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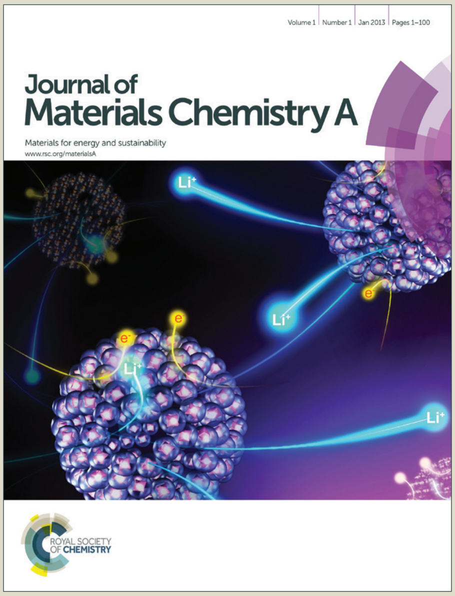

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ARTICLE TYPE

Retarding Charge Recombination in Perovskite Solar Cells Using Ultrathin MgO-coated TiO_2 Nanoparticulate Films

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MgO-coated TiO_2 nanoparticle (NP)-based electron collecting layers were fabricated to prevent charge recombination at the methylamine lead iodide/TiO_2 interface in perovskite solar cells. The open circuit voltage (V_{oc}) and fill factor (*ff*) for perovskite solar cells based on MgO-coated TiO_2 charge collectors were 0.89 V and 71.2%, respectively. These values were 4.7% and 6.1% higher than the pure TiO_2 based perovskite solar cells. Transient photovoltage decay data exhibited recombination times for MgO-coated TiO_2 NP-based perovskite solar cells about three times longer than those of TiO_2 NP based solar cells. The longer recombination time was responsible for enhancing the V_{oc} and *ff* of MgO-coated TiO_2 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 $10^5 cm^{-1}$), long absorption wavelength (>800nm), and unique electrical properties.[1,2] $CH_3NH_3PbI_3$ 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,[3-6] (b) replacing the halogen atom in the perovskite material that influences electron and hole mobility,[7,8] and (c) using efficient hole transport materials.[9,10] 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.[11]

Chlorine doped $CH_3NH_3PbI_3$ perovskite ($CH_3NH_3PbI_{3-x}Cl_x$) has an electron diffusion length of one order longer than $CH_3NH_3PbI_3$because of its faster transport because of its higher electron and hole mobility.[7] The longer electron diffusion length enabled the use of insulating Al_2O_3, and ZrO_2 nanoparticles (NPs) as mesoporous scaffold materials, consequently raising the open circuit voltage (V_{oc}) to 1.1 V.[11,12] However, in the case of pure $CH_3NH_3PbI_3$, the relatively short electron diffusion length led to the utilization of wideband gap semiconducting nanoparticles, such as TiO_2 and ZnO, as charge collecting layers, as well as scaffold layers.

At the interface between these nanoparticles and perovskite materials, injected photo-induced electrons may recombine with holes. This would deteriorate the open circuit voltage and fill factors (ff). In the case of dye-sensitized solar cells, a similar recombination is called back electron transfer. An effective way of controlling the charge recombination is to change the electrical properties of the wide band gap semiconductors by coating the nanoparticle surfaces. Several metal oxides, such as SrO, Al_2O_3, $CaCO_3$, and MgO have successfully suppressed charge recombination.[13-16] However, to the best of our knowledge, studies on controlling the interface between the wide band gap semiconductor and perovskite material has been sparse.[17]

In this report, we coated MgO nanolayers onto TiO_2 NP films using a sol-gel process. The increase in Mg-methoxide concentration of MgO coating solution improved the fill factor (*ff*) and open circuit voltage (V_{oc}), which was explained in terms of the retarded charge recombination at the interface between MgO and $CH_3NH_3PbI_3$.Consequently, energy conversion efficiency of the MgO-coated TiO_2-based perovskite solar cell increased from 11.4 % to 12.7 %.

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 CH_3NH_3I powder. The CH_3NH_3I was washed three times in diethyl ether and dried in a vacuum oven at 60°C for 6h. Magnesium methoxide (Mg $(OCH_3)_2$) solution was used to prepare MgO-coated TiO_2 core shell nano-architectures. Magnesium methoxide (6–10 wt % in methanol, Aldrich) and diethanolamine (98.5%, Aldrich) was used as a

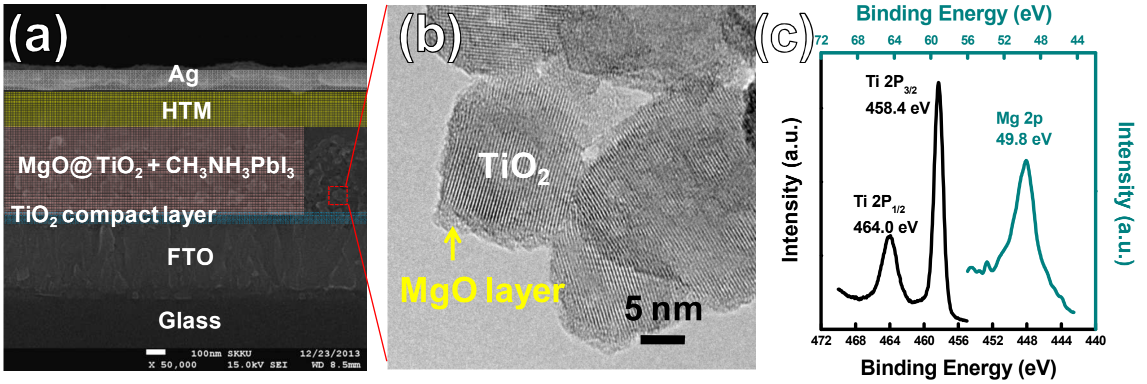

Figure 1. (a) Cross section field emission scanning electron microscopy (FESEM) image of MgO/TiO_2 core shell NP-based perovskite solar cell. (b) High-resolution transmission electron microscopy (HRTEM) image of MgO/TiO_2 NPs. (c) High-resolution X-ray photoelectron spectrum of Mg (dark cyan line, 1s) and Ti (black line, 2p).

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 ^{o}C.[16]

Fabrication of $CH_3NH_3PbI_3$ 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 diisopropoxide bis (acetylacetonate) solution in 1-butanol, which was dried at 120 °C for 10 min. Then 0.3 M titanium diisopropoxide 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 30min 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 15min.To prepare mesoporous TiO_2 film, TiO_2 NP (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 1h.

Perovskite solar cells were fabricated using a sequential deposition method with and without MgO-TiO_2 NP films.[3] 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_3NH_3I 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'-tetrakis-(N,N-dipmethoxyphenyl-amine) 9,9'-spirobifluorene), 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 (τ_R) was measured using a transient photocurrent-voltage spectroscopy setup, which is described elsewhere.[18] 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

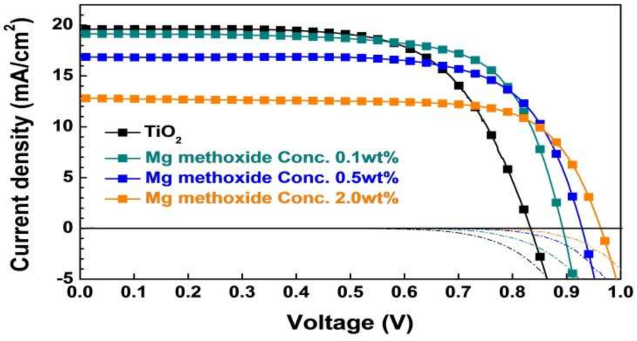

Figure 2. Representative *J-V* curves of pristine TiO_2 NP- and MgO/TiO_2 core shell NP-based perovskite solar cells with varying magnesium methoxide concentration (0.1 wt%, 0.5 wt%, and 2.0 wt %).

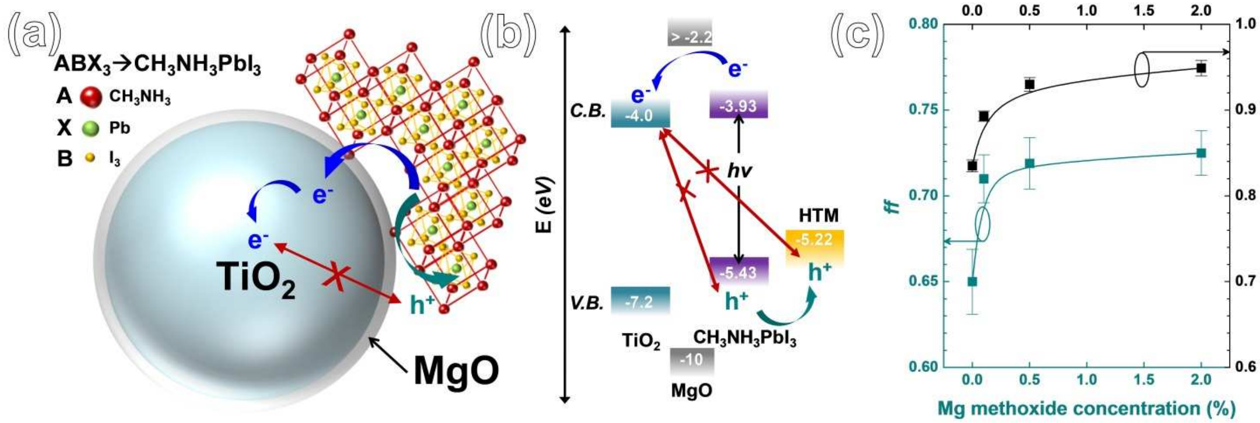

Figure 3. (a) Schematic representation of the charge transfer mechanism in theTiO$_2$ based perovskite solar cell with MgO layer. (b) Band energy diagram for the MgO/TiO$_2$ core shell NP-based perovskite solar cell. (c) Open circuit voltage (V_{OC}) and fill factor (*ff*) of MgO/TiO$_2$ core shell NP-based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

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 1nm thick) were observed. This implied the 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 photoelectron spectroscopy (XPS) spectra, confirming the presence of a MgO layer on TiO$_2$ nanoparticles. Ti 2p$_{3/2}$ peaks of Ti^{4+} ions and Mg 2p peaks of Mg^{2+} ions were observed in the range of 458.5–458.9eV and 49.3-51.6 eV, respectively.

Fig. 2 shows the *J-V* curves of the perovskite solar cells containing MgO-coated TiO$_2$ films as a function of weight percentage 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).

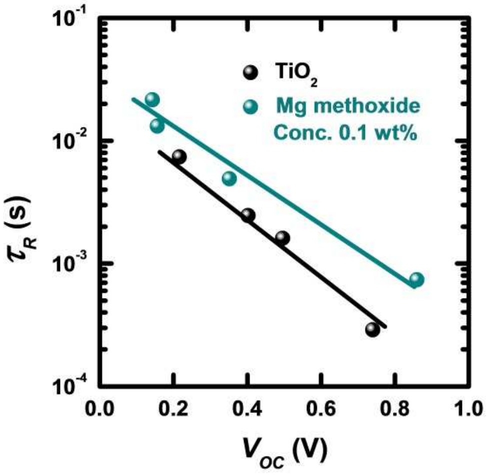

Figure 4. Electron lifetime of a MgO/TiO$_2$ core shell NP-based perovskite solar cell compared to a TiO$_2$NP-based perovskite solar cell.

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 0.95±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.[19,20]

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

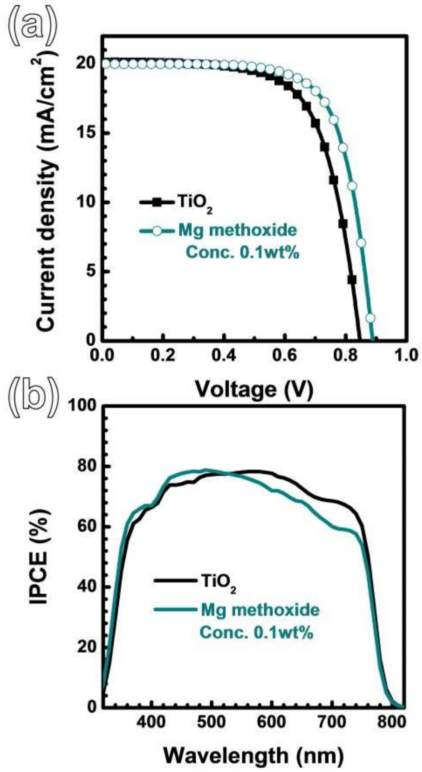

Figure 5. (a) *J–V* curves and (b) IPCE for the best performing cells; MgO/TiO$_2$ core shell NP- (dark cyan line) and TiO$_2$ NP- (black line) based perovskite solar cell.

shows the longer electron life time for the MgO-coated TiO$_2$ perovskite solar cell. The *J-V* curve characteristics of the best performing perovskite solar cells composed of the respective pristine TiO$_2$ and MgO-coated TiO$_2$ charge collecting layers are plotted in Fig. 5(a). In the case of the pristine TiO$_2$ perovskite cell, we achieved the characteristic values of 20.11mA·cm^{-2}, 0.85 V, 67.1%, and 11.4 % for J_{sc}, V_{oc}, ff, and the PCE (Supplementary Information 4), respectively. The MgO-coated TiO$_2$ perovskite cell exhibited the J_{sc}, V_{oc}, 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 V_{oc} and *ff* by retarding charge recombination at the TiO$_2$/perovskite or TiO$_2$/HTM interface.

Conclusions

In summary, we coated an MgO nanolayer onto a TiO$_2$ nanoparticle charge collecting film using a sol-gel process. The perovskite solar cells employing MgO-coated TiO$_2$ films exhibited an increase in *ff* and V_{oc} 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 TiO$_2$/CH$_3$NH$_3$PbI$_3$ surface, thereby extending the carrier life time. The optimized perovskite solar cell based on the MgO-coated TiO$_2$ films showed higher energy conversion efficiency: 12.7% in comparison to the 11.4% of the pristine TiO$_2$ perovskite cell. This was ascribed to the improved *ff* and V_{oc}. This study demonstrates that the employment of a thin MgO layer is a promising way to block the charge recombination at the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface in perovskite solar cells.

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† Electronic Supplementary Information (ESI) available: The representative photovoltaic characteristic values for each solar cell, Strandard deviation of photovoltaic properties, HR-TEM image of MgO thickness on TiO$_2$ nanoparticles as a function of magnesium methoxide concentration, and *J-V* characteristic for the best performance cells. See DOI: 10.1039/b000000x/

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Table of contents

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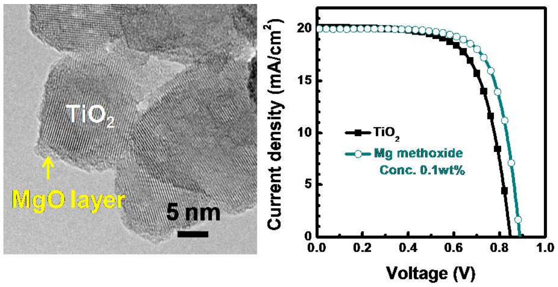

MgO ultrathin nanolayers are able to efficiently retard charge recombination in perovskite solar cells.