Selective Deposition of Insulating Metal Oxide in Perovskite Solar Cells with Enhanced Device Performance

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We report a simple methodology for the selective deposition of an insulating layer on the nanoparticulate TiO$_2$ (np-TiO$_2$) mesoporous layer of perovskite solar cells. The deposited MgO insulating layer mainly covered the bottom part of the np-TiO$_2$ layer with less coverage at the top. The so-called quasi-top-open structure is introduced to act as an efficient hole-blocking layer to prevent charge recombination at the physical contact of the transparent conducting oxide with the perovskite. This leads to an open-circuit voltage higher than that of the reference cell with a compact TiO$_2$ hole-blocking layer. Moreover, such a quasi-top-open structure can facilitate the electron injection from perovskite into the np-TiO$_2$ mesoporous layer and improve the spectral response at longer wavelength because of the less covered insulating layer at the top. This work provides an alternative way to fabricate perovskite solar cells without the need to use a conventional compact TiO$_2$ layer.

The field of electrical energy generation through photovoltaic energy conversion by solar cells has been growing rapidly to make use of the world’s most abundant clean energy source, sunlight. Historically, conventional photovoltaics, namely, crystalline silicon, are expensive and this has led to an increase of research interest in the field of low-cost solar technologies. Recently, a new class of hybrid organic–inorganic-based perovskites (CH$_3$NH$_3$PbX$_3$, X = halogen) has attracted great attention as light harvesters because of their excellent optical properties,[5–11] large absorption coefficient[2, 3] high carrier mobility,[4] and significant potential for high-efficiency solar cells.[6–11]

In perovskite solar cells, charge carriers are generated by the light excitation of the perovskite crystals and further separated by the injection of electrons to the electron-transporting materials and holes to the hole-transporting material (HTM). A competitive process also exists in which electrons and holes are annihilated in a reaction called recombination. Charge recombination at the interface of the transparent conducting oxide (TCO) and the perovskite is one of the major loss factors that decrease the open-circuit voltage of the device. To prevent this, an efficient hole-blocking layer is important for high-performance perovskite solar cell devices.[12–15] Conventionally, a compact TiO$_2$ layer is used to eliminate direct contact between TCO and perovskite.[16, 17] The TiO$_2$ compact layers are pre-deposited on the TCO substrate by different methods, such as a 20–100 nm TiO$_2$ by spray pyrolysis,[8, 18–21] one or two TiO$_2$ layers by spin-coating,[22, 23] and other physical or chemical vapor deposition methods.[24] It is difficult to control the quality of the compact layer as the thickness and coverage can affect the performances of the cell device significantly. A thin compact layer may cause the risk of insufficient film coverage on the TCO, which reduces its effectiveness to prevent electron recombination, whereas a thicker compact layer would increase the series resistance of the device.[13] Another method, namely, surface passivation is also effective to reduce the charge recombination. An example of surface passivation is the use of large-band-gap insulating metal oxide, such as Al$_2$O$_3$, CaCO$_3$, and MgO, coatings on the electron-transporting materials.[24] Generally, the use of these insulating materials as surface coatings or scaffolds can increase the open-circuit voltage, but at the same time they will hinder the electron injection into the electron-transporting materials and decrease the photocurrent.[25]

The generation of photocurrent depends on the light harvesting efficiency, charge generation efficiency, and charge collection efficiency. Although the organometal halide perovskites exhibit excellent harvesting ability in the UV/Vis/near-IR region, the absorption coefficient of the perovskite film at longer wavelengths is smaller than that at shorter wavelengths.[26] Therefore, the long-wavelength photons have a longer optical path length in perovskite film than the short-wavelength photons. In addition, excited electrons generated by the absorption of shorter-wavelength photons have a higher energy and can be injected easily from the perovskite film into the electron-transporting materials. In comparison, the electrons excited by the photons of a longer wavelength have a lower energy and comparably lower electron injection efficiency. The addition of an insulating overlayer on the electron-transporting materials would further hinder the injection of the lower-energy electrons generated by longer-wavelength photons. As a result, the overall electron injection efficiency decreases as a result of the insulating overlayer, which leads to a lower photocurrent. Therefore, it is a big challenge to gain both a high photovoltage and photocurrent by the deposition of insulating...
materials on the electron-transporting materials, especially with a simple methodology required for the development of low-cost perovskite solar cells.

In this work, we introduce a simple method for the selective deposition of an insulating MgO layer on the mesoporous TiO$_2$. The deposited MgO mainly covers the bottom part of the mesoporous layer with less at the top, which allows efficient hole-blocking at the bottom and efficient electron extraction, especially for long-wavelength light, at the top. Although the recent development of perovskite solar cell efficiency by using a compact TiO$_2$ hole-blocking layer combined with a mesoporous TiO$_2$ layer has achieved an efficiency of up to more than 20%, this new method for the selective deposition of insulating materials would pave the way to further enhance the device performance. Additionally, this method reveals the possibility to fabricate perovskite solar cells without the need for a conventional compact TiO$_2$ layer on the TCO substrate.

The deposition of the MgO overlayer on the nanoparticulate TiO$_2$ (np-TiO$_2$) is illustrated in Scheme 1. Firstly, insulating metal oxide precursor solution was spin coated onto the np-TiO$_2$ mesoporous film and dried by the slow evaporation of the solvent at room temperature. Secondly, the surface was washed by dripping ethanol onto the film during high-speed spinning. After thermal annealing, a quasi-top-open MgO blocking layer was formed at the surface of the bare TCO and np-TiO$_2$. The final perovskite layer was deposited by a one-step process from a DMSO solution of lead iodide and methyl ammonium iodide. The quasi-top-open implies that there is less insulating layer on the top part of the TiO$_2$ film than on the bottom part, which provides good contact between TiO$_2$ and perovskite for efficient electron injection. The bottom filling indicates that at the bottom part of the TiO$_2$ film the insulating metal oxide layer is intact and able to prevent electron recombination from the TCO to the perovskite.

A cross-sectional image of a perovskite solar cell using the above mentioned deposition method is shown in Figure 1a. The morphology of the perovskite layer is good with no undulating variation in the thickness. To characterize the inner MgO dispersion in the mesoporous TiO$_2$ layer, we performed X-ray energy dispersive spectroscopy (EDS) by using the EDS analyzer installed in the field-emission scanning electron microscopy (FE-SEM) equipment. The EDS spectrum taken from the cross-section of the mesoporous TiO$_2$ layer on a silicon wafer is shown in Figure S1. The EDS analysis shows that the layer is composed of Ti, Mg, O, and Si. A peak at around 1.253 keV, which corresponds to the energy level of Mg, is observed, which indicates the presence of Mg in the mesoporous TiO$_2$ layer. To further identify the presence of MgO in the mesoporous TiO$_2$ layer, EDS line scans for elemental analysis and element mapping of Mg are shown in Figure 1b and Figure S2. From the analysis, we can see that the intensity of Mg decreases gradually from the bottom to the top in the sample with surface washing, which indicates that MgO is mainly at the bottom part and less in the top part of the mesoporous TiO$_2$ layer. For the sample prepared without surface washing, the intensity of Mg does not decrease gradually, which indicates that the surface washing might help the bottom filling of MgO on np-TiO$_2$.

The current–voltage (I–V) curves of the cell measured under simulated AM1.5G solar irradiance (100 mW cm$^{-2}$) are shown in Figure 2a. The short-circuit current ($I_{SC}$) is 19.1 mA cm$^{-2}$, which is much higher than that of a reference cell without surface washing (15.8 mA cm$^{-2}$). Sufficient surface washing indicates
that the top part of the insulating metal oxide precursor solution is partially removed, which increases the electron injection efficiency. In comparison with the cell device prepared without surface washing, the quasi-top-open structure is able to reduce the possible loss in the electron injection from the perovskite to the photoanode. Therefore, washing by ethanol dripping on the surface of np-TiO$_2$ during the high-spinning process is crucial to remove Mg(CH$_3$COO)$_2$ from the top part of the np-TiO$_2$ film.

To study effect of the deposition of insulating metal oxide on the performance of the cell devices systematically, we used different concentrations of Mg(CH$_3$COO)$_2$ solutions (Figure 2b). The extracted photovoltaic parameters are summarized in Table 1. All of the cell devices except the reference cell (TiO$_2$) were prepared without a compact TiO$_2$ layer but with the post-deposition of Mg(CH$_3$COO)$_2$ solutions followed by surface washing.

The cell without a hole-blocking layer (np-TiO$_2$/perovskite on bare TCO) shows an open-circuit voltage ($V_{OC}$), $J_{SC}$, and fill factor (FF) of 721 mV, 16.10 mA cm$^{-2}$, and 0.42, respectively, to yield an overall power conversion efficiency (PCE; $\eta$) of 4.87%. Thus in the absence of an efficient hole-blocking layer, the device suffers from a very low $V_{OC}$ and FF that can be attributed to the increased recombination at the TCO surface within the device.

The addition of a 0.0025 m MgO overlayer accompanied with surface washing improves both the $V_{OC}$ and FF substantially to result in a PCE of 9.05%. With a further increase of the MgO concentration to 0.005 m, the PCE was enhanced significantly to 13.38% and the $V_{OC}$ increased to 1104 mV. To the best of our knowledge, this is one of the highest open-circuit voltages obtained with TiO$_2$-based solution-processable CH$_3$NH$_2$PbI$_3$ perovskite solar cells. It is clear that the insulating MgO deposition is a crucial and efficient way to obtain a high open-circuit voltage (Table 1). The reference cell, which has a compact TiO$_2$ hole-blocking layer prepared by spray pyrolysis, shows a lower $V_{OC}$ of 0.952 V. The performance parameters ($J_{SC}$, $V_{OC}$, FF, PCE) of cells based on compact TiO$_2$ blocking and MgO blocking are shown in Figure S3. The dark current of the cell prepared by the post-deposition of MgO was compared with that of the reference cell and the cell without a MgO overlayer (Figure S4). The onset voltage for the cell with “no MgO” is ~300 mV, and the onset shifts to ~800 mV for the cell prepared by the TiO$_2$ spray pyrolysis of a compact TiO$_2$ layer (~40 nm). A large shift in the onset voltage (~1000 mV) is observed in the sample prepared from 0.005 m MgO, which reveals a very dark current. An increased photovoltage performance and significantly reduced dark current in quasi-top-open MgO-based perovskite solar cells indicate the suppression of electron back-transfer from the TCO glass to the perovskite crystal, which is consistent with the $J$-$V$ data.

The cells prepared by the post-deposition method show higher $J_{SC}$ and $V_{OC}$ values but lower FF values than the reference cells. The low FF is probably because of the shunt, which is partially related to the quality of the hole-blocking layer and the morphologies of the perovskite layer. As we used the same method to deposit and control the quality of the perovskite layer, the main difference should be caused by the change in the hole-blocking layer. Previous work also found a relatively low FF (~0.60) in the cells prepared by the post-deposition of TiO$_2$ overlayer by the atom layer deposition (ALD) method.[15] The $J_{SC}$ in that work was also found to decrease gradually with the increase of the thickness of the TiO$_2$ overlayer, which confirmed that the deterioration of the photocurrent was caused by the full coverage of an insulating metal oxide or even a TiO$_2$ overlayer. In this work, the photocurrent of the quasi-top-open structure is higher than that of devices with no MgO or with a full MgO overlayer. The high $J_{SC}$ is a benefit of the design of the quasi-top-open MgO strategy. In addition, the active area of the cells is 1.0 cm$^2$, which is much bigger than that of most of the perovskite solar cells reported so far. This indicates that the selective deposition method can be applied easily in perovskite solar cells.
To explain the photocurrent loss in the fully covered structures, we measured the light absorption spectra (Figure S5) and incident photon-to-current conversion efficiency (IPCE) to further understand the device performance. Light absorption as a function of perovskite film thickness at light wavelengths of 500 and 700 nm is shown in Figure 3a. The light absorption, \( A \), is expressed by \( A = 1 - \exp(-p \alpha x) \), in which \( p \) is the porosity, which is \(-0.5\) for the np-TiO\(_2\) layer and \(1.0\) for the perovskite capping layer, \( \alpha \) is the light absorption coefficient of the CH\(_3\)NH\(_3\)PbI\(_3\) perovskite film (\(2 \times 10^5\) cm\(^{-1}\) at 500 nm and \(5 \times 10^5\) cm\(^{-1}\) at 700 nm),\(^{[26]}\) and \( x \) is the film thickness. The light absorption at the short wavelength (500 nm) increased rapidly up to \(\sim 90\%\) in the mesoporous layer, whereas the light absorption at the long wavelength (700 nm) increased relatively slowly with only \(50\%\) absorbed in the mesoporous layer (Figure 3a). In comparison, the incident light at the long wavelength absorbed in the perovskite capping layer has to travel a greater distance to the surface of the TiO\(_2\) film, which makes it more difficult for electron injection into the insulator-covered TiO\(_2\) film. Therefore, the IPCE spectrum of the devices fully covered by MgO is lower than \(70\%\), especially in the longer wavelength region (Figure 3b).

The IPCE data of the devices with quasi-top-open MgO are shown in Figure 3b. The IPCE increases in both the short- and long-wavelength range after surface washing in comparison with devices covered fully with MgO. However, the increase of the IPCE at the long wavelength is larger than that at the short wavelength. The IPCE at the short wavelength increases by \(\approx 8.5\%\) and that at the long wavelength increases by \(\approx 18.4\%\).

According to the absorption spectra (Figure S5), there is a negligible difference between the np-TiO\(_2\)/perovskite film with and without the top-open insulating layer. This indicates that the quasi-top-open strategy, which produces a semicoated MgO layer on the TiO\(_2\) film improves the electron injection greatly, especially in the long-wavelength range, which leads to an improvement of the photocurrent compared to the device coated fully with a MgO layer.

To further understand the hole-blocking effect, electrochemical impedance spectroscopy (EIS) on these devices was performed in the dark. The Nyquist plot measured at a voltage bias of 1.0 V is shown in Figure 4. From the measurements, we can extract the recombination resistance (\( R_{\text{rec}} \)) based on a simple equivalent circuit model, which has been applied widely in most perovskite solar cells.\(^{[27]}\) With the increase of the MgO overlayer concentration, the diameter of the semicircle increases, which indicates higher recombination resistance in the devices prepared with 0.005 m MgO than those with a lower MgO concentration or with a TiO\(_2\) compact layer. \( R_{\text{rec}} \) as a function of the applied voltage bias is shown in Figure S6. From these data, \( R_{\text{rec}} \) decreases as a function of applied voltage. The \( R_{\text{rec}} \) of “0.005 m-MgO” is higher than that of “0.0025 m-MgO” or the sample prepared with a TiO\(_2\) compact layer, and these values are all much higher than that of the “no MgO” sample. The increased recombination resistance reflects an efficient recombination blocking effect. This is in good agreement with the increase in \( V_{\text{oc}} \) with the increase of the MgO overlayer concentration.

In summary, we have developed an alternative way to block electron recombination by employing a quasi-top-open insulating MgO layer over nanoparticulate TiO\(_2\) (np-TiO\(_2\)), which eliminates the need to use a compact TiO\(_2\) layer in the perovskite solar cells. Our observation shows that this selective deposition of the MgO overlayer on the np-TiO\(_2\) film can facilitate the electron injection, especially under long-wavelength light, in comparison with the sample prepared with a full MgO layer, and retard electron–hole recombination to lead to an improved energy power conversion efficiency with a significant

![Figure 3](image1.png)

**Figure 3.** (a) Calculation of the light absorption as a function of distance in the film thickness at 500 and 700 nm. (b) IPCE data of the device with and without surface washing.

![Figure 4](image2.png)

**Figure 4.** Nyquist plot of the cell with no MgO (blue), cells with quasi-top-open 0.005 m MgO (red), 0.0025 m MgO (black), and TiO\(_2\) compact (brown) at an applied voltage of 1.0 V. The inset is the equivalent circuit model employed to fit the Nyquist plots.
high open-circuit voltage up to 1.10 V. The quasi-top-open deposition method can be extended to other metal oxide overlayers. This work gives a general guideline for future fabrication of effective hole-blocking layers, which is especially useful in practical perovskite photovoltaic technology.

Experimental Section

Fluorine-doped tin oxide (FTO) glass was washed in a detergent solution for 15 min with sonication, which was followed by consecutive washing. The anodic deposition was performed in an electrolyte solution containing 2.7% weight ratio of TiO$_2$ paste onto the substrate and annealed under 500 °C for 45 min. The produced 300 nm thick np-TiO$_2$ mesoporous film. After cooling to RT, Mg(CH$_3$COO)$_2$ solutions with different concentrations were spin-coated on the np-TiO$_2$ layer at a speed of 1000 rpm and then kept at RT to evaporate the ethanol slowly. The substrate was placed on the spin-coater to be accelerated to 5000 rpm. During spinning, the deposition was performed by a one-step process of a DMSO solution of lead iodide and methyl ammonium iodide.$^{[10]}$ The synthesized CH$_3$NH$_3$I (0.795 g) was mixed with PbI$_2$ (2.305 g) in anhydrous DMSO (4 mL) by stirring at 70 °C for several hours to attain a clear CH$_3$NH$_3$PbI$_3$ solution. To deposit the perovskite films, CH$_3$NH$_3$PbI$_3$ solution (50 μL) was dropped on the heated FTO glass with np-TiO$_2$-MgO, which was placed on the spin-coater. The spin-coater was accelerated at a rotation speed of 1000 rpm for 10 s and then further accelerated at 5000 rpm for another 30 s. Toluene (800 μL) was dropped at 10 s after the 5000 rpm spinning started. The deposited films were then heated to 100 °C for 10 min. The hole-transporting material was deposited by spin-coating at 3000 rpm for 30 s. The spin-coating solution was prepared by dissolving spiro-MeOTAD (2,2′,7,7′-tetrakis[N,N-di-p-methoxyphenylamine]-9,9′-spirobifluorene) (150 mg), a stock solution of lithium bis(trifluoromethanesulfonyl)imide in acetonitrile (75 μL, 170 mg mL$^{-1}$), Co$^{3+}$ complex (FK-102) solution in acetonitrile (58 μL, 300 mg mL$^{-1}$), and 4-tert-butylpyridine (36 μL) in chlorobenzene (2 mL). The device fabrication was finally completed by the thermal evaporation of 80 nm thick film of Au as the cathode. The reference cell with a compact TiO$_2$ hole-blocking layer was fabricated by spray pyrolysis.

Acknowledgements

This work was supported by the Core Research for Evolutional Science and Technology of Japan Science and Technology Agency.

Keywords: magnesium · nanoparticles · photochemistry · thin films · titanium

References


Received: April 15, 2015
Revised: June 22, 2015
Published online on July 21, 2015
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**Materials:** All solvents and chemicals were of reagent grade quality, purchased, and used without further purification. Unless specified otherwise, all materials were purchased from Sigma-Aldrich and used as received. Spiro-MeOTAD was purchased from Merck KGaA Corp. Methylammonium iodide (CH$_3$NH$_3$I) was synthesized by reported procedures.$^{51}$

**Characterization:** Cross-section image of the film was characterized by using a JSM-6500F field-emission scanning electron microscope. UV-Vis spectra were measured on Shimadzu UV/Vis 3600 spectrophotometer with an integrated sphere. Electrochemical impedance spectra (EIS) were obtained on an electrochemical work station (solartron 1287 and 1255B): the solar cell was kept in the dark under different bias potential at frequencies ranging from $10^6$-$10^1$ Hz. Current-voltage ($J$-$V$) curves were measured by using a digital source meter (2400, Keithley) under simulated AM 1.5 solar illumination of 100 mW cm$^{-2}$ (WXS-90L2, Wacom).$^{52}$ The simulated light intensity was calibrated with a silicon photodiode. The aperture area was 1.0 cm$^2$ determined by a mask slightly smaller than the active area. IPCE data were measured with mono-chromatic incident light of $10^{16}$ photon per cm$^2$ in DC mode (CEP-2000, Bunko-Keiki).
Figure S1. EDS spectra of the spot measurement at the top and bottom parts of the np-TiO$_2$ with MgO over layer (0.005M). It shows that the layer was composed of Ti, Mg, O, Si at the energy spectra: Ti-K$_{α}$=4.508 keV, Mg-K$_{α}$=1.253 keV, O-K$_{α}$=0.525 keV, Si-K$_{α}$=1.739 keV, respectively. Si signal is from silicon wafer that used for the substrate in case that FTO glass contain Mg element.
Figure S2 Element mapping of Mg
Figure S3. Statistics on performance parameters of 50 cells for TiO$_2$-compact and MgO blocking type cells: (a) $J_{SC}$, (b) $V_{OC}$, (c) FF, (d) efficiency.
Figure S4. The dark currents of the cells with (a) TiO$_2$ spray pyrolysis blocking layer (black), (b) no MgO (blue) and (c) 0.005M-MgO blocking layer (red).
**Figure S5.** Absorption spectra of CH$_3$NH$_3$PbI$_3$ perovskite films prepared on mesoporous TiO$_2$/ MgO (0.005 M)/perovskite with (Quasi-top-open) and without surface washing (fully-covered).
Figure S6. Recombination resistant ($R_{\text{rec}}$), estimated from the Nyquist plot of electrochemical impedance spectra, is plotted as a function of applied voltage for devices.

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