Revealing and Reducing the Possible Recombination Loss within TiO₂ Compact layer by Incorporating MgO Layer in Perovskite Solar Cells

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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 TiO_2 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 TiO_2 CL (50-60 nm) enhances V_{oc} of the cell significantly while the MgO layer coated on TiO_2 CL (TiO_2 -MgO bilayer) does not change the V_{oc} much. In combination with open-circuit voltage decay (OCVD) measurements, we reveal that recombination at FTO/ TiO_2 interface is a major factor regulating the voltage and efficiency of TiO_2 -based perovskite solar cells.

Keywords

Perovskite Solar cells, MgO thin layer, TiO_2 compact layer, TiO_2 -MgO bilayer, FTO/ TiO_2 interface recombination.

Graphical abstract

1. Introduction:

After our pioneering report on perovskite ($\text{CH}_3\text{NH}_3\text{PbX}_3$, $\text{X} = \text{I}, \text{Br}$) 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 TiO_2 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 TiO_2 which improves open-circuit voltage (V_{oc}) by up-shift of the conduction band edge of TiO_2 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, SnO_2 having lower 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 hour 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 sec 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 minutes. 80 mM TiCl_4 treatment was given at 70°C for 30 minutes and again the cells were annealed at 550°C for 30 minutes. 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 sec 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 sec 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 sec and annealing at 550°C for 30

min. Perovskite was deposited by sequential deposition method (Bruschka et. al., 2013; Yantara et. al., 2015). First, 1M PbI_2 solution in DMF was deposited on mesoporous coated substrate at 6500 rpm for 30 sec 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 sec. Then, the perovskite coated substrates were rinsed in 2-propanol and were dried using spin coater at 4500 rpm for 10 sec. 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 seconds. 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 (Peccell 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 milliseconds.

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 $Mg(CH_3COO)_2$ 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.

Figure 1: Schematics of device architecture of (a) TiO_2 CL, (b) MgO TL and (c) TiO_2 -MgO bilayer incorporated devices.

Figure 2: Cross sectional SEM images of the TiO_2 mesoscopic $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells with (a) TiO_2 CL, (b) MgO TL, (c) TiO_2 -MgO bilayer as interlayer's between FTO and TiO_2 mesoporous layer. Top surface SEM-Energy-Dispersive X-ray (EDX) spectroscopic images of (d) MgO TL and TiO_2 -MgO bilayer showing mapping of (e) Mg and (f) Ti.

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 (~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 deposition would further reduce the recombination loss. On the contrary, a dense 50-60 nm thick layer of TiO_2 exhibited lower V_{oc} . For the cells with TiO_2 CL (~50-60 nm), as

shown in histogram plot (Fig. 3a), V_{oc} varied from 0.8 V to 0.9 V with majority of the samples showing the V_{oc} of 0.86 V while the values for cells with MgO TL varied from 0.9 V to 1.02 V and majority of the samples showed a V_{oc} of 0.98 V. However, increase in V_{oc} by the MgO TL was accompanied with slight reduction in short-circuit current density (J_{sc}) (from $\sim 18.5 \text{ mA/cm}^2$, in TiO_2 CL devices, to $\sim 17.5 \text{ mA/cm}^2$). This decrease in J_{sc} as well as concomitant decrease in fill factor (FF) must be due to slight increase in resistance to electron transfer through thin MgO to FTO, which happens via tunneling (Chandiran et. al., 2014). As a result, the overall PCE ($\sim 9.5\%$ PCE for majority of devices as shown in histogram) of these cells were found to be same in both the cases; TiO_2 CL and MgO TL. Here, it was believed that MgO blocked the back transfer of electron from FTO to perovskite (at places where perovskite is in direct contact with FTO) and thereby improved V_{oc} . This result was then compared with the TiO_2 -MgO bilayer structure in which FTO surface was coated with TiO_2 CL followed by a thin layer of MgO on top of it. Although we expected further improvement of V_{oc} by use of double blocking structure (TiO_2 and MgO) against recombination, we found decrease in V_{oc} with this structure. As can be seen from Fig. 3a, the majority of the TiO_2 -MgO bilayer samples showed a V_{oc} of ~ 0.9 V, which is slightly higher than 0.86 V for cells with TiO_2 CL (free of MgO over-layer) but lower than V_{oc} (0.98V) of the cell with MgO TL. This indicated that MgO on FTO and on TiO_2 CL worked differently and there is a reasonable loss in V_{oc} due to the presence of TiO_2 CL itself. The main difference between MgO TL and TiO_2 -MgO bilayer is that the electron is finally collected, after passing the blocking layer, by FTO in case of MgO TL and by TiO_2 in case of TiO_2 -MgO bilayer, respectively.

Figure 3: Histogram plot of (a) V_{oc} , (b) J_{sc} , and (c) PCE of 48 devices of each kind of TiO_2 mesoporous perovskite solar cells; with TiO_2 CL (black), MgO TL (red) and TiO_2 -MgO bilayer (green). (d) $J-V$ curves of best performing devices with TiO_2 CL, MgO TL and TiO_2 -MgO bilayer.

Table 1 Photovoltaic characteristic (J_{sc} , V_{oc} , FF, PCE) of champion devices of each kind of TiO_2 mesoscopic perovskite solar cells; with TiO_2 CL, MgO TL and TiO_2 -MgO bilayer. FS and BS stands for forward scan (i.e. from short circuit to open circuit) and backward scan (i.e. from open circuit to short circuit) respectively.

Cases Studied	Scan Direction	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
TiO_2 CL	FS	20.3	0.85	0.58	10.1
	BS	18.8	0.85	0.67	10.8
MgO TL	FS	16.65	0.99	0.53	8.89
	BS	17.3	1.02	0.65	11.53
TiO_2 -MgO Bilayer	FS	21.6	0.9	0.58	11.3
	BS	21.4	0.89	0.62	11.8

In order to verify the active role of TiO_2 CL, devices with thinner TiO_2 CL, not visible in SEM (Fig. S2 (a)) and without CL (CL-free) (i.e. mesoporous TiO_2 layer directly deposited on FTO) (Fig. S2 (b)), were fabricated. Figure S3 depicts the J-V curves (under light and dark) of the best devices with TiO_2 CL (~50-60 nm), thin TiO_2 CL (not visible in SEM) and without TiO_2 CL. The histograms of V_{oc} , J_{sc} and PCE for 48 devices of each of the above three structures (CL-free, thin and thick TiO_2 CL) are given in Figure S4. Surprisingly, presence of TiO_2 CL (~50-60 nm or thin TiO_2 CL) did not essentially improve any of the photovoltaic parameters in the cell and showed the same V_{oc} (~0.85 V) as for the cells without the CL. This implied that either the bottom of the TiO_2 porous layer is sufficiently dense to act like CL to prevent perovskite from touching FTO directly or the recombination between FTO and perovskite is improbable (Ke et. al., 2013; Liu et. al., 2014). Additionally, in all the three cases, we also consider the

possible role of the remnant PbI_2 layer, which formed on FTO and TiO_2 , in preventing recombination by blocking back transfer of electron (Cao et. al., 2014). All the above results suggest that back transfer of electron from FTO or TiO_2 to perovskite is not significant and the lower V_{oc} of cells with TiO_2 CL compared to that with MgO TL is due to loss by TiO_2 CL.

Figure 4 shows the schematics of possible recombination mechanisms in a TiO_2 -based perovskite solar cell. The main recombination loss in a TiO_2 meso-structured perovskite solar cell can be by the carriers recombining between excited electron in TiO_2 (mesoporous) and hole in perovskite or HTM (Fig. 4a). Such recombination process can be suppressed by surface passivation of the TiO_2 particle (Han et. al., 2015). However, MgO layer, either on FTO or TiO_2 CL (as studied here), cannot prevent the recombination between porous TiO_2 and perovskite or HTM. In addition, the recombination of carriers at perovskite and HTM interface remains unaffected by any change in the CL. Therefore, the significant increment in V_{oc} by MgO TL is unlikely due to prevented back transfer from FTO to perovskite or HTM, which is already prevented by TiO_2 mesoporous layer and remnant PbI_2 (Cao et. al., 2014) (as evident from same V_{oc} for cells with and without CL) (Fig. S4 (a)). Here, important role of MgO is that electron once collected by FTO can never move to TiO_2 , where it ultimately undergoes a constant recombination due to trap states in the TiO_2 . It is known that there exist a lot of trap states in TiO_2 (or TiO_x) CL (Yuan et. al., 2015) and these trap states in TiO_2 , prepared by solution method, are of two types. The undercoordinated Ti^{4+} and oxygen vacancies act as electron trap centers while the hydroxyl groups act as hole trap centers (Mercado et. al., 2012; Wang et. al., 2010; Peter et. al., 2007; Bertoluzzi et. al., 2014). We consider that the TiO_2 compact layer prepared (solution method) for our study would contain undercoordinated Ti^{4+} and oxygen vacancies (annealing not done in oxygen rich atmosphere). These trap states can cause trap-assisted recombination in TiO_2 (Wang et. al., 2010; Wehrenfennig et. al., 2015; Bertoluzzi et. al., 2014; Leijtens et. al., 2013) as well as at the interface with perovskite (Fig. 4a) resulting in loss in V_{oc} . Also, as a minor effect, the holes in TiO_2 VB, generated by UV light absorption (Leong et. al., 2015), can also recombine with electron from FTO (Fig. 4a) however this needs further investigation

and is under progress. This V_{oc} loss via trap-state assisted recombination in TiO_2 CL was also evident from the open circuit voltage decay (OCVD) measurement. For OCVD measurement, the cells were kept under illumination (for 1 min) and the light is then switched off. The voltage decay was then monitored with time. Figure 5 depicts the OCVD graph for cells with different cases studied here. As can be seen in the figure 5, the device incorporating TiO_2 CL and TiO_2 -MgO bilayer showed similar and fast voltage decay while the voltage decay in case of MgO TL based cells was significantly slow. The similar decay behaviour of TiO_2 CL and TiO_2 -MgO bilayer based cells confirm that there is a reasonable loss in V_{oc} within TiO_2 CL itself. In the case of TiO_2 -MgO bilayer, however, the recombination at FTO/ TiO_2 interface is not prevented (Fig. 4c) and that is the reason why it does not show much increment in V_{oc} . The slight increment, from 0.86 to 0.9 V, is due to the coverage of TiO_2 CL and passivation of surface traps of TiO_2 CL by MgO TL. Additionally, dehydrogenative condensation reaction of $Mg(OH)_2$, which is formed as an intermediate product from the precursor $(Mg(CH_3COO)_2)$, is considered to improve interface contact between CL and mesoporous layer (Sakai et. al., 2014). As a result of which, J_{sc} also increased in the case of bilayer and the devices exhibited highest PCE (~12%) among all the device structures studied here.

Figure 4: Schematic diagram showing possible recombination mechanisms in TiO_2 mesostructure perovskite solar cells with (a) TiO_2 CL, (b) MgO TL and (c) TiO_2 -MgO bilayer.

Figure 5: Open-circuit voltage decay (OCVD) measurement of TiO₂ CL (blue trace), MgO TL (red trace) and TiO₂-MgO bilayer (black trace).

We also found that incorporation of MgO as a blocking material tends to stabilize the cell performance as a result of reduced recombination. Distribution of cell performance of MgO TL and TiO₂-MgO bilayer devices was in a narrow range (Fig. 3c) in comparison to the wider distribution observed in case of cells with (thick and thin) and without TiO₂ CL (Fig. S4 (c)), suggesting more uniform electrical property of MgO treated substrates over the area. The above result brings a hint about the desirable structure of perovskite solar cell with minimized recombination and we found that the effect of TiO₂ CL in suppressing recombination is limited.

Hysteresis in the J-V plot obtained from forward and reverse scan directions has been a commonly observed phenomenon in the perovskite solar cells (Snaith et. al., 2014) and several mechanisms such as ferroelectric polarization (Chen et. al., 2015), ion migration (Eames et. al., 2015), and carrier dynamics at the interface (Zhang et. al., 2015; Wojciechowski et. al., 2015; Shao et. al., 2014; Jena et. al., 2015) have been proposed in the literature. In our study here, we observed that although the perovskite in the bulk of meso-structure TiO₂ was the same, as the absorption spectra in all the three samples were found to be same (Fig. S5), the cells with MgO TL showed reasonable

hysteresis while the cells with TiO₂ CL and TiO₂-MgO bilayer exhibited negligible hysteresis (Fig. 3d). This indicates that hysteresis is much influenced by the carrier dynamics at the interfaces (Zhang et. al., 2015; Wojciechowski et. al., 2015; Shao et. al., 2014; Jena et. al., 2015). MgO thin layer on FTO is believed to change the charge transfer rate at the interface of mesoporous TiO₂ and FTO, which results in enhanced hysteresis and alters the carrier transfer rate at the interface and thereby enhances hysteresis in the cell.

3. Conclusions

MgO incorporated in TiO₂ mesostructure perovskite solar cell as a thin tunneling barrier layer on FTO enhanced the V_{oc} of the cells significantly (from 0.86 to 0.98 V) while the MgO layer on 50-60 nm TiO₂ CL (TiO₂-MgO bilayer) did not show much change in V_{oc} (from 0.86 to 0.9 V). The above results revealed that there is a reasonable recombination loss by trap assisted recombination within TiO₂ itself and by back transfer of electron from FTO to TiO₂ (as a minor effect). Therefore, the enhancement in V_{oc} by the MgO TL is most likely due to blocking the recombination pass way at FTO/TiO₂ interface, not at TiO₂/perovskite or TiO₂/Spiro-OMeTAD interface. Moreover, the cells with and without TiO₂ CL showed same V_{oc} , which confirmed that the TiO₂ CL does not necessarily help in preventing back transfer of electron from FTO to perovskite or HTM. Further investigation is needed to understand thoroughly the mechanism of recombination and its suppression by MgO at FTO/TiO₂ interface. However, our results suggest that interfacial modification on conductive FTO with thin tunneling barrier layer can further enhance the performance of perovskite solar cells.

ABBREVIATIONS

TL, Thin Layer; CL, Compact Layer; Spiro-OMeTAD, 2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene; MgO, Magnesium oxide; TiO₂, Titanium dioxide.

ASSOCIATED CONTENT

Supporting Information

Top surface SEM images of TiO₂ CL, MgO TL and TiO₂-MgO bilayer, Cross section SEM images of thin layer TiO₂ CL and without CL based device, J-V curves, device parameters, and histogram of TiO₂ CL (thick and thin) and without TiO₂ CL based devices.

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