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Retarding Charge Recombination in Perovskite Solar Cells Using Ultrathin MgO-coated TiO₂ Nanoparticulate Films

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Retarded charge recombination is an important issue for efficient operation and performance of perovskite solar cells (PSCs). MgO-coated TiO₂ nanoparticle (NP)-based electron collecting layers were fabricated to prevent charge recombination at the methylamine lead iodide/TiO₂ interface in perovskite solar cells. The open circuit voltage (Vₜₜ) and fill factor (ff) for perovskite solar cells based on MgO-coated TiO₂ charge collector were 0.89 V and 71.2%, respectively. These values were 4.7% and 6.1% higher than the pure TiO₂ based perovskite solar cells. Transient photovoltage decay data exhibited recombination times for MgO-coated TiO₂ NP-based perovskite solar cells about three times longer than those of TiO₂ NP-based solar cells. The longer recombination time was responsible for enhancing the Vₜₜ and ff of MgO-coated TiO₂ NP-based perovskite solar cells. By employing a MgO nanolayer, we observed that the power conversion efficiency (PCE) was increased from 11.4% to 12.7%, demonstrating that MgO ultrathin nanolayers are able to efficiently retard charge recombination in perovskite solar cells.

Introduction

Organometal halide perovskite materials have attracted a great deal of attention because of their higher light absorption coefficient (approximately 10⁶ cm⁻¹), long absorption wavelength (>800 nm), and unique electrical properties. CH₃NH₃PbI₃ perovskite has been considered to be the next generation solar material because of its excellent light absorption characteristics. There have been many attempts at improving the efficiency of perovskite solar cells, such as (a) using different scaffold materials which can contribute to efficient charge separation and charge transport, (b) replacing the halogen atom in the perovskite material that influences electron and hole mobility, and (c) using efficient hole transport materials. The combination of replacing scaffold materials and adding chlorine ions significantly boosted the power conversion efficiency (PCE) by retarding drops in the quasi Fermi energy and increasing the electron diffusion length.

MgO-coated TiO₂ nanoparticle (NP)-based electron collecting layers were fabricated to prevent charge recombination at the methylamine lead iodide/TiO₂ interface in perovskite solar cells. The open circuit voltage (Vₜₜ) and fill factor (ff) for perovskite solar cells based on MgO-coated TiO₂ charge collectors were 0.89 V and 71.2%, respectively. These values were 4.7% and 6.1% higher than the pure TiO₂ based perovskite solar cells. Transient photovoltage decay data exhibited recombination times for MgO-coated TiO₂ NP-based perovskite solar cells about three times longer than those of TiO₂ NP-based solar cells. The longer recombination time was responsible for enhancing the Vₜₜ and ff of MgO-coated TiO₂ NP-based perovskite solar cells. By employing a MgO nanolayer, we observed that the power conversion efficiency (PCE) was increased from 11.4% to 12.7%, demonstrating that MgO ultrathin nanolayers are able to efficiently retard charge recombination in perovskite solar cells.

Experimental

Materials

To synthesize the methyl-ammonium iodide (MAI), first hydroiodic acid (30 mL, 0.227 mol, 57 wt% in water) and methylamine (27.8 mL, 0.273 mol, 40% in methanol) were stirred in a round bottom flask at 0°C for 2 h. The solution was evaporated to precipitate white CH₃NH₃I powder. The CH₃NH₃I was washed three times in diethyl ether and dried in a vacuum oven at 60°C for 6 h. Magnesium methoxide (Mg(OCH₃)₂) solution was used to prepare MgO-coated TiO₂ core shell nanoarchitectures. Magnesium methoxide (6–10 wt % in methanol, Aldrich) and diethanolamine (98.5%, Aldrich) was used as a
precursor and stabilizer, respectively. The magnesium methoxide was dissolved in methanol at various concentrations (0.1, 0.5 and 2.0 wt%) by stirring at room temperature. The MgO coating was formed by spin-coating process. Initially, the magnesium methoxide solution was dropped onto the mesoporous TiO$_2$ NP layers. After sufficient penetration of the solution (~20 seconds), then the resultant films were spun at 3000 rpm. The magnesium methoxide molecules are chemisorbed onto the surface of TiO$_2$ by reacting with surface hydroxyl groups and adsorbed water molecules on TiO$_2$ NPs, which leads to the formation of MgO ultrathin layer after annealing at 500°C.

Fabrication of CH$_3$NH$_3$PbI$_3$ Perovskite solar cells

To prepare TiO$_2$ dense compact layers, cleaned fluorine doped tin oxide (FTO) glasses were spin coated with 0.15 M titanium dispropoxide bis (acetylacetonate) solution in 1-butanol, which was dried at 120°C for 10 min. Then 0.3 M titanium dispropoxide bis solution was twice coated onto the film using the same method. The films were then dried at 120°C and annealed at 500°C for 15 min. After cooling to room temperature, the substrates were treated with a 0.05 M aqueous solution of TiCl$_4$ for 30 min at 70°C to improve the surface properties of the TiO$_2$ layer. After that the substrates were rinsed in deionized (DI) water, dried by nitrogen blowing, and annealed at 500°C for 15 min. To prepare mesoporous TiO$_2$ film, TiO$_2$ NP solution (18NRT, Dyesol) paste diluted in ethanol (1:3.5 wt%) was spin coated onto the substrate and annealed at 500°C for 45 min. After cooling to room temperature, magnesium methoxide solution was spin coated on the mesoporous TiO$_2$ layer at optimized condition (3000 rpm for 30 s) and then annealed at 500°C for 1 h.

Perovskite solar cells were fabricated using a sequential deposition method with and without MgO-TiO$_2$ NP films. The prepared charge collectors were coated with PbI$_2$ (1.0M) and dimethylformamide (DMF,1mL) solution, which was dried at 70°C. The films were dipped in CH$_3$NH$_3$I and 2-propanol (10 mg·mL$^{-1}$) for 60 s, rinsed with 2-propanol, and dried at 70°C for 30 min. The HTM was deposited using a spin coating method with spiro-OMeTAD (2,2',7,7'-tetakis-(N,N-diphenylamino)-9,9'-spirobiferene), which was dissolved in chlorobenzene at 90 mg·mL$^{-1}$ (0.085 M), adding tert-butylpyridine (TBP) and Lithium-bis (trifluoro-methanesulphonyl) imide salt (Li-TFSI) additives. The 100 nm thick silver electrodes were deposited by using thermal evaporation.

Characterization

To realize the solar cells structures, cross-sectional images were observed using field emission scanning electron microscopy (FESEM, JEOL, JSM-7600F). The MgO-coated TiO$_2$ nanostructure was observed using high-resolution transmission electron microscopy (HRTEM, JEOL, JEM-3010). Elemental analysis was performed using high-resolution X-ray photoelectron spectroscopy (XPS, Theta Probe XPS Instrument, Thermo Fisher Scientific Co.). Photovoltaic properties were measured using a potentiostat (CHI660, CHI instrument). The solar spectrum at an AM 1.5 condition was simulated using a solar simulator (Oriel Sol 3A class AAA, Newport) to measure the current voltage characteristics (0.03V·s$^{-1}$ scan rate). The time constant for photo-generated electron recombination ($\tau$) was measured using a transient photocurrent-voltage spectroscopy setup, which is described elsewhere. The incident-photon-to-current conversion efficiency (IPCE) was measured using an IPCE measurement system (PV Measurements).

Results and discussion

The cross-sectional FE-SEM image of hybrid perovskite solar cells is shown Fig. 1(a). It is clearly seen that the TiO$_2$ compact layer and TiO$_2$ NP layer were deposited to about 50 nm and 400 nm in thickness, respectively. To ensure the presence of MgO on mesoporous TiO$_2$, HR-TEM images of MgO-coated TiO$_2$ powders detached from the electron collecting layer on FTO glass.

Figure 1. (a) Cross section field emission scanning electron microscopy (FESEM) image of MgO/TiO$_2$ core shell NP-based perovskite solar cell. (b) High-resolution transmission electron microscopy (HRTEM) image of MgO/TiO$_2$. (c) High-resolution X-ray photoelectron spectrum of Mg (dark cyan line, 1s) and Ti (black line, 2p).

Figure 2. Representative J-V curves of pristine TiO$_2$ NP- and MgO/TiO$_2$ core shell NP-based perovskite solar cells with varying magnesium methoxide concentration (0.1 wt%, 0.5 wt%, and 2.0 wt%).
were taken (Fig. 1(b)). The apparent lattice image for TiO$_2$
indicated that it was crystalline. At the TiO$_2$ surface, lattice
images were not found and amorphous-like ultrathin layers
(approximately 1 nm thick) were observed. This implied the
1 presence of amorphous MgO thin layers. Since the TEM image
for the MgO-coated TiO$_2$ NPs (Figure 1b) was randomly taken
from the powder samples detached from the mesoporous films on
FTO glasses, this result supports that the MgO ultrathin layer was
conformally coated to the inside part of the mesoporous TiO$_2$ NPs.
X-ray diffraction (XRD) analysis could not detect the MgO peak
due to its ultrathin thickness. Fig. 1(c) exhibits the X-ray
photocurrent density (19.88±0.32 mA·cm$^{-2}$). Increasing the
weight percentage of magnesium methoxide, which is related to
the thickness of the MgO layer, led to decreasing photocurrent
density (Supplementary Information 3). The photocurrent density
did not significantly change until the concentration of magnesium
methoxide reached 0.1 wt%. However, beyond 0.5 wt% of
magnesium methoxide concentration, the photocurrent density
remarkably decreased to 13.22±0.72 mA·cm$^{-2}$. This is attributed
to the restricted electron injection from the perovskite layer to the
TiO$_2$ particles that are associated with the large band gap in the
MgO nanolayer (7.8 eV).

Fig. 2 shows the $J$-$V$ curves of the perovskite solar cells
containing MgO-coated TiO$_2$ films as a function of weight
centre of magnesium methoxide in the MgO coating solution.
The average photovoltaic characteristic values for each solar cell
are summarized in Supplementary Information 1. The change in
each parameter, such as $J_{sc}$, $V_{oc}$, ff, and efficiency, is also plotted
in Supplementary Information 2. The pristine TiO$_2$ NP-based
perovskite solar cell (reference solar cell) showed the highest
photocurrent density (19.88±0.32 mA·cm$^{-2}$). Increasing the
weight percentage of magnesium methoxide, which is related to
the thickness of the MgO layer, led to decreasing photocurrent
density (Supplementary Information 3). The photocurrent density
did not significantly change until the concentration of magnesium
methoxide reached 0.1 wt%. However, beyond 0.5 wt% of
magnesium methoxide concentration, the photocurrent density
remarkably decreased to 13.22±0.72 mA·cm$^{-2}$. This is attributed
to the restricted electron injection from the perovskite layer to the
TiO$_2$ particles that are associated with the large band gap in the
MgO nanolayer (7.8 eV).

$V_{oc}$ increased with increasing magnesium methoxide solution
concentration. $V_{oc}$ of pristine TiO$_2$ and MgO-coated TiO$_2$ (2.0
wt%) based perovskite solar cells was found to be 0.84±0.01 V
and 0.93±0.01 V, respectively. As shown in Fig. 2, the dark
current of the pristine TiO$_2$ perovskite solar cell dropped at a
relatively low bias, implying that charge recombination is
facilitated at the TiO$_2$/perovskite interface. On the other hand, the
dark current drop for the MgO-coated TiO$_2$ perovskite solar cell
started at higher voltages, demonstrating the retarded charge
recombination.

As illustrated in Fig. 3(a) and 3(b), the insulating MgO
layer with a large band gap energy (approximately 8 eV) is
capable of blocking charge recombination at the TiO$_2$/perovskite
or TiO$_2$/HTM interface. The improved electron life time for
photovoltaic devices employing an ultrathin MgO layer has been
well known, especially in dye-sensitized solar cells. The MgO
layer was revealed to efficiently block electron recombination
with I$_3^-$ ionic electrolytes$^{13, 21}$. Therefore, the $V_{oc}$ increased with
increasing magnesium methoxide concentration, indicating the
effective retardation of charge recombination via an addition of a
large amount of MgO. It was also observed that the ff increased
with increasing magnesium methoxide solution concentration
(Fig. 3(c)). This provides more evidence for the retarded charge
recombination. To verify the effect of MgO coating on the
retardation of charge recombination, the transient photovoltage
decay behavior for the pristine TiO$_2$ and MgO-coated TiO$_2$
perovskite solar cells were characterized. Fig. 4 shows charge
recombination times of each cell as a function of $V_{oc}$. This clearly

![Figure 3](image_url)

**Figure 3.** (a) Schematic representation of the charge transfer mechanism in the TiO$_2$ based perovskite solar cell with MgO layer. (b) Band energy diagram for the MgO/TiO$_2$ core shell NP-based perovskite solar cell. (c) Open circuit voltage ($V_{oc}$) and fill factor (ff) of MgO/TiO$_2$ core shell NP-based perovskite solar cell with varying magnesium methoxide concentration (0.1 wt%, 0.5 wt%, and 2.0 wt%).

![Figure 4](image_url)

**Figure 4.** Electron lifetime of a MgO/TiO$_2$ core shell NP-based perovskite solar cell compared to a TiO$_2$NP-based perovskite solar cell.
Figure 5. (a) J–V curves and (b) IPCE for the best performing cells; MgO/TiO₂ core shell NP- (dark cyan line) and TiO₂ NP- (black line) based perovskite solar cell.

shows the longer electron life time for the MgO-coated TiO₂ perovskite solar cell. The J–V curve characteristics of the best performing perovskite solar cells composed of the respective pristine TiO₂ and MgO-coated TiO₂ charge collecting layers are plotted in Fig. 5(a). In the case of the pristine TiO₂ perovskite cell, we achieved the characteristic values of 20.11 mA·cm⁻², 0.85 V, 67.1%, and 11.4 % for Jₐc, Voc, ff, and the PCE (Supplementary Information 4), respectively. The MgO-coated TiO₂ perovskite cell exhibited Jₐc, Voc, ff, and PCE values of 20.02 mA·cm⁻², 0.89 V, 71.2 %, and 12.7 %, respectively. Figure 5(b) shows the IPCE spectra for each solar cell, which demonstrates that the employment of a MgO layer enhances a PCE by improving the Voc and ff by retarding charge recombination at the TiO₂/perovskite or TiO₂/HTM interface.

Conclusions
In summary, we coated an MgO nanolayer onto a TiO₂ nanoparticle charge collecting film using a sol-gel process. The perovskite solar cells employing MgO-coated TiO₂ films exhibited an increase in ff and Voc as a function of weight percentage of magnesium methoxide in the MgO coating solution. However, because of the insulating nature of MgO, the photocurrent decreased with the magnesium methoxide content. The transient photovoltage study revealed that the MgO nanolayer retarded the electron/hole recombination at the TiO₂/CH₃NH₃PbI₃ surface, thereby extending the carrier life time. The optimized perovskite solar cell based on the MgO-coated TiO₂ films showed higher energy conversion efficiency: 12.7% in comparison to the 11.4% of the pristine TiO₂ perovskite cell. This was ascribed to the improved ff and Voc. This study demonstrates that the employment of a thin MgO layer is a promising way to block the charge recombination at the TiO₂/CH₃NH₃PbI₃ interface in perovskite solar cells.

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Notes and references
MgO ultrathin nanolayers are able to efficiently retard charge recombination in perovskite solar cells.