

Unraveling the Function of an MgO Interlayer in Both Electrolyte and Solid-State SnO₂ Based Dye-Sensitized Solar Cells

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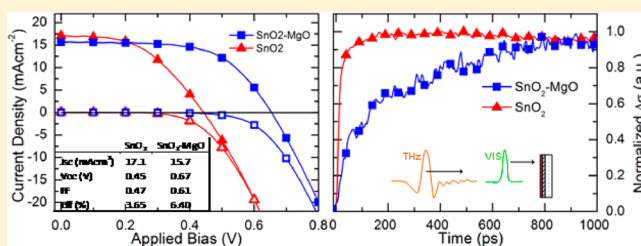
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S Supporting Information

ABSTRACT: The coating of n-type mesoporous metal oxides with nanometer thick dielectric shells is a route that has proven to be successful at enhancing the efficiency of some families of dye-sensitized solar cells. The primary intention is to introduce a “surface passivation layer” to inhibit recombination between photoinduced electrons and holes across the dye-sensitized interface. However, the precise function of these dielectric interlayers is often ambiguous. Here, the role of a thin MgO interlayer conformally deposited over mesoporous SnO₂ in liquid electrolyte and solid-state dye-sensitized solar cells is investigated. For both families of devices the open-circuit voltage is increased by over 200 mV; however, the short-circuit photocurrent is increased for the solid-state cells, but reduced for the electrolyte based devices. Through electronic and spectroscopic characterization we deduce that there are four distinct influences of the MgO interlayer: It increases dye-loading, slows down recombination, slows down photoinduced electron transfer, and results in a greater than 200 mV shift in the conduction band edge, with respect to the electrolyte redox potential. The compilation of these four factors have differing effects and magnitudes in the solid-state and electrolyte DSCs but quantitatively account for the difference in device performances observed for both systems with and without the MgO shells. To the best of our knowledge, this is the most comprehensive account of the role of dielectric shells in dye-sensitized solar cells and will enable much better interfacial design of photoelectrodes for DSCs.



1. INTRODUCTION

The dye-sensitized solar cell (DSC)^{1,2} is a very attractive low-cost technology for photovoltaic devices. Their reasonably high efficiency and projected low cost of manufacture have garnered a considerable amount of attention over the last two decades.^{3,4} However, more progress needs to be made before they become a viable alternative to the established silicon photovoltaic devices. DSCs are composed of a transparent conductive oxide (TCO), typically fluorine-doped tin oxide, over which a mesoporous layer of a metal oxide is deposited. This mesostructure is then sensitized with a light absorbing dye, filled with a hole transporter, typically a redox active electrolyte, and finally capped with a regenerating top contact, typically platinum. Photovoltaic action arises from photoexcited electrons in the sensitizer, which are transferred to the conduction band (CB) of the metal oxide and then transported through the mesostructure to the TCO. Meanwhile, the hole on the dye is regenerated by the electrolyte which then diffuses through to the platinum counter-electrode.

One aspect that is particularly critical for efficient device operation is the interaction of charges at the interface between the metal oxide and the electrolyte/hole transporter, as well as with the dye. Recombination between holes in the hole-

transporter and electrons in the metal oxide, occurs across this interface. Minimizing this loss as well as correctly matching the energy levels of the photoexcited sensitizer to the CB of the metal oxide requires careful engineering of the interface to achieve maximum power conversion efficiencies. There are many ways through which to tune the nature of the interface, from coabsorption of small organic molecules with the dye to depositing conformal shells of metal oxides over the whole mesostructure.^{5–8}

Shells of metal oxides have a profound impact on the different solar cell performance parameters, as they affect diverse characteristics from inhibiting recombination, to enabling a higher degree of dye loading depending on the isoelectric point.^{8–10} Of particular interest is a thin MgO layer over SnO₂-based DSCs, as it enables the efficient operation of this type of devices under normal simulated sunlight conditions, where devices barely reach 1% power conversion efficiencies without treatment in some cases and can reach over 7% after the addition of the MgO layer.^{6,11,12} This choice of material as

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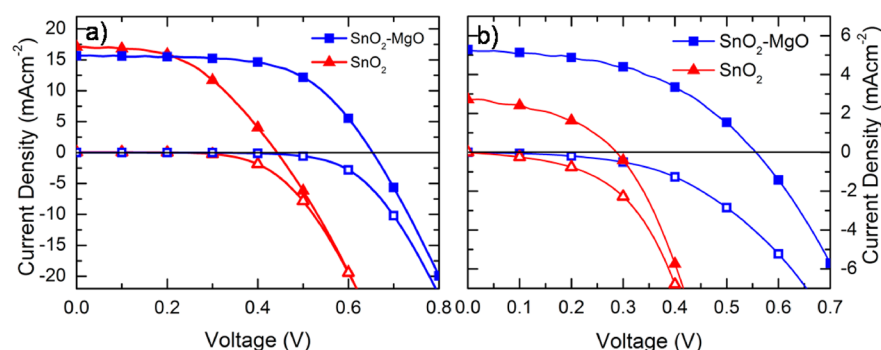


Figure 1. Current–voltage characteristics of devices incorporating a thin MgO layer (blue squares) and no surface treatment, labeled bare (red triangles): (a) liquid electrolyte based devices; (b) solid-state based devices.

the mesostructure does not deliver quite as high power conversion efficiencies as TiO_2 based devices, which can reach up to 11% power conversion efficiency with the iodide/triiodide redox couple,³ mainly due to its early stage of development. However, the use of TiO_2 as the mesostructured material limits the choice of dyes that can transfer charge efficiently to its CB, which in state-of-the-art devices typically means an optical band gap of about 1.48 eV. In SnO_2 , the CB is located about between 0.3 and 0.5 eV farther from vacuum than TiO_2 , which allows us to target narrower band gap sensitizers in combination with currently available electrolyte/hole-transport systems, which in turn opens up the possibility of aiming for higher achievable power conversion once all losses have been minimized.¹³ Beyond possible efficiency motivations, concerning stability, SnO_2 has a band gap of 3.8 eV and is a less effective photocatalyst than TiO_2 which should give less stringent demands for UV filtration.

For the conventional electrolyte system based on iodide/triiodide, there is a loss to power conversion efficiency not only due to charge recombination but also due to hole regeneration, because a large overpotential is required to activate the multistep process in the redox active electrolyte.¹⁴ A way to minimize this loss is to move away from the established electrolyte system and replace it with a solid-state hole transporter, typically Spiro-OMeTAD,^{13,15} where no intermediate products are necessary to regenerate the holes in the dye. Power conversion efficiencies with this system have been reported to be over 7%;¹⁶ however, equally importantly, when the TiO_2 in the mesostructure is substituted for SnO_2 and a conformal, thin shell of MgO is deposited, a near unity internal photon-to-electron conversion efficiency has been observed.¹⁷ Despite MgO having been extensively employed for SnO_2 based DSCs, there is still not a clear understanding of its complete function in the solar cells. In this work, we have studied the effects of the deposition of a shell of MgO over SnO_2 based DSCs on their electronic properties, using both a conventional low volatile iodide/triiodide “robust” liquid electrolyte and Spiro-OMeTAD as the hole transporter. Our study elucidates the precise role of the MgO interlayer in this system.

2. RESULTS AND DISCUSSION

For the remainder of the article, solar cells incorporating a thin MgO layer chemically deposited via a 20 mM ethanolic bath of Mg acetate for 1 min under boiling conditions over the SnO_2 mesostructure prior to dyeing will be referred to as “ SnO_2 –MgO” devices. Devices where the surface was not modified will

be referred to as “bare” or “ SnO_2 ”. In Figure 1 we show the current–voltage curves for both liquid electrolyte (a) and solid-state (b) DSCs. In all previous reports on SnO_2 based DSCs the introduction of a MgO interlayer results in a significant increase in the photocurrent generated by the solar cell. In our study, however, we have repeatedly observed the contrary and the bare SnO_2 devices already exhibit extremely high photocurrents, as shown in Figure 1a where the cell generates 17.1 mA cm^{-2} . For the SnO_2 –MgO liquid electrolyte based solar cells, we observe that the short-circuit current is reduced, as shown in the example of Figure 1 where the SnO_2 –MgO device generates 15.7 mA cm^{-2} under 100 mW cm^{-2} AM 1.5 simulated solar light. However, for the solid-state DSCs we observe the expected trend, where the current increase with the addition of MgO from 2.7 to 5.2 mA cm^{-2} . The results are summarized in Table 1. We note that these currents are lower

Table 1. Summary of the Photovoltaic Parameters Resulting from the *JV* Curves from the Representative Cells Shown in Figure 1^a

	electrolyte		solid state	
	SnO_2	SnO_2 –MgO	SnO_2	SnO_2 –MgO
J_{sc} (mA cm^{-2})	17.1	15.7	2.7	5.2
V_{oc} (V)	0.45	0.67	0.28	0.57
FF	0.47	0.61	0.42	0.48
Eff (%)	3.65	6.40	0.33	1.40

^aFor a typical batch of 6 solid-state DSCs, a standard deviation of 0.3 mA cm^{-2} was found for short circuit current, 0.03 V for open circuit voltage, 0.05% for power conversion efficiency and 0.03 for the fill factor.

than previously reported for SnO_2 -based solid-state DSCs, this is due to a different SnO_2 paste being used in this study. For comparison, the best TiO_2 -based dye-sensitized solar cells incorporating the indoline dye used here, termed D149, exhibit currents of about 20 mA cm^{-2} , and power conversion efficiencies exceeding 9%.¹⁸ In the case of solid-state dye-sensitized solar cells fabricated from TiO_2 photoanodes and the indoline dye used (D102), currents of over 7 mA cm^{-2} and power conversion efficiencies of over 4% have been presented.¹⁹

Both solid-state and electrolyte based cells show an overall significant increase in efficiency upon MgO treatment. However, the contrary shifts in short-circuit photocurrent indicate that multiple competing factors may be at play. In previous studies, increased photocurrent has been explained by the higher isoelectric point of MgO compared to SnO_2 , which

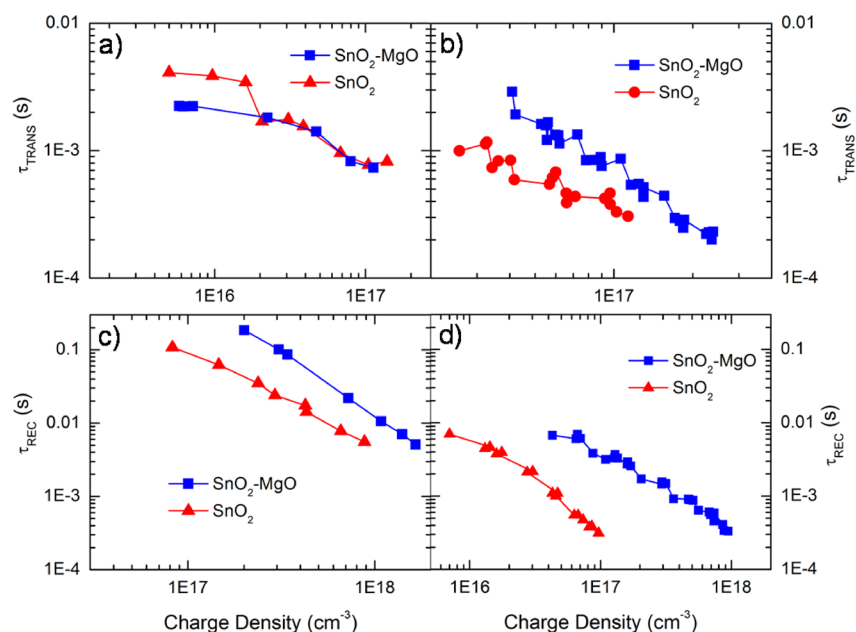


Figure 2. (a) and (b) are the transport lifetimes (τ_{TRANS}) extracted at short-circuit conditions, and (c) and (d) are the recombination lifetimes (τ_{REC}) extracted at open-circuit conditions, plotted against charge density for devices incorporating a thin MgO layer ($\text{SnO}_2\text{-MgO}$, blue squares) and devices with no surface treatment (SnO_2 , red triangles). (a) and (c) correspond to devices fabricated with a liquid electrolyte, and (b) and (d) correspond to devices fabricated with a solid-state hole transporter. Error bars are not shown for clarity as they are the same size as the plot points shown. To estimate the uncertainty in the measurement, a batch of three cells fabricated with the same materials were measured, and then the standard deviation from the resulting lifetime values was extracted.

would allow a higher dye loading.^{6,10} We do indeed observe higher dye loading; however, absorption spectra for films with and without the MgO surface treatment indicate that the magnitude of the increase in light absorption, which is only a 9% difference over the solar spectrum, does not account for the difference in short-circuit current (see Supporting Information).

In addition to the changes in photocurrent, for both liquid and solid-state cells an increase in open-circuit voltage of $\sim 200\text{--}300$ mV for $\text{SnO}_2\text{-MgO}$ devices is observed, as compared to the bare devices. Solid-state devices fabricated from TiO_2 nanoparticles incorporating this surface treatment show a trend similar to the one observed for electrolyte devices, although in this case, the gain in voltage does not offset the loss in current and hence no gains in performance were observed (see Supporting Information). In the past, the change in voltage has been attributed either to a CB shift, due to a possible surface dipole formation after the addition of this layer, or to reduced recombination at the SnO_2 /hole transporter interface.^{6,9,11,12,20–24} It is also possible that during the chemical bath deposition of the insulating metal oxide precursor, a Sn-Mg-O composite may be formed, which would also result in a CB shift; this has been demonstrated to occur with a ZnO and MgO alloy.²⁵

To further elucidate the role of this layer in our devices, we have performed small perturbation transient photocurrent and photovoltage measurements to extract information about the transport and recombination. In Figure 2 we show the transport and recombination characteristics of the DSCs incorporating the MgO coating and bare devices, plotted against charge density. All measurements are taken under a background illumination from white light diodes with a range of light intensities ranging from an equivalent 100 mW cm^{-2} solar illumination to 2.5 mW cm^{-2} . See the Experimental Section for

a description of the technique. The transport lifetimes at short-circuit conditions for the devices with and without the MgO coating are overlapping at most points studied in the electrolyte cells, as shown in Figure 2a). For the solid-state cells, although slightly different, the transport lifetimes are close at high illumination conditions, indicating that the MgO treatment has little influence on the transport limiting trap sites. We note that the charge collection rate in the solid-state cells is a few times faster than the electrolyte cells, presumably due to the thinner films employed (2 versus $8\text{ }\mu\text{m}$).

Concerning the electron recombination lifetimes, there appears to be an upward shift to longer times in the curves of recombination lifetime versus charge density; i.e., the MgO treated cells have slower recombination under the same charge density conditions. For liquid electrolyte devices, the change is small at just about twice the recombination lifetime at the same charge density, whereas the trend for the solid-state cells is much more pronounced, where a change of almost an order of magnitude is observed. The difference between liquid electrolyte and solid-state devices may be related to the different recombination mechanisms; i.e., recombination in electrolyte devices is a two-electron process where an intermediate complex must be formed.²⁶ The fact that reduced recombination is observed suggests that the MgO layer is passivating the surface states, or presenting a physical barrier inhibiting recombination.²⁷ We are more inclined to believe that the MgO is passivating recombination sites, because this method for deposition only results in what appears to be a monolayer coating of MgO upon the SnO_2 surface.¹⁷ This is also consistent with a study by Prasittichai et al. on Al_2O_3 coated SnO_2 via ALD, where recombination is mainly retarded by the first layer deposited.⁸ Although the reduction in the recombination lifetime is significant (2-fold for electrolyte and 10-fold for solid-state DSCs), it is not enough to explain

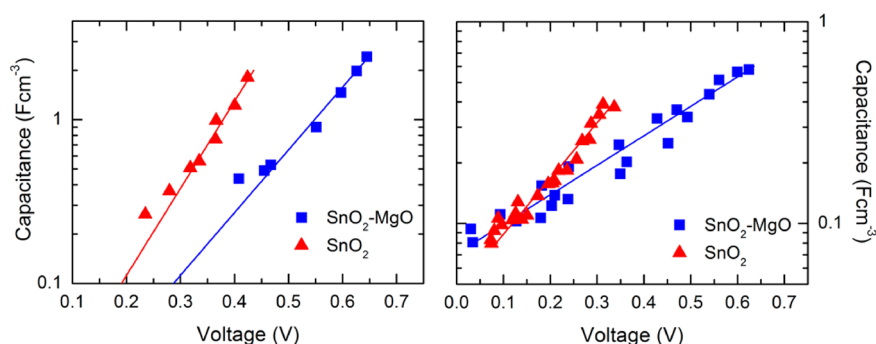


Figure 3. Voltage against capacitance plot of devices incorporating a thin MgO layer (SnO_2 -MgO, blue squares) and devices without a surface treatment (SnO_2 , red triangles). (a) corresponds to liquid electrolyte based devices, and (b) to corresponds devices fabricated with a solid-state hole transporter. Solid lines correspond to exponential fits of the experimental data that were used to calculate the charge density of Figure 2a,b.

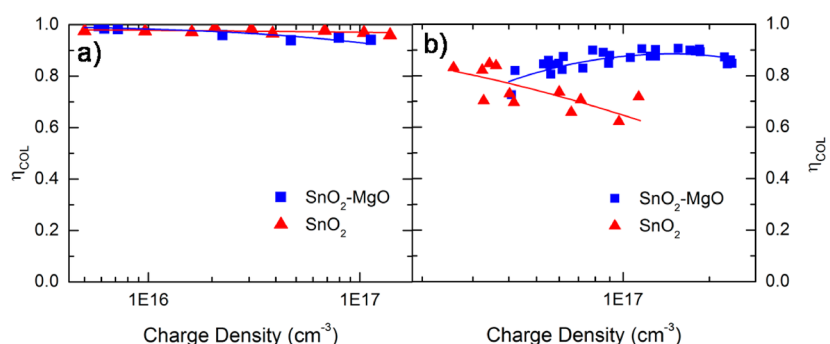


Figure 4. Charge collection efficiencies (η_{COL}) against charge density for electrolyte cells (a) and solid-state solar cells (b), for devices incorporating a thin MgO layer (SnO_2 -MgO, blue squares) and devices without a surface treatment (SnO_2 , red triangles). The lines are the result of interpolating the experimental data.

the 200–300 mV shift of the open-circuit potential. We would require over a 100-fold increase in the recombination lifetime to induce such a shift in open-circuit voltage.²⁸ If the total increase in open-circuit voltage cannot be accounted for by inhibited recombination, then it is possible that the addition of the MgO interlayer results in a shift in the surface potential of the oxide. Indeed, such a shift has been postulated before for both SnO_2 and ZnO coated with MgO or Al_2O_3 .^{8,25} To probe this, we have again used the transient photovoltage and charge collection measurements to extract a differential capacitance as a function of open-circuit voltage. This capacitance–voltage data is presented in Figure 3 and is representative of the location and shape of the tail of the density of sub-band gap states in the metal oxide with respect to the electrolyte/hole-transporter redox potential. The substrate capacitance was found to be several orders of magnitude smaller than that of the mesoporous metal oxide (see Supporting Information) and was therefore disregarded. For the electrolyte and solid-state cells there is a clear positive shift in the position of the “density-of-states” (DOS) of around 200 mV at high capacitances. The small change in slope in the capacitance–voltage data presented indicates that in addition to a shift in the surface potential, there is also a passivation of surface states, consistent with other reports in literature.²⁴ We note that as only the tail of the conduction band states can be measured with our setup, the actual conduction band edge shift could be larger than the one measured, and hence only a lower bound can be determined in this study. For the solid-state devices presented, the change in slope after the addition of the insulating interlayer is much more pronounced. This may be the result of passivation of the deepest surface traps by the MgO interlayer, which are more

visible due to the lower charge density in the film for these type of devices. This result may explain why the recombination lifetimes are increased by an order of magnitude for the solid-state devices, whereas only a factor of 2 is observed for the electrolyte devices. The combination of the surface potential shift and recombination inhibition quantitatively account for the relative shift in open-circuit voltage observed in the *JV* curves of the solar cells presented in Figure 1.

To check whether the shift in short-circuit current for solid-state devices is due to poor charge collection efficiency, we have estimated the recombination lifetime at short-circuit as a function of light intensity (in galvanostatic mode, or constant current transient photovoltage decay). In combination with the results from Figure 2a,b, we have calculated the charge collection efficiency for both electrolyte and solid-state devices, as shown in Figure 4. With the MgO interlayer, the solid-state cells exhibit a charge collection efficiency of over 85%; however, this drops to as low as 60% for the bare devices at full solar light intensity conditions. Coupled with a slight reduction in dye loading, this quantitatively accounts for the reduction in short circuit current for the bare solid-state cells. In the case of liquid-electrolyte based devices, Figure 4a), the charge collection efficiencies for both devices incorporating the MgO interlayer and bare mesostructures are remarkably similar, at over 95% for the whole range studied. This is in contradiction to most literature on this subject where usually bare devices incur extreme recombination losses that lead to poor charge collection efficiencies, completely limiting the device performance to under 1% power conversion efficiencies.^{6,12,21} For the liquid electrolyte devices fabricated in this study, the main role of the thin MgO layer is that of a surface potential shift toward

a vacuum. The fact that recombination characteristics only vary by a factor of 2 for both treated and untreated cells is particularly important to the viability of using SnO_2 as the mesoporous metal oxide for low band gap dyes. Comparing the overall recombination rate for the electrolyte based cells to the solid-state cells, as shown in Figure 2, is helpful to understand why a much stronger inhibition to recombination is observed for the solid-state cells upon MgO treatment. For the bare devices under a similar charge density of 10^{17} cm^{-3} , the recombination for the electrolyte cells is 300-fold slower than the solid-state cells, and for the SnO_2 –MgO devices under a charge density of 10^{18} cm^{-3} the electrolyte cells are 30-fold slower. The characteristic slow recombination in the iodide/triiodide system is due to specific nature of the multistep charge generation and recombination mechanism.^{26,29} This exceptionally slow reaction appears to be the rate determining process, rather than changes to the metal oxide surface.

Almost all the results can be explained by the influence of the MgO treatment upon recombination and surface potential. However, the apparent anomaly of higher photocurrent observed in the bare electrolyte cells still requires explanation. We note that we have observed this trend every time, with a number of different SnO_2 pastes over tens of experiments. To probe possible changes to charge generation, we have employed time-resolved terahertz-pump optical-probe photoconductivity spectroscopy. The samples we have studied are dye-sensitized mesoporous SnO_2 in vacuum where Z907 is used as the sensitizer. We note there is no electrolyte or hole-transporter present to purely probe the electron transfer phenomena. We have used Z907 as the sensitizer here because D102 gave very little signal in the terahertz set up, possibly due to the requirement for the presence of a polar medium to operate effectively.³⁰ As the terahertz radiation passes through the sample, it accelerates mobile charge carriers and is hence attenuated. The magnitude of the change in transmission of the terahertz pulse following photoexcitation of the system is proportional to the photoinduced change in conductivity ($\Delta\sigma$) and hence representative of the number of free carriers injected into the SnO_2 conduction band ($\Delta\sigma = e\Delta n\mu$) where e is the charge of an electron, Δn is photoinjected electron density, and μ is its mobility). In Figure 5 we show the normalized transient photoconductivity signal. Complete charge injection in SnO_2

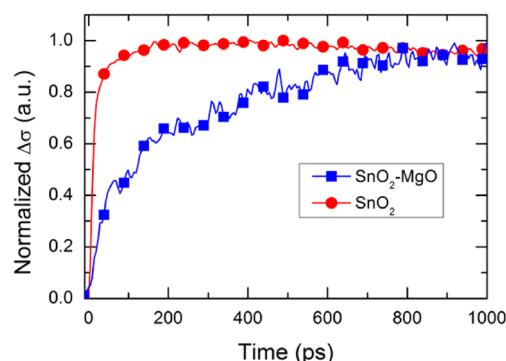


Figure 5. Photoconductivity dynamics measured in mesoporous SnO_2 sensitized with Z907 dye, without (red line, circles) and with (blue line, squares) MgO treatment, using optical-pump terahertz-probe (OPTP) spectroscopy. Photoexcitation was carried out with 550 nm wavelength 90 fs pulses with 7×10^{14} photons/ cm^2 fluence. The curves have been normalized at their respective maxima, for trend comparison.

sensitized with Z907 takes place within the first few hundred picoseconds, slightly slower than TiO_2 though still fast.³¹ However, in the case of MgO treated SnO_2 , charge injection is significantly slower and still not complete within the nanosecond measurement window. As will be discussed elsewhere,³² there is a light-soaking effect in sensitized SnO_2 films, both with and without MgO treatment, where injection and photocurrent improve during illumination. Data in Figure 5 is shown for the final steady-state value in both cases. The absolute photoconductivity values cannot be directly compared with each other, due to sample-to-sample variation; however, the general trend observed is that higher photoconductivity values at 1 ns are observed for bare devices.

The time-resolved photo conductivity measurements are consistent with faster and more efficient electron transfer in the bare dye-sensitized systems. The slower injection in the dye-sensitized SnO_2 –MgO films is consistent with poorer electron transfer and at this rate of hundreds of picoseconds to nanoseconds, we would expect the injection to not compete entirely favorably with nonradiative decay channels. Hence this spectroscopy is entirely consistent with the slightly higher short-circuit photocurrent for the bare SnO_2 liquid electrolyte cells.

3. CONCLUSIONS

The role of a thin MgO layer, chemically deposited over mesoporous SnO_2 structures in liquid electrolyte and solid-state dye-sensitized solar cells has been investigated. The treatment has four significant influences upon the optical and electronic characteristics of the solar cells, and these effects have differing levels of importance for either solid-state or liquid electrolyte based solar cells:

1. There is at least a 200 mV **positive shift in the conduction band edge**, which is the predominant factor increasing the open-circuit voltage in both cells.
2. There is an **increase in the electron lifetime** by approximately 2-fold for electrolyte and 10-fold for solid-state cells. This has only a small influence on the electrolyte cells, though it significantly contributes to further increased open-circuit voltage and increased photocurrent (charge collection efficiency) for the solid-state cells.
3. There is a **reduction in the electron injection rate and efficiency**, which results in a marginal drop in photocurrent for the electrolyte cells upon MgO treatment. Notably for the solid-state cells, the possibility of reductive quenching of the excited dye (where hole transfer can occur prior to electron transfer) may negate this aspect.
4. There is a **marginal increase in the dye loading** upon MgO treatment, which will contribute slightly to increasing the photocurrent in the solid-state cells but will have negligible influence upon the thicker electrolyte cells.

These clear findings ascertain the viability of using SnO_2 electrodes for DSCs and indicate that careful choice and control of the surface coating could result in competitive electrodes for DSCs and open new possibilities for low band gap dyes and stability.

4. EXPERIMENTAL SECTION

Substrate Preparation. Fluorine-doped tin oxide (FTO) coated glass sheets (15 $\Omega/\square$ Pilkington) were etched with zinc powder and HCl (2 Molar) to obtain the required electrode pattern. The sheets were then washed with soap (2% Hellmanex in water), deionized water, acetone, and methanol and finally treated under an oxygen plasma for 10 min to remove the last traces of organic residues. The FTO sheets were subsequently coated with a compact layer of SnO₂ (100 nm) by aerosol spray pyrolysis deposition of butyltin trichloride 95% (Sigma-Aldrich) mixed with ethanol in a 1:10 precursor:ethanol ratio at 450 °C using air as the carrier gas. During the deposition of the compact layer, the electrodes were masked so that the SnO₂ only covered the FTO and not the etched glass (otherwise short-circuiting would occur).

A homemade SnO₂ mesoporous paste prepared in the same way as Ito et al.³³ from <100 nm particle size nanopowder (549657 Sigma-Aldrich) was then doctor bladed by hand using scotch tape and a pipet on the SnO₂ compact layer coated FTO sheets for the solid-state DSCs to achieve a final thickness of 1.5 μm . For liquid electrolyte DSCs, the paste was screen-printed, in the shape of a square with a 5 mm side, several times to achieve a thickness of $\sim 8 \mu\text{m}$. The sheets were then slowly heated to 500 °C (ramped over 1 1/2 h) and baked at this temperature for 30 min in air. After cooling, slides were cut down to size and soaked in 20 mM Mg acetate in ethanol bath for 1 min on a hot plate set at 100 °C (boiling the ethanol in the bath). After rinsing with ethanol and drying in air, the electrodes to be used in solid-state DSCs were coated with a paste of Al₂O₃ nanoparticles (see below for details of paste) to give a buffer layer with a dry film thickness of 100 nm, whereas the electrodes to be used in liquid electrolyte DSCs were not coated with this Al₂O₃ layer. The substrates were subsequently baked once more at 500 °C for 45 min in air, then cooled down to 70 °C and finally immersed in a dye solution for 1 h.

Solid-State Solar Cell Assembly. The indolene dyes used were D102,³⁴ and D149 0.2 mM in a 1:1 volume ratio of *tert*-butanol and acetonitrile. 2,2',7,7'-Tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) was dissolved in chlorobenzene at 15 vol% concentration and after fully dissolving the hole transporter, 4-*tert*-butylpyridine (tBP) was added with a volume to mass ratio of 1:26 $\mu\text{L mg}^{-1}$ tBP:spiro-OMeTAD. Lithium bis(trifluoromethylsulfonyl)imide salt (Li-TFSI) was predissolved in acetonitrile at 170 mg mL⁻¹ and added to the hole transporter solution at 1:12 $\mu\text{L mg}^{-1}$ of Li-TFSI solution: Spiro-OMeTAD. The dyed films were rinsed briefly in acetonitrile and dried in air for 1 min. Immediately after drying, a small quantity of the hole transporter solution (22 μL) was dispensed onto each substrate and left to wet the films for 20 s before spin-coating at 700 rpm for 40 s in air. After spin-coating the hole transporter, the films were left overnight in an air atmosphere in the dark before placing them in a thermal evaporator where 150 nm thick silver electrodes were deposited through a shadow mask under high vacuum (10⁻⁶ mbar). To measure the photovoltaic properties correctly, the active areas of the devices were defined by metal optical masks with 0.09–0.125 cm² apertures that were glued onto the illuminated side. The typical photoelectrode area as defined by the overlap between the silver electrode and the FTO was around 0.15 cm².

Liquid Electrolyte Solar Cell Assembly. The indolene dye used was D149,³⁴ 0.2 mM in a 1:1 volume ratio of *tert*-

butanol and acetonitrile. The robust Z646 electrolyte used was composed of a mixture of 1.0 M PMII, 30 mM I₂, 0.5 M 1-butyl-1*H*-benzimidazole (NBB), and 0.1 M GuNCS in 3-methoxypropionitrile (MPN). After being washed by acetonitrile and dried under air flow, the sensitized electrodes were assembled with the counter electrode by melting a 25 μm thick Surlyn gasket. To prepare the platinum coated counter electrode, first a hole was sandblasted into an FTO slide. A drop of 5 mM (H₂PtCl₆) ethanolic solution was then spread over the FTO and then it was heated to 400 °C for 15 min under air. The internal space between the working and the counter electrodes was filled with Z646 electrolyte using a vacuum backfilling system. The hole was finally clogged with a melted Surlyn sheet and a thin cover slide.

Solar Cell Characterization. Solar simulated AM 1.5 sunlight was generated with an ABET solar simulator calibrated to give 100 mW cm⁻² using an NREL calibrated KG5 filtered silicon reference cell. The *JV* curves were recorded with a Keithley 2400. The solar cells were masked with a metal aperture defining the active area of the solar cells, which were approximately 0.12 cm². The photovoltage decay measurement was performed by a method similar to that by O'Regan et al.³⁵ and as described elsewhere.^{36–39} In essence, a steady-state background white illumination from an array of diodes (Lumiled Model LXHL-NWE8 whitestar) is first applied to the cell, filling up a fraction of the available sub-bandgap states that will be proportional to the intensity applied. Then, a short pulse was generated from red light diodes (LXHLND98 redstar, 200 μs square pulse width, 100 ns rise and fall time), which is irradiated on the cell and its response is recorded with an oscilloscope. The perturbation light source was set to a suitably low level such that the decay kinetics were monoexponential. This enabled the charge recombination rate constants to be obtained directly from the exponential decays measured with a 1 GHz Agilent oscilloscope. When the measurement is performed at fixed potential conditions, i.e., potentiostatic mode, the oscilloscope is set with the 50 Ω port and the generated charge (ΔQ) by the pulse can be directly extracted by integrating the photocurrent decay curve. When the measurements are performed at fixed current conditions, i.e., galvanostatic mode, the oscilloscope is set with the 1 M Ω port and the current generated through the small perturbation pulse is not allowed to exit the device and hence the response measured with oscilloscope is purely dependent on the recombination kinetics of the system, and the perturbation voltage (ΔV) can be extracted. By doing these two measurements at either open or short circuit, we can directly measure the differential capacitance as a function of voltage for the system as $C(V) = \Delta Q / \Delta V$.

To extract the transport lifetimes as a function of charge density, the monoexponential decay dynamics of the cells were measured in potentiostatic mode with different applied background light intensities with a suitably low perturbation pulse. The charge density was then extracted as explained below. The diffusion coefficient (D_e) can be calculated as $D_e = t^2 / 2.35 \tau_{\text{trans}}$, where t is the thickness of the film,⁴⁰ and τ_{trans} is the transport lifetime at short circuit conditions.

To extract the charge density of the films at short circuit conditions, the transport lifetime (τ) against short circuit current (J) was fit as $\tau(J) = A J^B$.⁴¹ After the relationship between short circuit current and transport lifetime was established, the current density ($J = J_0 e^{-t/\tau(J)}$) was calculated iteratively as

$$\begin{aligned}\Delta J_n &= J_n(t) - J_n(t+\Delta t) \\ &= J_0(e^{-t/\tau(J)} - e^{-(t+\Delta t)/\tau(J)}) \\ &= J_n(1 - e^{-\Delta t/AJ_n^B})\end{aligned}$$

$$J_n = J_{n-1} - \Delta J_{n-1}$$

The resulting values for the short circuit current were then integrated to find the charge density.

■ ASSOCIATED CONTENT

■ Supporting Information

Current–voltage characteristics of solid-state TiO₂ devices. Absorption spectra. Plots of recombination lifetimes vs charge density. Voltage against capacitance plot. This information is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

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