide (FTO) conductive substrate in order to avoid direct contact between FTO and perovskite and/or hole transporting material (HTM). Moreover, such dense CLs made on FTO are also believed to prevent recombination caused by back transfer of electron from FTO to either perovskite or HTM. To avoid such recombination, even modification of TiO₂ CL (Zuo et al., 2015), ZnO layer with self-assembled monolayers (Liu et al., 2015) have been found to enhance the overall PCE. MgO is an insulating material and has been employed in perovskite solar cells to reduce recombination (Wang et al., 2015; Han et al., 2015). It has been reported that CL made of Mg-doped TiO₂ which improves open-circuit voltage (V_{oc}) by up-shift of the conduction band edge of TiO₂ and thereby reducing recombination (Wang et al., 2015). A recent study employing MgO in mesoscopic perovskite solar cell has shown enhancement in V_{oc} by avoiding direct contact between FTO and perovskite (Yue et al., 2015). However, there are several reports that contradict the presumption of recombination at conductive substrates and perovskite interface. For instance, planar architecture cells made with perovskite directly grown on FTO (Ke et al., 2015) and indium doped tin oxide (ITO) (Liu et al., 2014) have been found to generate V_{oc} as high as 1 V, suggesting that the recombination at this interface is improbable. Further, SnO₂ having lower

Abbreviations: TL, thin layer; CL, compact layer; Spiro-OMeTAD, 2,2',7,7'-Tetraakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirofluorene; MgO, magnesium oxide; TiO₂, titanium dioxide.

* Corresponding authors.

E-mail addresses: ashish.kulkarni786@gmail.com (A. Kulkarni), jenajay@gmail.com (A.K. Jena), willchen@toin.ac.jp (H.-W. Chen), sanehira@toin.ac.jp (Y. Sanehira), ikegami@toin.ac.jp (M. Ikegami), miyasaka@toin.ac.jp (T. Miyasaka).

conduction band edge than TiO_2 has been found to generate V_{oc} of above 1 V in perovskite solar cells (Song et al., 2015) indicating that the recombination between CL and perovskite or HTM interface is also small. Therefore, the mechanisms of recombination in perovskite solar cells are still unclear and need to be investigated with various CL and device configuration for better understanding. In this report, we focus on the relevance of TiO_2 CL to electron transfer rectification by inserting a thin non-conductive layer of MgO at the interface of FTO- TiO_2 mesoporous layer and TiO_2 CL-mesoporous TiO_2 layer. Although the role of MgO in carrier transport regulation has not been clear, our investigation here reveals that TiO_2 CL itself is responsible for reasonable voltage loss in TiO_2 based perovskite solar cells, which is a major finding here in addition to the passivation effect of MgO.

2. Experimental methods

Unless otherwise stated, all the materials were purchased from Sigma-Aldrich or Wako and were used as received. Spiro-OMeTAD was purchased from Merck and used as received.

2.1. Methylammonium iodide synthesis

Methylammonium iodide was synthesized following the procedure given here in short. 24 mL of methylamine solution (33% in ethanol) was diluted with 100 mL of ethanol (anhydrous). Under constant stirring, 10 mL of hydroiodic acid (57 wt.%) was added to the prepared solution. After the reaction time of 1 h at room temperature, the MAI was obtained by evaporating ethanol by using a rotor evaporator. The obtained white solid was washed twice with dry diethyl ether and finally re-crystallized from ethanol.

2.2. Device fabrication

FTO-coated transparent glass sheets ($8 \Omega \text{sq}^{-1}$, Nippon Sheet Glass, 1.1 mm in thickness) were patterned by etching off FTO with Zn powder and 3 M HCl. Then, the substrates were cleaned with ultrasonication in 2% hellmax soap solution, deionised water and ethanol for 15 min each. After oxygen plasma treatment done to remove the traces of organic residues for 10 min, ~ 50 – 60 nm TiO_2 CL was deposited by spin coating 0.15 M and 0.3 M titanium diisopropoxide bis(acetylacetonate) (75 wt.% in isopropanol, Aldrich) in isopropanol (Wako). First, 0.15 M solution was spin coated at 2000 rpm for 30 s followed by annealing at 125°C for 5 min. The same procedure was followed twice to deposit 0.3 M and finally the substrates were annealed at 550°C for 30 min. 80 mM TiCl_4 treatment was given at 70°C for 30 min and again the cells were annealed at 550°C for 30 min. In case of MgO thin layer, on FTO, 25 mM solution of magnesium acetate tetrahydrate was dissolved in ethanol and was stirred at 100°C for 1 min prior to deposition at 3000 rpm for 30 s followed by annealing at 100°C for 5 min (Docampo et al., 2012). In case of bilayer, after deposition of TiO_2 CL, 25 mM magnesium acetate solution in ethanol was deposited by spin coating at 3000 rpm for 30 s followed by annealing at 100°C for 5 min.

For all the devices, mesoporous layer was obtained by spin-coating a commercially available TiO_2 paste (Dyesol, 18NR-T) in ethanol (1:3) at 4000 rpm for 30 s and annealing at 550°C for 30 min. Perovskite was deposited by sequential deposition method (Bruschka et al., 2013; Yantara et al., 2015). First, 1 M PbI_2 solution in DMF was deposited on mesoporous coated substrate at 6500 rpm for 30 s followed by drying at 70°C for 30 min. After cooling down, the substrates were dipped in methylammonium iodide solution in 2-propanol (10 mg/mL) for 50 s. Then, the

perovskite coated substrates were rinsed in 2-propanol and were dried using spin coater at 4500 rpm for 10 s. The substrates were then heated at 70°C for 30 min. The HTM solution was prepared by dissolving 84 mg of spiro-OMeTAD, 14.053 μL of 4-*tert*-butylpyridine (TBP, Aldrich), 27.013 μL of a stock solution of 520 mg/mL of lithium bis(trifluoromethylsulfonyl)imide in acetonitrile in 1 mL of chlorobenzene. The prepared spiro-OMeTAD solution was deposited on perovskite by spin-coating at 3000 rpm for 30 s. After spiro-OMeTAD coating, the substrates were stored in dark and ambient atmosphere overnight before the deposition of 80 nm Au as back contact electrode by thermal evaporation. All the perovskite deposition preparative work was carried out under ambient atmosphere with uncontrolled humidity.

2.3. Device characterization

Photovoltaic characterization of the devices was done by measuring current on voltage scan in forward (-0.1 V to 1.1 V) and backward (1.1 V to 0 V) directions both under light (100 mW/cm^2 AM1.5, 1 sun intensity) provided by a solar simulator (Pecell Technologies PEC-L01) and dark. A Keithley source meter (Model 2400) was used for all electrical measurements. The voltage scan speed used to obtain photocurrent density–voltage (J–V) curves was kept at 200 mV/s. The active area of the device was 0.09 cm^2 . The cross-sectional scanning electron microscopy images and Energy dispersive X-ray spectroscopy (EDX) of all the devices were taken with a HITACHI SEM instrument (SU8000). Optical properties of perovskite were measured by UV–vis spectrophotometer (UV–vis 1800, Shimadzu). Open circuit voltage decay (OCVD) measurement was performed by oscilloscope TDS 3012B (Tektronix) having mechanical shutter (Sumga Seiki, F776) connected to solar simulator as the illumination source. The solar cells were kept in open circuit condition under 1 sun illumination for 1 min for stabilizing the V_{oc} and then the shutter was closed. The decay in V_{oc} was measured over 20 ms.

3. Results and discussion

To investigate the back electron transfer and loss in V_{oc} at FTO/ TiO_2 CL interface we have deposited a thin layer (TL) of MgO, both as an independent layer directly on FTO and as a bilayer with TiO_2 CL as bottom layer by spin coating 25 mM solution of $\text{Mg}(\text{CH}_3\text{COO})_2$ in ethanol. The device structures are depicted in Fig. 1. From the cross sectional scanning electron micrographs (SEM) (Fig. 2), it is evident that a thick (~ 50 – 60 nm) TiO_2 CL (Fig. 2a) was formed while MgO layer was too thin to be visible (Fig. 2b). However, the top view SEM image of MgO layer (Fig. S1 (b)) shows small MgO particles in the valleys between large FTO grains and SEM energy dispersive X-ray (EDX) (Fig. 2d) mapping of the surface confirms coverage of the FTO substrate with Mg as MgO. However, it can be seen that a very thin MgO layer (thickness less than several nm) is formed but with many pin-holes exposing the FTO surface. The MgO layer coated on the TiO_2 CL (TiO_2 -MgO bilayer) also showed MgO particles that were spread over the TiO_2 underlayer (Sakai et al., 2014) (Fig. S1 (c)). In TiO_2 CL, however, many pores were seen (Fig. S1 (a)), which were covered partially by MgO particles and some MgO aggregates of rod shape were also seen scattered over the substrate. This morphology also shows that TiO_2 -MgO bilayer has some places where TiO_2 can have electrical contact with perovskite.

The MgO TL on the FTO surface as a substitute to ~ 50 – 60 nm thick TiO_2 CL enhanced V_{oc} of the cell significantly ($\sim 16\%$) despite having many pin holes where perovskite can directly touch FTO. However, we believe that thin layer (5 nm) of MgO with complete coverage which can be made by other methods like vapor deposi-

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