Subnanometer Ga$_2$O$_3$ Tunnelling Layer by Atomic Layer Deposition to Achieve 1.1 V Open-Circuit Potential in Dye-Sensitized Solar Cells

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Supporting Information

ABSTRACT: Herein, we present the first use of a gallium oxide tunnelling layer to significantly reduce electron recombination in dye-sensitized solar cells (DSC). The subnanometer coating is achieved using atomic layer deposition (ALD) and leading to a new DSC record open-circuit potential of 1.1 V with state-of-the-art organic D-π-A sensitizer and cobalt redox mediator. After ALD of only a few angstroms of Ga$_2$O$_3$, the electron back reaction is reduced by more than an order of magnitude, while charge collection efficiency and fill factor are increased by 30% and 15%, respectively. The photogenerated exciton separation processes of electron injection into the TiO$_2$ conduction band and the hole injection into the electrolyte are characterized in detail.

KEYWORDS: Atomic layer deposition, dye-sensitized solar cell, gallium oxide, tunnelling layer, electron recombination

Dye-sensitized solar cells (DSC) have attracted considerable attention from the energy market and researchers alike thanks to the flexibility it offers in terms of material selection, low cost, and chemical stability.\cite{1-7} The electrochemical system is sandwiched between two transparent conductive oxide (TCO) glass substrates and comprises a printed dye-sensitized mesoporous titania (TiO$_2$) film infiltrated with a redox electrolyte and a platinum-coated counter electrode. Solar photons with an energy equal to or greater than the HOMO–LUMO gap of the dye are absorbed generating electron–hole (e$^−$–h$^+$) pairs. These excitons are separated at the titania–sensitizer–electrolyte interfaces where the electrons are injected into the TiO$_2$ conduction band and the holes into the electrolyte.\cite{15} While the cell’s short-circuit photocurrent density ($J_{sc}$) is mainly determined by the light harvesting ability of the dye over the visible light spectrum, the open-circuit potential ($V_{OC}$) of the device is determined by the difference between two energetic positions: the quasi-Fermi level ($\mu$E$_F$) of electrons in the TiO$_2$ and the redox potential of the electrolyte medium. At open-circuit, the rate of e$^−$–h$^+$ injection into the TiO$_2$ is equal to the rate of recombination with the oxidized form of the redox couple, while the steady-state electron density ($n_e$) in the TiO$_2$ film determines the position of $\mu$E$_F$. For a given redox potential, slower recombination kinetics shifts the $E_F$ toward the conduction band of TiO$_2$ leading to an increase in $V_{OC}$.\cite{8,9}

Recently, research efforts have shifted from the development of panchromatic Ru(II) polypyrpyl dyes sensitizers regenerated using the standard iodide/triiodide (I$^-$/I$_3^-$) electrolyte to organic or phorphyrin dyes with finely tuned electron donor, π-bridge, and acceptor groups coupled with alternative single electron redox shuttles, like disulfide/thioleate, ferrocene, or cobalt complexes to achieve new record power conversion efficiencies (PCE) of 12.3% at 1 sun and 13.1% at 0.5 sun.\cite{10-15} Cobalt complex-based redox mediators offer tunable redox potentials and require less dye regeneration overpotentials to significantly enhance the $V_{OC}$.\cite{16} In spite of these advantages, Co($II$/III) complexes suffer from faster recombination dynamics of photogenerated electrons with the oxidized species in the electrolyte than that of the two electron iodide/triiodide limiting potential gains in $V_{OC}$ and overall PCE.\cite{12,16-18}

Thin metal oxides films have been shown in the past to efficiently passivate surface states and block the back reaction. However, conventional solution-based passivation techniques often lead to the formation of inhomogeneous films thicker than $\approx 1$ nm which significantly hampers electron injection into the TiO$_2$ conduction band.\cite{19-22} The recent development of atomic layer deposition (ALD) for the growth of ultrathin conformal films on high aspect ratio nanostructures, down to atomic layer thickness, has compelled DSC researchers to revisit this strategy.\cite{23-27} ALD is a self-limited growth process determined by the density of reactive sites on host’s surface. To summarize, the organometallic precursor and oxidizing agent are pulsed subsequently into a vacuum chamber using an inert gas as carrier to effectively avoid gas-phase reaction in the reactor, preventing the formation of thick oxide layers.\cite{28,29} However, previous reports on TiO$_2$ passivation by ALD of...
ZrO$_2$, HfO$_2$, and Al$_2$O$_3$ in $\Gamma$/I$_1$-based DSC showed a significant decrease in $J_{SC}$ without the significant $V_{OC}$ improvement associated with an effective blocking of the recombination pathway leading to a decrease in the overall power conversion efficiency (PCE). With that said, Snaith et al. and Li et al. have shown that MgO and ZrO$_2$ overlayers, respectively, could slightly improve all the photovoltaic parameters in low-efficiency solid-state DSC using an organic hole transport material. In addition, Tetreault et al. have been able to improve all photovoltaic parameters using TiO$_2$-passivation of Al-doped ZnO and SnO$_2$ in a $\Gamma$/I$_1$-based DSC, owing to a small reduction in recombination and a shift in the conduction band. However, to achieve true tunnelling behavior, there should be no available density of states between the dye excited state ($S^*$) and conduction band (CB) of the electron accepting material. Theoretically, the tunneling process can only occur through a barrier material, that possesses a larger bandgap, due to the strong electric field between the $S^*$ and CB. Considering the compromises and limitations described in the literature, we present herein a novel strategy using a highly insulating subnanometer gallium oxide (Ga$_2$O$_3$$_{-2.95}$ eV vs vacuum) ALD overlayer as tunnelling barrier to effectively balance injection and recombination in DSCs. The insulating Ga$_2$O$_3$ was also selected due its ability to form conformal layer on the mesoporous TiO$_2$, unlike Al$_2$O$_3$ where the deposition progresses following an island growth mode. In conjunction with a state-of-the-art organic D-$\pi$-A dye (Y123) and a novel single electron Co(bipyridine-pyrazole) redox mediator, we present a new record open-circuit potential of 1.1 V coupled to an increase in $V_{OC}$ and fill factor (ff) in the device. Through a complete characterization of the electron-transfer processes, we show that this is primarily due to an order of magnitude reduction in the recombination kinetics and an increase in electron collection efficiency.

Experimental details for the photoanode preparation, ALD, photovoltaic and material characterization as well as the electrochemical impedance spectroscopy (EIS) and photo-induced absorption (PIA) conditions are presented in the experimental section of the Supporting Information.

Different numbers of ALD cycles of Ga$_2$O$_3$ were deposited into a 2.7 ± 0.1 μm thick mesoporous TiO$_2$ film in a highly conformal manner using sequential exposures to tris(dimethyl) amido gallium and H$_2$O. A relatively thin TiO$_2$ film thickness was chosen to ensure uniform Ga$_2$O$_3$ deposition throughout the film and was limited by the diffusion length of the metal organic precursor in the mesopores. The reference (0 cycle) and the Ga$_2$O$_3$-passivated TiO$_2$ samples were characterized using X-ray photoelectron spectroscopy. Both the reference and passivated films show two binding energy peaks at 459.45 ± 0.15 and 465.05 ± 0.1 eV, corresponding to the Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ transitions (Figure 1 inset), respectively, indicating that the Ti$^{4+}$ oxidation state is preserved after passivation. In addition, a peak at 1118.65 ± 0.1 eV is observed for the surface treated films that is assigned to the Ga 2p$_{3/2}$ transition confirming the presence of the Ga$^{3+}$ valence state expected for Ga$_2$O$_3$ (Figure 1). It can be noted that the Ga 2p$_{3/2}$ binding energy peak intensity increases with the number of ALD cycles and, hence, the increase of Ga content on the surface. The growth rate of Ga$_2$O$_3$ by ALD was estimated to be ~1 Å per cycle by spectroscopic ellipsometry on Si wafer covered using the same ALD conditions. However, the growth rate for the first few cycles will be dependent on the surface chemistry of the host material, and thus, we should expect some deviation of the growth rate of Ga$_2$O$_3$ on the Si native oxide and that on TiO$_2$.

To test the performance of the tunnelling overlayer in DSCs, mesoporous TiO$_2$ photoanodes printed on a fluorine-doped tin oxide (FTO) glass substrate were covered by ALD of Ga$_2$O$_3$, covering both the TiO$_2$ host and the exposed FTO surface. Then, the photoanodes were sensitized with Y123 (Figure 2A) and infiltrated with the Co(bipyridine-pyrazole)$^{2+/3+}$PF$_6$ redox mediator (Figure 2B). This dye and electrolyte combination was chosen specifically for the high molar extinction coefficient of the D-$\pi$-A Y123 sensitizer (48 000 M$^{-1}$ cm$^{-1}$) and the standard redox potential of the Co(bipyridine-pyrazole)$^{2+/3+}$ (0.86 V vs NHE), enabling efficient light harvesting and high open-circuit potential, respectively. Figure 3 shows the $J$–$V$ performance of these cells as measured in the dark and at full sun (AM 1.5G). The onset of the dark current for the reference cell (black dashed curve) is observed at about 400 mV and is increased by about 500 mV, to 900 mV, upon deposition of 4 Ga$_2$O$_3$ ALD cycles (blue dashed line) to significantly block dark current generation. Under full illumination, the $J$–$V$ characteristics of the reference cell were found to be $V_{OC}$ = 692 mV, $J_{SC}$ = 3.6 mA/cm$^2$, and ff = 56.0%, leading to a modest PCE of 1.4% (black solid line). A substantial increase in $V_{OC}$ to 1000 mV is obtained after 1 Ga$_2$O$_3$ ALD cycle (red solid line) before reaching the record-breaking photovoltage of 1100 mV after 4 ALD cycles (blue solid line). In addition, we found that both the photocurrent and the ff increased to $J_{SC}$ = 5.1 mA/cm$^2$ and ff = 70.8% to increase the cell efficiency to reach PCE = 4.0%. Further Ga$_2$O$_3$ deposition only slightly raised the $V_{OC}$ to 1118 mV at a great expense for the $J_{SC}$ that is significantly decreased to 2.8 mA/cm$^2$ after 6 ALD cycles (dark-yellow solid line). The full $J$–$V$ characteristics and efficiencies are presented in Table 1. Finally, in order to better deconvolute the effects of photovoltage loss at the FTO-electrolyte and TiO$_2$-electrolyte interfaces, a 5 nm thick TiO$_2$ blocking underlayer was deposited on the FTO-glass to avoid contact with the electrolyte. The complete photovoltaic properties of the cells were investigated after a different number of cycles of Ga$_2$O$_3$ deposition covering both the mesoporous film and the underlayer. The $J$–$V$ curves are presented in Figure S1, Supporting Information, and
the corresponding photovoltaic data are presented in Table S1, Supporting Information. Although the $V_{OC}$ (1022 mV) of the cell with underlayer and without Ga$_2$O$_3$ was found to be higher than the reference cell. The blocking behavior of the TiO$_2$ was found to have a lesser effect than the tunnelling behavior obtained with Ga$_2$O$_3$. The increase in the $V_{OC}$ to 1070−1100 mV is observed with the simultaneous enhancement of the $J_{SC}$ and the $ff$ up to 3−4 cycles of Ga$_2$O$_3$. This shows that the back reaction is predominant at the FTO−electrolyte interface with a significant fraction observed at the TiO$_2$−electrolyte interface. However, the presence of tunneling Ga$_2$O$_3$ layer is found to suppress the back reaction at both the interfaces. The increase in the $J_{SC}$ in the latter case is supported by the incident photon-to-electron conversion efficiency (IPCE) shown in Figure S2, Supporting Information.

This dramatic increase of the open-circuit potential (Table 1) could be explained by a reduction of the trap-state density of the TiO$_2$ or reduction of the recombination rate between electrons in the TiO$_2$ and the oxidized form of the redox couple. However, no significant modification of the density of trap states upon Ga$_2$O$_3$ ALD could be measured using transient photocurrent measurements. But, the ability of the Ga$_2$O$_3$ overlayer to significantly decrease the recombination kinetics was revealed by transient photovoltage decay measurements. Figure 4A shows the recombination rate measured at different open-circuit potential obtained by varying the light bias on the cells. At the operating voltage, one Ga$_2$O$_3$ ALD cycle (red dots) is found to decrease the recombination rate by

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Figure 2. (A) Molecular structure of the organic D-π-A sensitizer coded as Y123. (B) Molecular structure of Co(bipyridine-pyrazole)$_{2/3+}$ PF$_6$− redox mediator used in the present DSCs.

Figure 3. Photocurrent−voltage ($J$−$V$) characteristics for DSC photoanodes subjected to different number of Ga$_2$O$_3$ ALD cycles as well as for the bare reference (black). Solid and dashed lines correspond to measurements under simulated AM1.5G solar irradiance (100 mW cm$^{-2}$) and in the dark, respectively.

Table 1. Photovoltaic Characteristics ($J_{SC}$, $V_{OC}$, $ff$, and PCE) for Photoanodes with Different Numbers of Ga$_2$O$_3$ ALD Cycles$^a$

<table>
<thead>
<tr>
<th>no. of Ga$_2$O$_3$ ALD cycles</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (mV)</th>
<th>$ff$ (%)</th>
<th>PCE (%)</th>
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<td>692</td>
<td>56.0</td>
<td>1.4</td>
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<td>1</td>
<td>4.9</td>
<td>995</td>
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<tr>
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<td>2.9</td>
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<td>2.3</td>
</tr>
</tbody>
</table>

$^a$Reference = 0 cycle. Experimental errors are within ±10 mV for $V_{OC}$, ±0.2 mA/cm$^2$ for $J_{SC}$, and ±0.5% for $ff$.  

Figure 4. (A) Transient photovoltage decay measurements showing the recombination rate of photogenerated electrons as a function of open-circuit potentials for DSCs with different numbers of Ga$_2$O$_3$ ALD cycles as well as for the reference. (B) Nyquist plot showing the evolution of the high-frequency semicircle corresponding to the interfacial charge-transfer resistance ($R_{CT}$) for mesoporous TiO$_2$ photoanodes with no Ga$_2$O$_3$ tunnelling overlayer and after different numbers of Ga$_2$O$_3$ ALD cycles. The measurements were carried out at 0.55 V forward bias in the dark with a cell configuration analogous to the DSC but without a sensitizer.
about 1 order of magnitude compared to the reference cell
(black squares). Further increase in the overlayer thickness
decreases the rate of electron transfer to the Co3+ by another
order of magnitude up to the sixth ALD cycle. Hence, the 2
orders of magnitude improvement in the lifetime (recombina-
tion rate−1) of the photogenerated electrons at open circuit
increases the steady-state electron density in the TiO2, shifting
the quasi-Fermi level toward vacuum and leading to a dramatic
increase of the VOC from 692 to 1120 mV.

This was confirmed by EIS to further analyze the
recombination kinetics of the reference and Ga2O3-passivated
photoanodes at the oxide–electrolyte interface.45 Figure 4B
compares the Nyquist plot of the two photoanodes measured at
0.550 V forward bias in the dark. All spectra exhibit a high-
frequency semicircle that corresponds to the interfacial charge-
transfer resistance (RCT) and a low-frequency semicircle
attributed to the diffusion resistance of Co3+ toward the
counter electrode. The high-frequency semicircle was fitted to a
Randles equivalent circuit shown in Figure S3, Supporting
Information to extract RCT.46 The RCT for the reference cell
was calculated to be 32.3 Ω and found to steadily increase with each
Ga2O3 ALD cycle to reach RCT = 230.7 Ω. This trend of
increasing RCT correlates well with the transient photovoltage
decay measurements where the recombination rate was found to
decline significantly with each additional ALD cycle and
further confirms that the gain in potential is a result of
considerable reduction in the recombination kinetics at the
photoanode.

The recombination rate of electrons in the cells with the
ALD TiO2 underlayer is presented in Figure S4, Supporting
Information, as the function of voltage. We can see that the
increase in the number of cycles of Ga2O3 deposition decreases
the recombination rate, which confirms the suppression of the
back reaction from the TiO2-electrolyte interface.45 Figure 4B
shows that the Ga2O3 passivation of the TiO2, these four parameters are analyzed separately. The light
harvesting efficiency is calculated from the absorption spectra
on the sensitized TiO2 films (Figure S5B, Supporting
Information). The ΦLHE is found to be close to 100% for
both the bare and the surface passivated TiO2 from 350 to 500
nm and drops following the trend of the absorption spectrum.
Since the ΦLHE is found to be similar for both the photoanodes,
this parameter cannot properly explain the observed increase
in IPCE upon passivation. The absorbed photon-to-electron
conversion efficiency (APCE) is cumulatively defined by the
last three parameters in eq 1 giving the true quantum yield of
photocurrent:

\[
\text{APCE} = \frac{\Phi_{LHE}}{\Phi_{LHE}} = \Phi_{inj} \Phi_{reg} \Phi_{coll}
\]

To rationalize the increase in IPCE for the Ga2O3-passivated
TiO2, these four parameters are analyzed separately. The light
harvesting efficiency is calculated from the absorption spectra
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\]

Figure S6, Supporting Information, shows the APCE
calculated by dividing the IPCE by ΦLHE follows the general
profile of the IPCE. In order to analyze specifically the kinetics
of the photoexcited electron injection into the conduction band
of the semiconductor, the fluorescence decay of Y123 for the
reference and Ga2O3-passivated TiO2 is measured using time-
resolved single photon counting (TRSPC) as proposed by S. E.
Koops et al.47,48 A qualitative comparison on the injection
capability is made between the reference electrode and the
electrode containing four cycles of Ga2O3. From Figure S7,
Supporting Information, it can be seen that the fluorescence
decay is faster for the reference cell (black curve) and when the
Ga2O3 is introduced, the emission decay is slightly delayed
(blue curve). The long-lived excited state of the dye indicates
the reduction in the injection kinetics of photogenerated
electrons in the semiconductor through the tunnelling
overlayer. This clearly shows that the subnanometer thick
Ga2O3 tunnelling overlayer does slow down the electron
injection, but at the same time, it is reducing the recombination
kinetics by about 2 orders of magnitude.23,24

The third parameter, the dye regeneration efficiency is
investigated using intensity modulated photoinduced absorp-
tion spectroscopy (PIA).44,49 Figure 6A compares the PIA
spectra of the Y123 on TiO2 and Ga2O3-passivated TiO2
infiltrated with acetonitrile or the Co2+/Co3+ redox electrolyte
with an excitation wavelength of 470 nm and a frequency
modulation of 36 Hz. For the reference photoanode in
acetonitrile (black solid line), three distinct absorption peaks
are observed at 672, 790, and 1540 nm in the differential PIA
spectrum (red arrows) indicating the presence of the transient
dye cations. When the Co2+/Co3+ electrolyte medium is
introduced (black dotted line), the absorption intensities of the
corresponding cations drop owing to the rapid reduction of the
oxidized dye by Co2+. However, the peaks do not disappear

Figure 5. IPCE as a function of wavelength for DSC electrodes with
and without the Ga2O3 tunneling overlayer (4 ALD cycles).
completely, which is indicative of incomplete regeneration. This might be due to the lower driving force for dye regeneration as well as poor electronic coupling between the dye and the bulky Co-complex.16 When using the Ga2O3 tunnelling overlayer, a strong negative peak at 694 nm, a weak shoulder peak at 790 nm, and a positive absorption peak at 1540 nm are observed. The negative peak at 694 nm corresponds to the fluorescence decay of excited electrons from the LUMO to the HOMO now competing with the slowed down injection. The shoulder peak at 790 nm is representative of dye cation absorption as evidenced by the phase shift observed with respect to the modulated excitation shown in Figure S8, Supporting Information (solid blue line, red arrow). When the electrolyte is introduced, the shoulder peak disappears, and the peak intensity at 1540 nm is reduced indicating more efficient but still incomplete dye regeneration.

Finally, the charge collection efficiency (Φcoll) cumulatively takes into account the transport and recombination dynamics and is defined by the following equation:

\[
\Phi_{\text{coll}} = 100 \times \frac{\text{transport rate}}{\text{transport rate} + \text{recombination rate}}
\]

(3)

The plot of Φcoll as a function of open-circuit potentials is shown in Figure 6B. For the reference cell at voltages close to 0, the Φcoll is found to be about 90%. However, at operating voltages closer to 600 mV, the Φcoll significant drops as low as 50%. With the deposition of just 1 Ga2O3 ALD cycle, the tunnelling layer is found to greatly enhance Φcoll, which is maintained between 80 and 90% over all the voltages. With increasing thickness of the tunnelling overlayer, Φcoll is further increased and remains above 90%. This improvement in the collection efficiency shows that the presence of the tunnelling layer prevents the loss of photogenerated electrons from the semiconductor to Co3+ at short-circuit.43

Thus, out of four parameters defining the IPCE, the ΦLHE and Φorg have remained largely constant upon addition of the Ga2O3 tunnelling overlayer on the TiO2 photoanodes. In contrast, an appreciable gain in charge collection efficiency dominates the loss in injection efficiency and serves to explain the significant increase in Jsc observed for DSCs that include the Ga2O3 tunnelling layer.43

In conclusion, the surface of the porous TiO2 photoanode for DSC was passivated using a subnanometer thick Ga2O3 tunnelling overlayer by ALD. The numerous effects of the Ga2O3 were investigated in DSCs using a high molar extinction coefficient D-π-A organic sensitizer (Y123) and the state-of-the-art Co(bipyridine-pyrazole) redox electrolyte. The addition of the Ga2O3 tunnelling overlayer was found to increase the open-circuit potential of the device from 690 mV to a new record of 1.1 V after 4 ALD cycles. In addition, 42% and 15% increase in short-circuit current density and fill factor, respectively, were observed to improve the overall DSC efficiency at PCE = 4.0%. The remarkable increase in Voc was shown using transient photovoltage decay and EIS to be caused by 2 orders of magnitude decrease of the recombination rate between electrons in the TiO2 CB and the oxidized form of the redox couple. In spite of a small reduction in the electron injection efficiency after the addition of the tunnelling overlayer, the Jsc was increased due to a significant improvement in charge collection efficiency, which results from a decline in charge recombination at short-circuit. Further work on the ALD precursor chemistry to enhance the diffusion length in the mesopores will be necessary to implement this technological advance into thicker TiO2 photoanodes in order to harvest the whole visible solar spectrum in high-efficiency DSCs. The decrease in the molecular size of the ALD metal precursors and the increase in the pore diameter of the mesoporous titania film by means of polymer additives can be considered as the possible options to augment the diffusion of precursors in the thicker photoanodes. The existing deposition technology can be directly implemented in the 1D nanowire-based solar cells as the precursors do not have to diffuse through the random pore orientation to cover the whole photoanode, like in the mesoporous structures. The development of this tunnelling overlayer opens a new parameter space of research on new single-electron redox mediators or hole transport materials suffering from fast recombination kinetics. This should allow this technology to break new grounds and reach higher efficiencies in both liquid and solid-state DSCs. However, the authors do not expect the system to enhance the open-circuit potential significantly with an iodide/triiodide electrolyte due to its slow two electron recombination process for the conversion of I3- to I-.8

ASSOCIATED CONTENT

Supporting Information
The photovoltaic data table and curves for the solar cells with 5 nm TiO2 underlayer, the corresponding IPCE plot, equivalent
circuit used to fit Nyquist plots representing the charge-transfer resistance, absorption and light harvesting efficiency spectra of dye-sensitized photoanodes, APCE spectrum, fluorescence decay, and photoinduced transient absorption spectra plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

NOTE ADDED AFTER ASAP PUBLICATION

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