

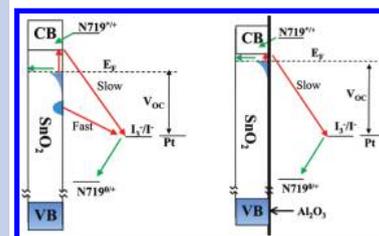
Surface Modification of SnO₂ Photoelectrodes in Dye-Sensitized Solar Cells: Significant Improvements in Photovoltage via Al₂O₃ Atomic Layer Deposition

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ABSTRACT We report here the exploitation of ultrathin layers of Al₂O₃ deposited via atomic layer deposition (ALD) on SnO₂ photoanodes used in dye-sensitized solar cells featuring the I₃⁻/I⁻ couple as the redox electrolyte. We find that a single ALD cycle of Al₂O₃ increases the lifetimes of injected electrons by more than 2 orders of magnitude. The modified SnO₂ photoanode yields nearly a 2-fold improvement fill factor and a greater than 2-fold increase in open-circuit photovoltage, with a slight increase in short-circuit photocurrent. The overall energy conversion efficiency increases by roughly 5-fold. The effects appear to arise primarily from passivation of reactive, low-energy tin-oxide surface states, with band-edge shifts and tunneling based blocking behavior playing only secondary roles.

SECTION Energy Conversion and Storage



Dye-sensitized solar cells (DSSCs) have garnered considerable attention within the solar cell community. With comparatively low manufacturing cost, ease of fabrication, and fair solar-to-electrical efficiency, these cells are potential candidates to replace conventional Si-based solar cells in specialized applications. A standard DSSC employs a Ru-based dye, which has a moderate molar absorption coefficient.^{1–3} With this limitation on the absorption coefficient, the system needs a high surface area substrate for the dye—typically nanoparticulate TiO₂—in order to achieve good light harvesting efficiency (LHE). Since electron transport is fairly slow in nanoparticulate TiO₂,^{4,5} the system also requires a slow redox shuttle (i.e., slow with respect to interception of injected electrons), usually I⁻/I₃⁻. Due to the otherwise sluggish reactivity of the shuttle, an energy of roughly 600 mV is required for regenerating the initial state of the dye molecule at an acceptable rate. The inclusion of this driving force reduces the achievable open circuit voltage almost by half. Many groups have experimented with alternative redox shuttles to address this loss in voltage.^{6–8} Conversely, if another semiconductor with higher electron mobility were used as the high-area substrate, electron transport would be faster, and a more reactive redox shuttle could be employed.⁹

Of the semiconductors that have been considered to replace TiO₂, SnO₂ is a recurring candidate. The use of SnO₂ as the high area electrode is not without drawbacks. Namely, the rate of electron interception by the redox electrolyte is much faster with SnO₂ than with traditional TiO₂. Durrant and co-workers found that the back electron transfer rate from SnO₂ (to the redox shuttle) is in the microsecond range, roughly 3 orders magnitude faster than with TiO₂.¹⁰ This is possibly due to the reactive, low-energy trap states in SnO₂.¹¹ In principle, coating the electrode with a layer of a high-bandgap metal

oxide such as MgO,¹⁰ ZrO₂,¹² SiO₂,¹³ or Nb₂O₅¹⁴ could passivate these states and make the rate of electron interception slower. Typically, the technique referred to as “dip-coating” has been employed to apply the barrier layer. However, this technique often creates layers with irregular, unpredictable thicknesses, as well as pinholes that reach the surface of the semiconductor.¹⁵ In contrast, atomic layer deposition (ALD) conformally coats high surface area materials.¹⁶ The self-terminating process in ALD enables angstrom-scale control over the coating thicknesses. The deposited layer's thickness is precisely controllable based on the number of ALD cycles. All of these benefits make ALD suitable for applying ultrathin barrier layers on photoelectrodes. In fact, ALD has been utilized in many recent alternative photoanode configurations.^{2,3,17–24} In this letter, we show that coating a SnO₂ electrode with a fraction of a monolayer of redox-inactive Al₂O₃ via ALD effectively slows down the rate of electron recombination with triiodide by 2 to 3 orders of magnitude, while substantially boosting the attainable photovoltage. With the addition of Al₂O₃, SnO₂ becomes viable as an electrode for DSSCs. In particular, because the conduction band-edge for SnO₂ is ca. 0.4 V less negative than that for TiO₂, incorporation of tin oxide in DSSCs should make possible the use of far-red-absorbing chromophores having excited states too low in energy to inject into TiO₂.

Figure 1 shows the effect that coating one cycle of Al₂O₃ has on DSSCs based on nanoparticulate SnO₂ electrodes. The short-circuit current density from the naked electrode is nearly

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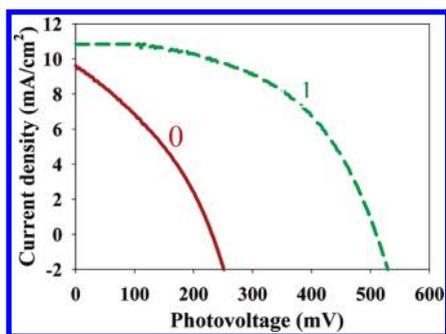


Figure 1. J - V curves for DSSCs based on naked SnO_2 (solid red line) and on SnO_2 coated with one cycle of Al_2O_3 (dashed green line).

10 mA/cm^2 , which is almost as large as the values obtained from transparent TiO_2 of the same thickness. The open-circuit photovoltage (V_{oc}), however, is significantly lower. With only one ALD cycle of Al_2O_3 , the short-circuit current density marginally increases. As in other reports involving thicker layers,^{10,15} the V_{oc} increases substantially; here it more than doubles, from 230 mV to 510 mV. The fill factor also improves from 35% to 65%, indicating near ideal diode-like behavior and an increase of the shunt resistance in the cell. The results were replicated with two additional sets of naked and alumina-coated photoelectrodes, showing very similar trends (ca. $\pm 5\%$ deviation).

Several factors could contribute to the observed V_{oc} enhancement. First, the conduction band-edge of the SnO_2 electrode may be negatively shifted by the layer of Al_2O_3 , resulting in a higher quasi-Fermi level under illumination and a higher V_{oc} . A conduction band-edge shift of a few hundred millivolts in response to a submonolayer coating of metal-oxide, however, would be unprecedented; more typical are shifts of around 100 mV or less.²⁵ Cyclic voltammetry experiments with and without an alumina coating (see Supporting Information) imply little shift in the conduction band edge (e.g., ca. -10 mV for one cycle of alumina and -60 mV for five cycles). We therefore disregard this possibility as the primary explanation. Second, Al_2O_3 could act as a tunneling barrier, slowing the rate of electron interception by the redox electrolyte. From the diode equation,²⁶ for every order of magnitude that the rate of interception decreases (for whatever reason), the photovoltage will increase by $\gamma \cdot 59 \text{ mV}$. (γ is the diode-quality factor; ideally its value is 1, but experimentally it typically ranges from 1 to ca. 1.5.) The observed photovoltage increase is 280 mV, corresponding to a ca. 3 order-of-magnitude decrease in the interception rate. Recall that the average thickness of one cycle of Al_2O_3 is only 1.1 \AA —far too thin to engender a tunneling based attenuation of this magnitude. Thus, we also disregard the tunneling possibility as the primary explanation. (See below for further discussion of tunneling.)

Bisquert et al.²⁷ have suggested that electron interception can occur not only via thermal population of the conduction band, but also directly via trap states (surface states) below the conduction band. The origin of these states (surface states) could be incomplete (or “incorrect”, e.g., hydroxyl rather than oxo) coordination of Sn(IV) sites on the surface of the

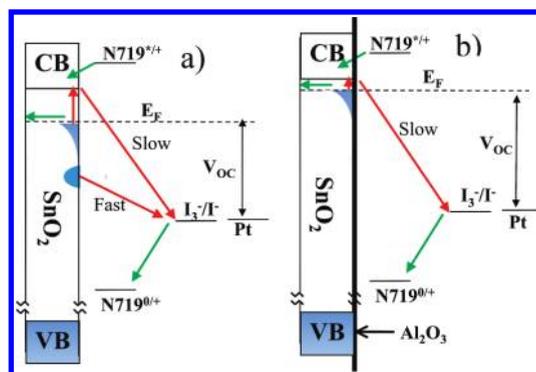


Figure 2. Proposed schematic diagram of electron interception at the SnO_2 electrode/solution interface: (a) without and (b) with an Al_2O_3 passivation layer.

nanoparticles. When the semiconductor surface is exposed to a single pulse of the aluminum precursor and a single pulse of water in ALD, the tin presumably achieves complete oxo coordination, resulting in diminished surface electronic states on the SnO_2 . While there might be other contributors to the observed increases in the overall performance, we suggest that the chief cause is passivation of sub-band-edge surface states in the semiconductor. Figure 2 illustrates the idea.

The survival times of injected electrons (τ_n) in both cells were measured by the open-circuit photovoltage decay technique. The relationship between photovoltage decay and charge carrier lifetime is given by²⁸

$$\tau_n = \frac{k_B T}{q} \left(\frac{dV_{oc}}{dt} \right)^{-1}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and q is the positive elementary charge.

As shown in Figure 3, with only one ALD cycle of Al_2O_3 on the SnO_2 electrode, the charge lifetimes increase by more than 2 orders of magnitude, indicating a reduction in the rate of electron interception, in good agreement with expectations from the observed increase in V_{oc} .

With the aim of producing additional increases in photovoltage and overall performance, the Al_2O_3 thickness was increased. Although the charge lifetime and the photovoltage increased as the thickness of Al_2O_3 increased (demonstrated in Figure 3), the current densities decreased (see Supporting Information). This likely reflects slowing, by the blocking-layer, of the kinetics of electron injection, resulting in lower injection yields and, therefore, lower current densities. In principle, this problem could be overcome by turning to dyes featuring longer-lived excited states.

A plot of the light intensity dependence of the open-circuit photovoltage of the coated electrode had a slope of 79 mV/decade (see Supporting Information). This near ideal diode-like behavior of the coated electrode indicates that the back electron transfer from the coated semiconductor has first-order kinetics, as seen in the literature for naked and coated electrodes.^{8,29,30} The measured lifetime of an injected electron in the photoelectrode is proportional to the inverse of the rate of electron interception [$\tau_n \alpha (1/k_{ET})$]. If the Al_2O_3 coating

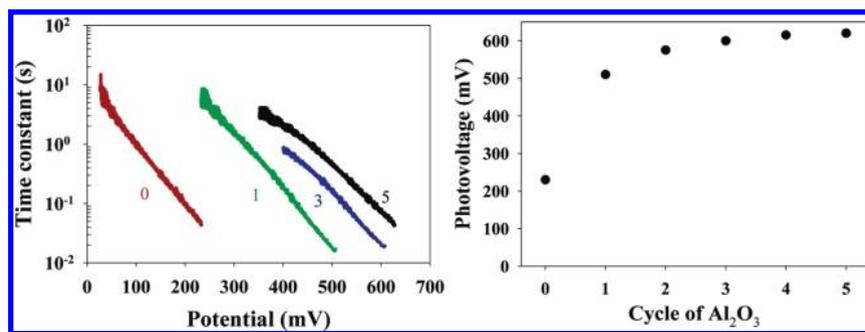


Figure 3. Open-circuit charge lifetimes and photovoltage of SnO₂ electrodes with different numbers of coating cycles of Al₂O₃. For clarity, data for two and four cycles are omitted from the voltage decay plot.

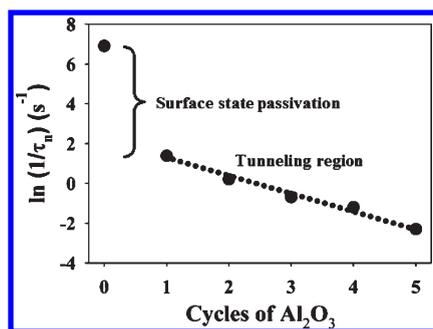


Figure 4. Plot of the logarithm of the electron interception rate by the redox shuttle ($1/\tau_n$) as a function of number of cycles of Al₂O₃ deposition. Comparisons were made at $V = 400$ mV. The dotted line shows the tunneling-attenuation region for the coated photoelectrode.

acts as a simple tunneling barrier, a plot of $\ln(1/\tau_n)$ and the thickness of the coating Al₂O₃ should yield a straight line with a slope of $-\beta$, the damping constant for the Al₂O₃ barrier.^{31,32} Given that the growth rate of the Al₂O₃ is 1.1 Å/cycle, the graph in Figure 4 gives a β value of 1 Å⁻¹, similar to the result observed in another coated electrode system, albeit with ferrocenium/ferrocene as the redox shuttle.⁸

In summary, we have shown that only one ALD cycle of Al₂O₃ (i.e., a fraction of a monolayer) on a SnO₂ photoelectrode is sufficient to extend the electron survival time within the electrode by 2 to 3 orders of magnitude. The immediate consequences are (a) an approximate doubling of open-circuit photovoltages in ruthenium-based DSSCs (230 mV → 510 mV), (b) a near doubling of the fill factor, (c) a modest increase in short-circuit photocurrent, and (d) a ca. 5-fold increase in energy conversion efficiency (0.76% → 3.7%). Thicker layers of Al₂O₃ act as a simple tunneling barrier with a β value of 1 Å⁻¹. With these modifications, the SnO₂ electrode could potentially be useful for dyes that are known to be energetically incapable of injecting into TiO₂. Such studies are underway.

EXPERIMENTAL SECTION

All chemicals, unless otherwise noted, were purchased from Sigma-Aldrich and used without further purification. Fluorine-doped tin oxide (FTO)-coated glass was sonicated in an acetone bath for 20 min and dried. Twenty nanometers of SnO₂ blocking layer was deposited by ALD (Savannah 100,

Cambridge Nanotechnology) using tetrakis(dimethylamino)titanium (TDMASn, Gelest) and H₂O₂ as precursors. Films were grown at 150 °C using exposure times of 1 and 0.03 s for TDMASn and H₂O₂, respectively, and 30 s of nitrogen between the pulses. This blocking layer was deposited to create effective shunt resistance between the FTO-coated glass and the electrolyte as was demonstrated in previous work.⁸ The SnO₂ was deposited concurrently on a Si chip. Ellipsometry (AJA Woolam Co. M2000) was performed on the silicon chip, and the obtained deposition rate was 1.2 Å/cycle, in good agreement with the published value.³³ SnO₂ nanoparticles (~20 nm in diameter) were fabricated according to a published procedure¹⁰ and placed on the FTO-coated glass by a doctor blade using Scotch tape as a spacer. The samples were then heated in air at 500 °C for 30 min. The thickness of the transparent SnO₂ electrode, as measured by profilometry (P10, Tencor), was ~4 μm.

Ultrathin layers of Al₂O₃ were deposited using trimethylaluminum (TMA) and water as precursors. The layers were deposited at 200 °C using exposure times of 8 s for TMA and for water, with 30 s of nitrogen between each pulse. After ALD, electrodes were immediately soaked in an ethanolic solution of 0.5 mM (Bu₄N)₂[Ru(4,4'-dicarboxy-2,2'-bipyridine)₂-(NCS)₂] (“N719” Dyesol, B2) overnight. The samples were then rinsed with ethanol and dried with a N₂ stream. A 25 μm-thick Surlyn spacer was used to meld the photoanode to a predrilled platinized piece of FTO-coated glass. A solution consisting of 0.6 M butylmethylimidazoliumiodide (TCI America), 0.03 M I₂, 0.1 M guanadinium thiocyanate, and 0.5 M 4-*tert*-butylpyridine in 85:15 acetonitrile/valeronitrile was introduced to the cell by vacuum back-filling through the hole on the dark electrode. A cover glass and a second piece of Surlyn spacer were used to seal the hole on the dark electrode.

The electrical characteristics and photovoltaic properties of each cell were measured with a CH-Instrument 1202 electrochemical analyzer interfaced with a Jovin Yvon Spex Fluoro-Log-3 fluorometer. The slit width was adjusted to achieve illumination of 100 mW/cm².

SUPPORTING INFORMATION AVAILABLE Plots of photovoltage as a function of light intensity, $J-V$ curves of naked and coated SnO₂ photoelectrodes, and cyclic voltammograms of naked and coated photoelectrodes. This material is available free of charge via the Internet at <http://pubs.acs.org>

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