

## Multistep Electron Transfer Processes on Dye Co-sensitized Nanocrystalline TiO<sub>2</sub> Films

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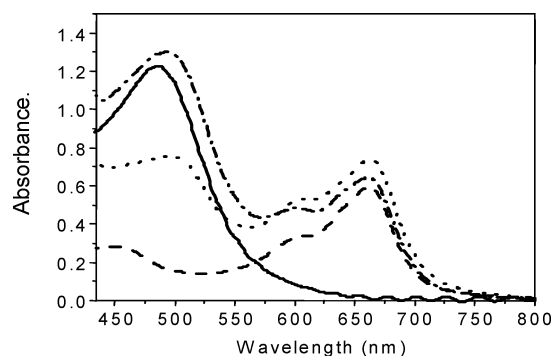
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Heterogeneous electron transfer systems based on the coupling of molecular dyes to inorganic nanoparticles are attracting extensive interest for technological applications ranging from electrochromic displays to photoelectrochemical energy conversion. Such electron transfer systems have to date largely been limited to the immobilization of a single molecular species to the nanoparticle surface. Several studies have addressed the interfacing supramolecular systems to nanoparticles and nanocrystalline electrodes ("heterosupramolecular chemistry") achieving for example, super-sensitizer function, panchromatic sensitization, and light-driven redox switches.<sup>1–5</sup> Attempts to sensitize such electrodes with multiple dyes have achieved only limited success to date.<sup>6</sup> A recent study has shown improved efficiencies by using dye multilayers.<sup>7</sup> In this communication we report an alternative approach to achieving a molecular electron-transfer cascade at a dye/TiO<sub>2</sub> interface, employing two spatially separated layers of distinct sensitizer dyes to achieve a vectorial movement of the oxidized dye species away from the TiO<sub>2</sub> surface.<sup>8</sup> Crucially this electron transfer cascade is achieved with simple molecular dyes without requiring complicated synthetic procedures and should therefore be generically applicable to a wide range of molecular sensitizer dyes.

Our novel co-sensitization strategy is based upon the deposition of a secondary metal oxide layer between the absorption of the first and the second sensitizer dyes, as illustrated in Scheme 1. This strategy is employed to achieve three key objectives: (i) to achieve an increased dye adsorption relative to that achievable by direct co-sensitization; (ii) to achieve an interfacial charge-transfer cascade on the TiO<sub>2</sub> nanoparticles. The two dyes are spatially and energetically organized so as to achieve hole transfer from the inner dye closer to the TiO<sub>2</sub> surface than to the outer dye, thereby increasing the distance between oxidized dye species and injected electrons and resulting in suppression of the charge recombination reaction; and (iii) to achieve an improved red sensitivity of the dye-sensitized film.

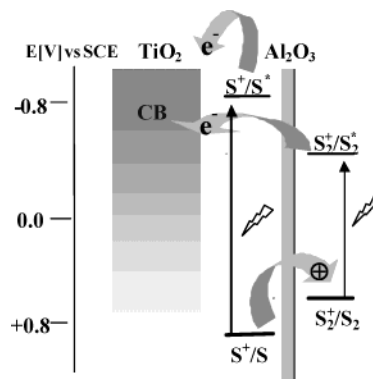
Our study employs two sensitizer dyes Ru(dcbpy)<sub>2</sub>(CN)<sub>2</sub>-RuL<sub>2</sub>(CN)<sub>2</sub> and RuPc (chemical name: bis(3,4-dicarboxypyridine)-(1,4,6,11,15,18,22,25-octamethyl phthalocyanato)ruthenium(II)). The secondary Al<sub>2</sub>O<sub>3</sub> layer was deposited by immersion of a RuL<sub>2</sub>(CN)<sub>2</sub>-sensitized TiO<sub>2</sub> film in an anhydrous solution of aluminum isopropoxide at 25 °C. Full experimental details are given in the Supporting Information.

Figure 1 compares absorption spectra for 4 μm mesoporous TiO<sub>2</sub> films sensitized by our novel co-sensitization strategy against control films employing conventional sensitization routes. As can be seen,



**Figure 1.** Absorption spectra of 4 μm mesoporous sensitized TiO<sub>2</sub> films as follows: TiO<sub>2</sub>/RuL<sub>2</sub>(CN)<sub>2</sub> (—), TiO<sub>2</sub>/RuPc (---), TiO<sub>2</sub>/RuL<sub>2</sub>(CN)<sub>2</sub>:RuPc (···) and TiO<sub>2</sub>/RuL<sub>2</sub>(CN)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/RuPc (· - · - ·)

**Scheme 1.** Charge Transfer Processes in Multilayer Co-sensitized Nanocrystalline TiO<sub>2</sub> Films (S = RuL<sub>2</sub>(CN)<sub>2</sub>, S<sub>2</sub> = RuPc)

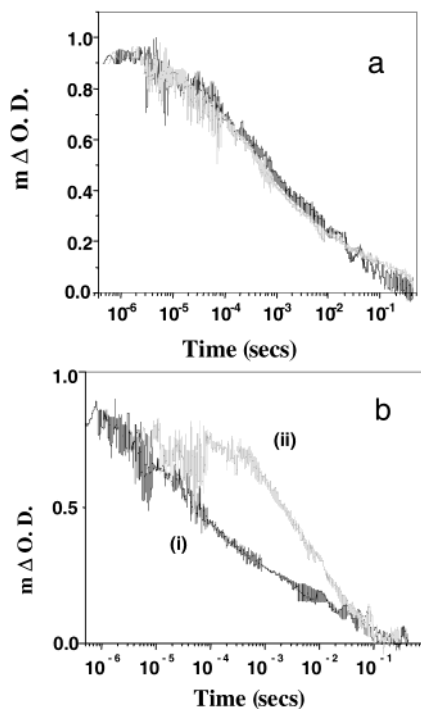


the multilayer co-sensitized approach results in the adsorption of near monolayer coverages of both dyes. The deposition of the secondary metal oxide layer was essential to achieve such high dye loading. Attempts to adsorb RuPc onto TiO<sub>2</sub> film already sensitized with a full monolayer of RuL<sub>2</sub>(CN)<sub>2</sub> were unsuccessful, resulting in gradual RuL<sub>2</sub>(CN)<sub>2</sub> desorption from the photoelectrode.

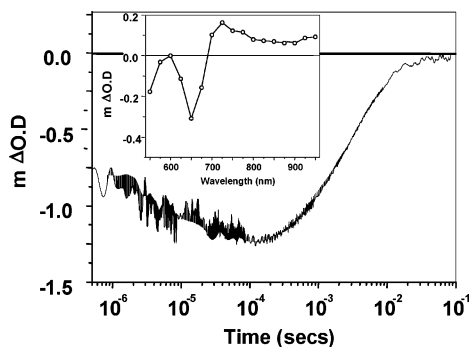
Transient absorption spectroscopy was employed to investigate the achievement of the desired electron-transfer cascade, employing low-intensity excitation conditions (~0.1% dye molecules excited per pulse). We consider first a control RuL<sub>2</sub>(CN)<sub>2</sub>-sensitized TiO<sub>2</sub> film (Figure 2a) with and without the secondary metal oxide layer postdeposition; it is apparent that the postdeposition of the Al<sub>2</sub>O<sub>3</sub> layer has no influence on either the electron injection yield or the charge recombination dynamics of this film. We thus deduce that the deposition of the Al<sub>2</sub>O<sub>3</sub> layer does not disrupt the adsorption of the RuL<sub>2</sub>(CN)<sub>2</sub> underlayer. We now turn to the second dye layer,

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**Figure 2.** Transient absorption data monitoring dye cation absorption for (a)  $\text{TiO}_2/\text{RuL}_2(\text{CN})_2$  (black) and  $\text{TiO}_2/\text{RuL}_2(\text{CN})_2/\text{Al}_2\text{O}_3$  films (gray) ( $\lambda_{\text{ex}} = 490$  and  $\lambda_{\text{pr}} = 800$  nm) and (b) (i)  $\text{TiO}_2/\text{RuPc}$  and (ii)  $\text{TiO}_2/\text{RuL}_2(\text{CN})_2/\text{Al}_2\text{O}_3/\text{RuPc}$  films ( $\lambda_{\text{ex}} = 670$  nm and  $\lambda_{\text{pr}} = 725$  nm).



**Figure 3.** Transient kinetics observed for a  $\text{TiO}_2/\text{RuL}_2(\text{CN})_2/\text{Al}_2\text{O}_3/\text{RuPc}$  film ( $\lambda_{\text{ex}} = 490$  nm,  $\lambda_{\text{pr}} = 650$  nm), probing the grow in and decay of the RuPc bleach. Inset: Difference absorption spectra recorded at 100  $\mu\text{s}$ .

employing 670 nm excitation to ensure direct excitation of the RuPc alone, Figure 2b compares the transient kinetics in our novel  $\text{TiO}_2/\text{RuL}_2(\text{CN})_2/\text{Al}_2\text{O}_3/\text{RuPc}$  system with those of the control film  $\text{TiO}_2/\text{RuPc}$ . In this case, the results are similar to those we have previously reported for the insertion of  $\text{Al}_2\text{O}_3$  barrier layers between the  $\text{TiO}_2$  film and a sensitizer dye,<sup>9,10</sup> namely that, for suitable barrier layer thicknesses, the barrier layer does not reduce the electron injection yield but results in a significant retardation of interfacial charge recombination dynamics. In this case, it is apparent that the charge recombination half time ( $\tau_{50\%}$ ) for the RuPc cation is slow from 0.13 ms for the  $\text{TiO}_2/\text{RuPc}$  film to 5 ms for the multilayer film. No such retardation was observed for co-sensitized films in the absence of the  $\text{Al}_2\text{O}_3$  layer. It can thus be concluded that our sensitization strategy indeed results in the desired spatial organization of the two sensitizer dyes, with  $\text{RuL}_2(\text{CN})_2$  adsorbed directly to the  $\text{TiO}_2$  surface and the RuPc localized further from the  $\text{TiO}_2$ .

We turn now to consideration of the hole transfer between the  $\text{RuL}_2(\text{CN})_2$  and RuPc dyes. Figure 3 shows transient absorption

data obtained for our  $\text{TiO}_2/\text{RuL}_2(\text{CN})_2/\text{Al}_2\text{O}_3/\text{RuPc}$  system following optical excitation of the  $\text{RuL}_2(\text{CN})_2$  dye at 490 nm. The main figure shows the transient kinetics observed at 650 nm, the maximum of the RuPc ground-state absorption bleach. The inset shows the transient spectrum observed 100  $\mu\text{s}$  after excitation. The RuPc ground-state bleach is clearly present in the co-sensitized film data, clearly demonstrating efficient hole transfer from the initially excited  $\text{RuL}_2(\text{CN})_2$  to RuPc, consistent with the difference in oxidation potentials for these dyes (Scheme 1). Simulation of this spectrum from those for the singly sensitized films indicates a hole transfer yield to the RuPc of >70% (see Supporting Information). The kinetic data indicate that this hole transfer is rapid, being over 50% complete within 500 ns (at the probe wavelength the  $\text{RuL}_2(\text{CN})_2$  cation yields a small positive signal, the opposite sign to the negative RuPc bleach signal). The subsequent signal recovery, assigned to charge recombination, exhibits a  $\tau_{50\%}$  of 5 ms, in agreement with Figure 2b.

The transient absorption data reported here therefore confirm that the co-sensitization route we have employed here achieves the desired electron transfer cascade illustrated in Scheme 1. We note that our data do not indicate the detailed structure of the  $\text{Al}_2\text{O}_3$  barrier layer. Most probably our deposition strategy results in  $\text{Al}_2\text{O}_3$  deposition interspaced between the  $\text{RuL}_2(\text{CN})_2$  dyes, rather than as a continuous barrier layer, and may indeed not result in complete hydrolysis of the precursor to the  $\text{Al}_2\text{O}_3$  oxide. Notwithstanding such uncertainties, it is apparent that this layer achieves the desired functionality.

The results we present here demonstrate the viability of a novel route to the co-sensitization of nanocrystalline  $\text{TiO}_2$  films. Initial studies of the use of this route in dye-sensitized solar cells are already promising, indicating efficient current generation from both sensitizer dyes and achieving an order of magnitude improvement in photocurrent generation relative to direct co-sensitization without the  $\text{Al}_2\text{O}_3$  layer (see Supporting Information). Further development of this strategy employing optimized blue and red absorbing sensitizer dyes therefore presents an attractive route to the panchromatic sensitization of dye-sensitized solar cells.

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**Supporting Information Available:** Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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