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Suppression of Forward Electron Injection from Ru(dcbpy)$_2$(NCS)$_2$ to Nanocrystalline TiO$_2$ Film As a Result of an Interfacial Al$_2$O$_3$ Barrier Layer Prepared with Atomic Layer Deposition

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ABSTRACT Subnanometer-thick Al$_2$O$_3$ barrier layers on nanocrystalline TiO$_2$ film were prepared with atomic layer deposition (ALD). The method allowed variation of barrier thicknesses at atomic resolution also deep in nanoporous structures, which makes it a superior method as compared to, e.g., sol–gel techniques. In this letter we present results on the effect of Al$_2$O$_3$ barriers of various thicknesses on forward electron injection in dye-sensitized solar cells. A decrease in the amplitude of the oxidized Ru(dcbpy)$_2$(NCS)$_2$ dye absorption signal due to singlet injection was observed already after one deposition cycle that produces a discontinuous layer with nominal thickness of 1 Å. More than two layer coatings also slowed down the triplet injection. The findings indicate suppression of total electron injection, which is probably due to the Al$_2$O$_3$-induced weakening of electronic coupling between the dye and TiO$_2$ as well as modification of the TiO$_2$ electronic structure.

SECTION Kinetics, Spectroscopy
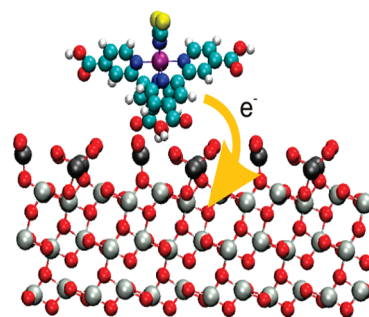
Electron transfer from the excited state of ruthenium complex dye (Ru(dcbpy)$_2$(NCS)$_2$, also called RuN3, dcbpy = 4,4′-dicarboxy-2,2′-bipyridine[1]) to the conduction band of the semiconductor (TiO$_2$) is one of the key processes determining the current output from dye-sensitized solar cells (DSSCs).[2] After excitation the RuN3 singlet state undergoes ultrafast electron injection to the semiconductor (~50 fs) and intersystem crossing (~70 fs) to triplet state localized on the bipyridine ligands of the RuN3 molecule.[3–5] The injection from the triplet state is a heterogeneous process occurring on a picosecond time scale.[6] The excited state absorption of the dye attached on TiO$_2$ occurs in the wavelength region of 630–760 nm and that of oxidized dye occurs from 760 to 940 nm with correlated time evolution, which is indicative of a reactant-to-product reaction.[4,7] The oxidized dye absorption dominates over triplet state absorption at 860 nm as evidenced by an isosbestic point in the excited state absorption signal of RuN3 dye in solution at this wavelength. Thus, 860 nm is an ideal probe wavelength for oxidized dye formation.

Recombination reactions of the injected electron with the oxidizing agent of the electrolyte (I$_3^-$) limit the photocurrent of the DSSC. As an effort to suppress recombination, the nanocrystalline semiconductor film has been coated with high band gap metal oxide layers, which act as barriers for the interfacial electron transfer. Several metal oxide materials have been studied as potential barrier materials, e.g., Al$_2$O$_3$,[8–12,14] ZrO$_2$,[8] SiO$_2$,[8] and ZnO.[13] While the effect of these materials on recombination rates and power conversion efficiency of the DSSC has been extensively studied, few reports on their effect on forward electron injection rates exist.[14]

In liquid-phase methods (the primary methods applied to Al$_2$O$_3$ layer preparation in DSSC, e.g., surface sol–gel processes[15]), incomplete penetration of the solution to the nanoporous TiO$_2$ film results in an uneven coverage of the nanosized cavities of the semiconductor.[14] Chemical vapor phase methods, such as atomic layer deposition (ALD),[16,20] allow the reactants to penetrate even the most distant nanopores near the interface between the semiconductor film and the conducting layer of the substrate[11] as was found in a Rutherford back-scattering (RBS) measurement of a 8 nm thick ALD-Al$_2$O$_3$ film on nanoporous TiO$_2$ (data not shown). ALD is based on sequential surface reactions where precursors react with the surface in a saturative manner. This allows production of smooth, continuous films and straightforward control of the thickness of the deposited film by adjusting the

number of reaction cycles. In the TMA/H$_2$O process[20] used in this work, the growth per cycle is ~1 Å. As a result of the saturative nature of ALD, surface reactions allow rather reliable calculation of layer thicknesses from growth per cycle (see Supporting Information). For submonolayer films, i.e., films deposited with less than five deposition cycles, only nominal thicknesses can be estimated since the submonolayer films are discontinuous. To our knowledge, ALD has been applied to barrier layer preparation in DSSCs only in a few cases.[10−12] We report the first study of the effect of ALD Al$_2$O$_3$ barrier layers on the forward electron injection from RuN3 dye to the conduction band of TiO$_2$ as a function of barrier thickness by femtosecond transient absorption spectroscopy.

All samples were sensitized to the same optical density (absorbance) 0.5 OD. This allows us to compare the amplitudes of the transient absorption signals directly. In Figure 1, signals from excited state absorption of the dye and absorption of the oxidized dye are shown in two time domains. In the region of singlet injection ($\tau < 1$ ps), the signal amplitude decreases as the barrier thickness increases.[3,4] The smaller the amplitude (Table 1) the smaller the oxidized dye number density in the excitation volume after excitation. This decrease in amplitude implies suppression of the fast electron injection from the singlet state of the dye. The oxidized dye absorption accounts for ~75% of the amplitude of the transient absorption signal in this spectral range, and the
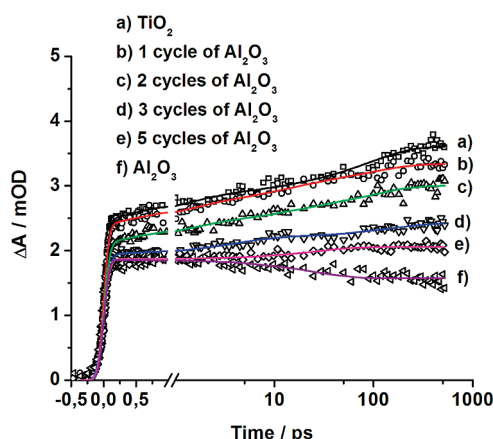

Figure 1. Time dependencies of the absorbance changes (in mOD) of excited state of the RuN3 dye and of the oxidized dye probed at 860 nm after 540 nm excitation on uncoated TiO$_2$, on TiO$_2$ with Al$_2$O$_3$ barrier layers, and on Al$_2$O$_3$. Solid lines are exponential fits to the experimental data (symbols).

~25% is due to the excited state absorption remaining after singlet injection.[4,17] It is obvious from Figure 1 that the signal amplitude in the time domain $\tau > 1$ ps up to 200 ps also diminishes as the barrier thickness increases, leading to a decrease in the quantum yield of triplet injection as well.[3,4] Vibrational relaxation of related ruthenium complexes has been reported to take place in a few picoseconds,[18] and these processes may well compete with the slow injection channel.

The quantum yield of the total electron injection can be determined by calculating the contribution of the oxidized dye to the total signal from the data in Figure 1 according to[14]

$$S(860\,\text{nm}, t) = N_{ex}(t)A_{ex}(860\,\text{nm}, t) + N_{ox}(t)A_{ox}(860\,\text{nm})$$

$$(1)$$

where $S(860\,\text{nm}, t)$ is the measured signal at time t and at the given wavelength and $N_{ex}(t)$ and $N_{ox}(t)$ represent the relative populations of the excited state and the oxidized form of the dye, respectively. $A_{ex}(860\,\text{nm}, t)$ is the time-dependent absorption of the excited state, i.e., that of the RuN3/Al$_2$O$_3$ sample, and $A_{ox}(860\,\text{nm})$ is the absorption of the oxidized dye determined from the RuN3/TiO$_2$ signal at 520 ps, i.e., after injection has completed. For the excited state, a time-dependent absorption signal is used because of the small decay due to vibrational energy relaxation, while a constant value can be used for the oxidized dye because it has no significant time dependence. The amplitude of the oxidized dye signal directly represents the quantum yield of electron injection, and from Figure 2 it can be seen that the quantum yield decreases by 15% after the first deposition cycle of Al$_2$O$_3$ and falls 70% with five deposition cycles, i.e., a monolayer of Al$_2$O$_3$.

The electron injection from the dye to the semiconductor follows the classical Marcus electron transfer theory in the nonadiabatic limit. The slowing down of injection as electronic coupling between the dye and the semiconductor weakens has been demonstrated by Asbury et al.[19] with the introduction of CH$_2$ spacer groups between the bipyridine and the semiconductor binding carboxylate groups. The Al$_2$O$_3$ barrier layer also increases the distance between the electron donating bipyridine orbitals of the dye and the conduction band of TiO$_2$, leading to weaker electronic coupling. The gradual decrease of the transient absorption amplitude (Figure 1) may be due to the discontinuous nature of the layers prepared with less than five deposition cycles (<5 Å nominal thickness).[20] It is possible that some dye molecules are still able to bind to TiO$_2$ in samples where the barrier is prepared with one or two deposition cycles, and these consequently have stronger average electronic coupling than

Table 1. Oxidized Dye Formation Time Constants (τ) and Relative Amplitudes (In Percentages of the Total Amplitude) on Bare TiO$_2$ and Al$_2$O$_3$ Films and Al$_2$O$_3$-Coated TiO$_2$ Films Obtained from Fitting the Data in Figure 1[a]

	TiO$_2$	1 cycle of Al$_2$O$_3$	2 cycles of Al$_2$O$_3$	3 cycles of Al$_2$O$_3$	5 cycles of Al$_2$O$_3$	Al$_2$O$_3$
instrument limited rise	68%	71%	70%	80%	91%	100%
τ_1 (ps)	1.2 ± 0.1 (−11%)	1.2 ± 0.1 (−10)	1.2 ± 0.1 (−10%)	3.9 ± 0.4 (−11%)	26 ± 3 (−9%)	25 ± 3 (19%)
τ_2 (ps)	11.0 ± 1.1 (−3%)	11.0 ± 1.1 (−8%)	11.0 ± 1.1 (−7%)	145 ± 15 (−9%)		
τ_3 (ps)	95 ± 10 (−18%)	95 ± 10 (−10%)	95 ± 10 (−13%)			

[a] Time resolution of the present experiment did not allow resolving the fast singlet injection rate, which is buried under the instrument limited rise.[3,4] Decay amplitudes are given in parentheses.
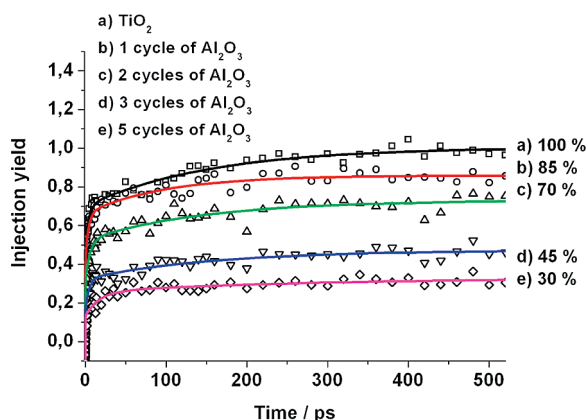
Figure 2. Injection yields calculated using eq 1 from the data in Figure 1. The numbers are total electron injection yields relative to RuN3/TiO$_2$.

samples where the dye binds only to Al$_2$O$_3$. If the dye is unable to bind to TiO$_2$ even after one deposition cycle, then the increasing distance with increasing number of deposition cycles would explain the gradual change in electronic coupling and the observed amplitude. A more detailed study of the slowing down of electron transfer as a function of barrier layer thickness will be presented elsewhere.

The injection kinetics on a picosecond time scale of the samples with one and two cycles of Al$_2$O$_3$ are almost identical as compared to the kinetics on uncoated TiO$_2$ film, while in samples with three or more deposition cycles the triplet injection is suppressed (Table 1). The efficiency of the triplet state injection is dependent on the conduction band energetics of the semiconductor. For the N3—TiO$_2$ system, the low-energy triplet states of the dye lie below the conduction band edge and are thus associated with slow, possibly thermally activated electron transfer. This was found in studies where slower triplet injection kinetics resulted from excitation of the dye in the red part of its absorption spectrum compared to excitation at maximum absorption.[17] A shift in the conduction band energy of TiO$_2$ will change the density of electron accepting states with respect to the excite state energy level of the dye and this will appear as a change in injection kinetics - especially in the picosecond time scale (injection from triplet state). The band energetics of TiO$_2$ show Nernstian pH-depedence.[21] Being an alkaline coating material (isoelectric point 8−9),[22] Al$_2$O$_3$ also shifts the TiO$_2$ energy levels upward.[11−13] Lin et al. have studied this effect with ultraviolet photoelectron spectroscopy.[11] They suggested that after two deposition cycles of Al$_2$O$_3$, the dye lowest unoccupied molecular orbital (LUMO) would still remain above the TiO$_2$ Fermi level, but after five cycles the Fermi level rises above the LUMO, impeding electron injection. Our results are consistent with this picture in the sense that we observe suppression of the triplet state injection in samples with three or more deposition cycles of Al$_2$O$_3$. However, since somewhat efficient injection is still taking place in the sample with five deposition cycles of Al$_2$O$_3$, we doubt that the Fermi level would have risen high enough to be able to halt electron injection as suggested by Lin et al.

In conclusion, we have shown already that one ALD cycle of Al$_2$O$_3$ results in a barrier that slows down electron injection from the singlet excited state of RuN3 dye and decreases the overall injection efficiency. With more than three ALD cycles of Al$_2$O$_3$, the triplet state injection is also suppressed, indicating a shift in the TiO$_2$ density of states.

SUPPORTING INFORMATION AVAILABLE TiO$_2$ thin film preparation, ALD of Al$_2$O$_3$ barrier layers, sensitization with RuN$_3$, and time-resolved transient absorption spectroscopy (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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