

Organisation and Reactivity of Nanoparticles at Molecular Interfaces. Part II.⁺ Dye Sensitisation of TiO₂ Nanoparticles Assembled at the Water | 1,2-Dichloroethane Interface

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KEYWORDS:

colloids · dyes · liquid|liquid interfaces · photocurrents · titanium oxide

Dye sensitisation of wide bandgap semiconductors has been extensively studied in the fields of photography and photovoltaics.^[1, 2] Strong electronic coupling between dyes featuring suitable anchoring groups and metal oxides can lead to electron injection from the excited state into the solid in the subpicosecond domain.^[3–9] Time-resolved transient absorption studies of TiO₂ and ZrO₂ nanoparticles sensitised by alizarin have demonstrated that ultrafast injection may occur not only into the conduction band but also into empty surface states located in the bandgap.^[4] These studies also showed that the lifetime of the charge separated state in the TiO₂–alizarin system exhibits a multiexponential relaxation with a fast component of the order of 430 fs. However, a substantial fraction of the charge separated state feature lifetimes beyond the nanosecond time scale. Previous studies by Moser and Grätzel have shown that the slower component is of the order of 500 μs.^[10] This slow back electron transfer has been rationalised in terms of the inverted Marcus region for electron transfer.^[10, 11] On the other hand, Haque et al. have indicated that population/depopulation dynamics in traps levels can be the determining factor in the rate of back electron transfer in dye-sensitised mesoporous TiO₂ nanocrystalline photoelectrodes.^[12]

The lifetime of the charge separated state is one of the key points behind the high quantum efficiencies exhibited by dye sensitised nanocrystalline (DSNC) solar cells.^[11] In these systems, the fast injection process is followed by the regeneration of the

dye by a redox couple present in the electrolyte phase. This process is equivalent to the cosensitisation reaction employed in photography. Assuming that all injected electrons arriving to the back contact are collected in the external circuit (short-circuit conditions), the photocurrent efficiency is determined by the diffusion of electrons across the mesoporous film and the rate of electron capture by species in solution. Independent measurements of both parameters revealed opposite dependencies on the light intensity, which is consistent with the weak relationship between the incident photon-to-current conversion efficiency (IPCE) and the illumination intensity.^[13–16]

In our previous publication, we explored a fundamentally different approach in which TiO₂ colloids and redox couples are separated by a polarisable liquid|liquid junction.^[17] Under potentiostatic (short-circuit) conditions, the origin of the photoresponses is connected to charge transfer processes across the boundary between the two immiscible electrolyte solutions. For instance, the transfer of valence band holes from the particles in the aqueous electrolyte to an electron donor in the organic phase manifests itself by a photocurrent signal.^[17] In the present communication, we demonstrate that photocurrent responses originating from the photooxidation of ferrocene can be extended into the visible region by dye sensitisation of TiO₂ particles assembled at the water|1,2-dichloroethane (DCE) interface.

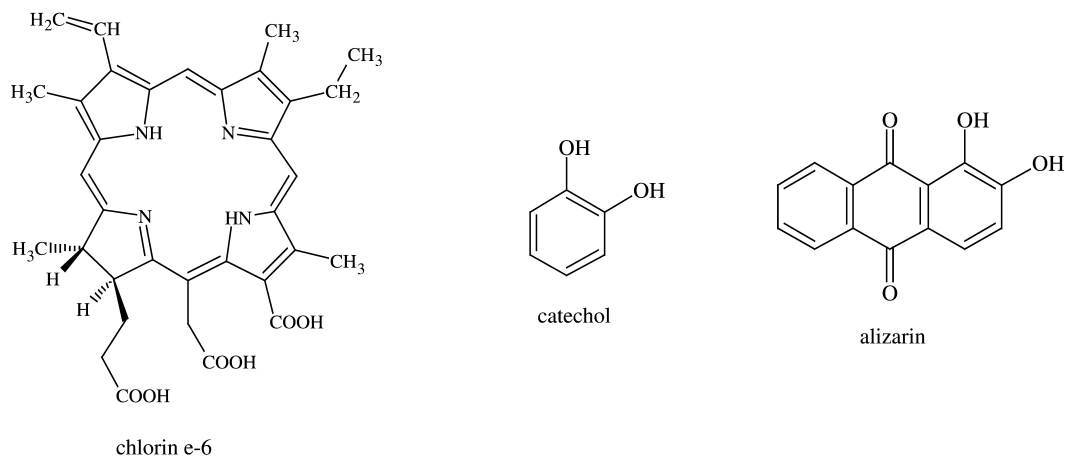
The sensitisation of TiO₂ nanoparticles in the aqueous phase was carried out by homogeneous complexation in the presence of chlorin e-6, catechol or alizarin (Scheme 1), as well as by interfacial complexation involving alizarin in the DCE phase. A representation of the electrochemical cell employed in all measurement is shown in Scheme 2. Cyclic voltammograms in the presence of these dyes as well as TiO₂ colloids do not show any faradaic responses within the polarisable window. The positive and negative limits of the potential window are determined by the transfers of Li⁺ and Cl[–] ions from water to the DCE phase.^[18]

Photocurrent spectra for various concentrations of TiO₂ particles in the presence of chlorin e-6 are shown in Figure 1. In the absence of the particles, the photocurrent responses are rather small mainly due to low coverage of the dye at the interfacial boundary.^[19] No photoresponses are observed in the absence of ferrocene in the organic phase, indicating that the photocurrent originates from heterogeneous electron transfer involving the organic phase donor. Upon increasing concentration of TiO₂ to 1.0 g L^{–1}, the photocurrent is increased approximately ten-fold at wavelengths around 650 nm. These results contrast remarkably with the photocurrent spectra obtained in the absence of dyes, where the photocurrent onset coincides with the TiO₂ bandgap (413 nm).^[17] It is also observed that the photocurrent responses show a weak dependence on the TiO₂ concentration above 0.5 g L^{–1}, which indicates a saturation of the particle density at the interface. Previous differential capacitance and photocurrent studies have shown that the organisation of TiO₂ at water|DCE boundary is affected by lateral interaction forces that counteract the aggregation and determined a maximum surface coverage of the order of $3 \times 10^{10} \text{ cm}^{-2}$.^[17]

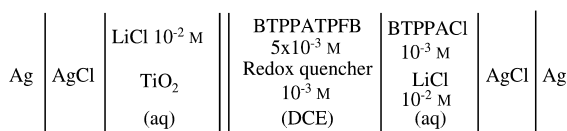
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Scheme 1. Molecular structures of chlorin e-6, catechol and alizarin.



Scheme 2. Schematic representation of the electrochemical cell. BTPPATPFB = bis(triphenylphosphoranylidene) ammonium tetrakis(pentafluorophenyl)borate.

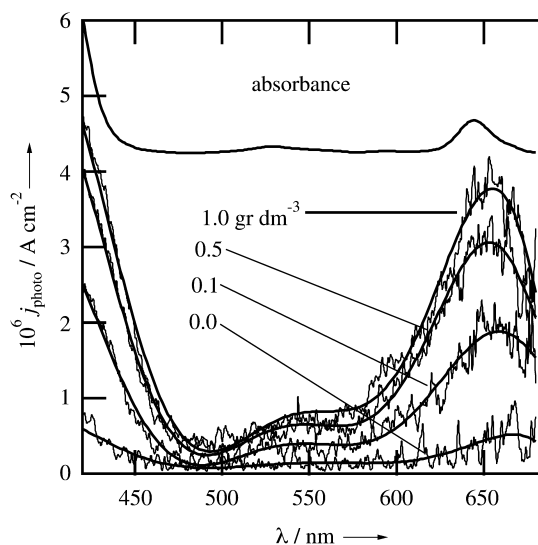


Figure 1. Photocurrent spectra for 1.0, 0.5, 0.1, and 0.0 g L⁻¹ concentrations of TiO₂ in the aqueous phase in the presence of 2.0 × 10⁻⁶ M chlorin e-6. The absorption spectrum of chlorin e-6 is also superimposed. The Galvani potential difference was 0.125 V.

The sensitisation of TiO₂ by alizarin and catechol was performed by slow addition of 1 mM ethanolic solution of the dyes into an aqueous solution containing TiO₂ and LiCl. The concentrations of the particles and dye after dilution were 0.1 g L⁻¹ and 40 μM respectively. These dyes have a strong affinity for TiO₂ surfaces, leading to the formation of metal-to-ligand charge transfer absorption bands, where Ti^{IV} acts as the metal centre.^[4] The absorption features associated with the TiO₂-catechol and TiO₂-alizarin complexes are displayed in Figure 2.

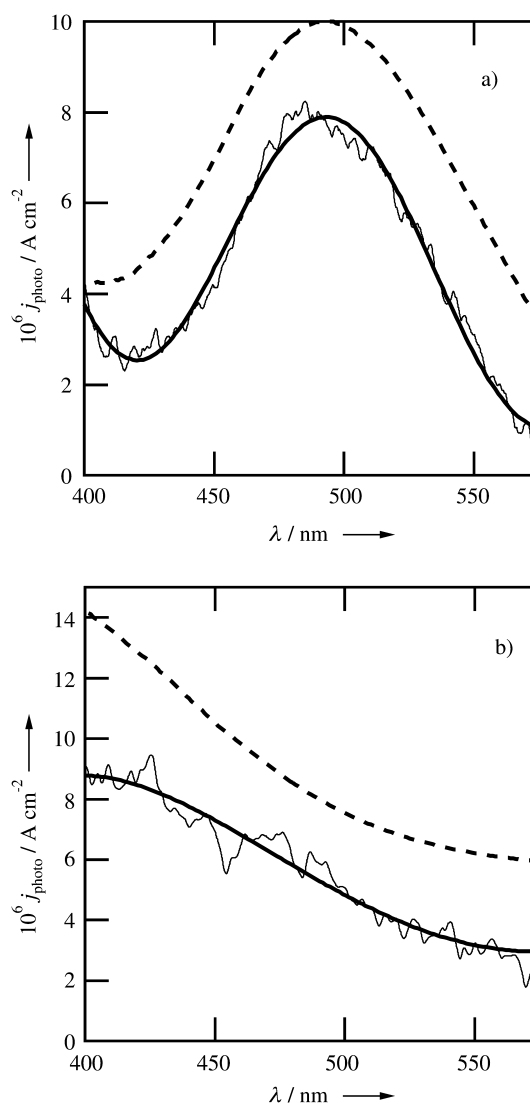


Figure 2. Absorption (---) and photocurrent (—) spectra for TiO₂ colloidal solution sensitised by a) alizarin and b) catechol in the presence of 1.0 × 10⁻⁶ M ferrocene in the organic phase. The concentration of TiO₂ was 1.0 g L⁻¹ and the Galvani potential difference was 0.300 V.

Assuming a donor–acceptor separation distance of the order of 6 Å for the TiO_2 –alizarin complex, the characteristic matrix element coupling of the ground state to the charge-transfer excited state can be calculated employing the Mulliken–Hush equation to be of the order of $3 \times 10^3 \text{ cm}^{-1}$.^[4] This rather strong electronic overlap manifests itself by charge injection on the femtosecond scale.

The photocurrent action spectra shown in Figure 2 were obtained in the presence of catechol- and alizarin-sensitised TiO_2 in the aqueous phase and $1.0 \times 10^{-3} \text{ M}$ ferrocene in the organic phase. As in all previous experiments, no photocurrent responses are observed in the absence of either TiO_2 or ferrocene. The photocurrent spectra exhibit identical features to the absorption spectra of the sensitised nanoparticles. These results clearly demonstrate that the origin of the photocurrent is connected to an ultrafast electron injection from the photoexcited dye into the nanoparticle followed by a heterogeneous electron transfer from ferrocene.

Further studies of alizarin sensitisation of TiO_2 reveal that interfacial complexation at the water|DCE junction also provided photocurrent spectra identical to the one displayed in Figure 2a. Photocurrent spectra with a maximum at 490 nm were obtained for TiO_2 colloidal solution in contact with a DCE phase containing $1.0 \times 10^{-4} \text{ M}$ alizarin and $1.0 \times 10^{-3} \text{ M}$ ferrocene. In this case, the TiO_2 –alizarin complex responsible for the photoelectrochemical signal is generated at the liquid|liquid boundary. Evidence linking the photocurrent responses with the interfacial assembly of nanoparticles is illustrated in Figure 3. The differential capacitance curves in Figure 3a show the characteristic increase in the excess charge upon positive polarisation of the interface in the presence of alizarin-sensitised TiO_2 at pH 3.5. This excess charge is associated with the potential induced assembly of nanoparticles at the interface.^[17] On the other hand, the photocurrent–potential curve in Figure 3b features an onset potential close to -0.1 V , which coincides with the onset potential for the formation of the particle assembly. The common potential dependencies of the photocurrent and the excess charge confirm that the photoinduced heterogeneous electron transfer involving the TiO_2 –alizarin complex takes place in the region where the nanoparticles are assembled at the liquid|liquid boundary. Taking into account that the photon flux is of the order of $10^{17} \text{ cm}^{-2} \text{ s}^{-1}$, neglecting reflection losses, the maximum IPCE at 442 nm is close to 0.001%. This rather low efficiency is determined by the small fraction of photons collected by the sensitised particles at the liquid|liquid boundary. Assuming that the maximum particle density is of the order of $3 \times 10^{10} \text{ cm}^{-2}$,^[17] and a photon capture cross section of $5 \times 10^{-15} \text{ cm}^2$, the quantum yield is approximately 10%.

The origin of the photoelectrochemical response for the alizarin-sensitised TiO_2 can be rationalised in terms of the mechanism highlighted in Figure 4. Similar to the homogeneous sensitisation process in the presence of chlorin e-6 and catechol, the ultrafast injection from the alizarin excited state into the particle is followed by interfacial electron transfer from ferrocene to the oxidised dye. Consequently, the quantum yield of the photoelectrochemical process is determined by the competition between back electron transfer from the particle to the oxidised

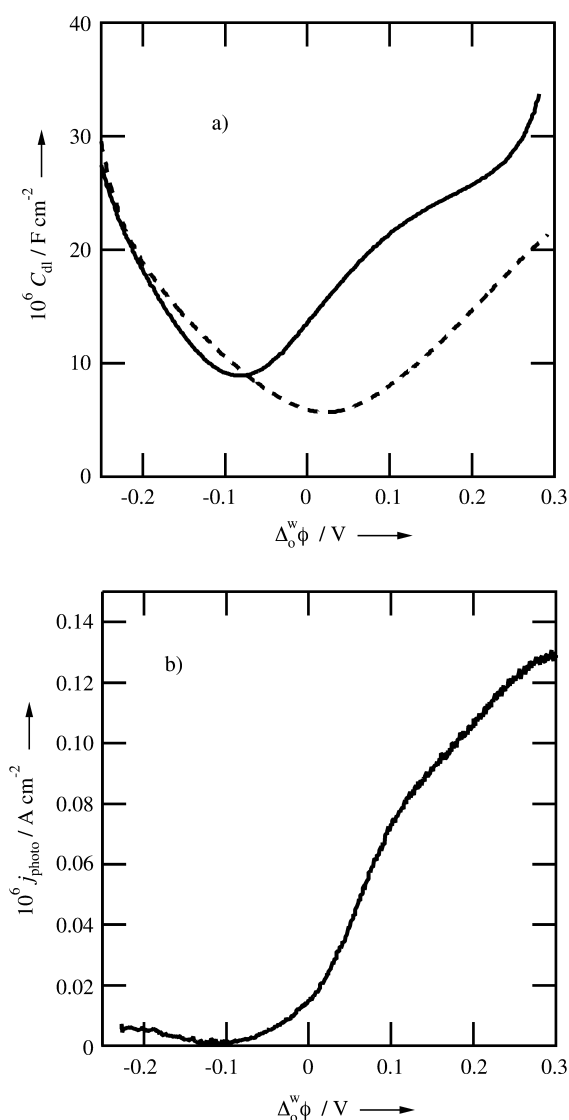


Figure 3. a) Capacitance and b) photocurrent voltage curves obtained for $1.0 \text{ g L}^{-1} \text{ TiO}_2$ in the aqueous phase and $1.0 \times 10^{-4} \text{ M}$ alizarin and $1.0 \times 10^{-3} \text{ M}$ ferrocene in the DCE phase. The capacitance response in the absence of the nanoparticles is displayed as a dashed line. The photocurrent signal was obtained by laser illumination at 442 nm in total internal reflection from the organic phase.

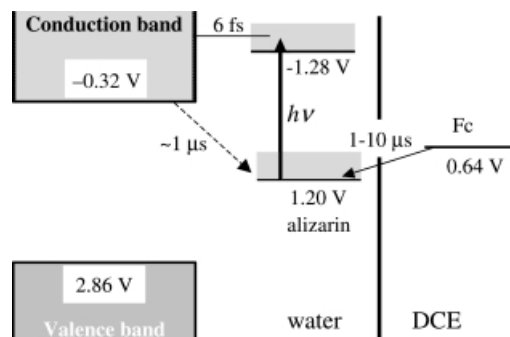


Figure 4. Schematic representation of the mechanism behind the photoresponses observed for alizarin-sensitised TiO_2 particles at the water|DCE junction. The characteristic time constant for the main processes involved are also indicated.^[3, 20]

dye and the interfacial regeneration of the dye by ferrocene. As we mentioned previously, the charge separated state in the TiO_2 -alizarin complex exhibits a highly multiexponential decay, in which more than 10% extends into the microsecond scale.^[4, 10] On the other hand, heterogeneous electron-transfer reactions across the water|DCE interface featuring ferrocene derivatives also provide time constants of the order of several microseconds for similar driving forces.^[20] Although the early estimation of the effective quantum yield remains approximate, the magnitude of the photocurrent responses appears roughly consistent with the dynamics of the processes indicated in Figure 4.

Despite some obvious similarities with DSNC photoelectrodes, the origin of the photoelectrochemical responses involving dye sensitised TiO_2 at the water|DCE interface is rather different. In the case of DSNC solar cells, the photocurrent is determined by the collection of injected electrons at the conducting support of the mesoporous TiO_2 film. The electron transport phenomena exhibit a complex dependence on the dynamics of population and depopulation of trap states distributed across the film. By contrast, the efficiency of the photoresponses at the water|DCE junction is determined by the competition between back electron transfer from the particle and the regeneration of the oxidised dye. Considering the processes taking place across the whole photoelectrochemical cell, the flux of electrons tunnelling through the liquid|liquid boundary is matched by the diffusion of the redox species in the organic phase as well as the removal of injected electrons from the particles at the interface. The magnitude of the photocurrent is rather small under the present conditions; therefore the diffusion of the redox species in the organic phase does not appear as the limiting step of the photoreaction. However, the effect of oxygen as well as other electron acceptor species in the aqueous phase remains to be explored. We believe that by increasing the dynamics of electron capture by species in the aqueous electrolyte, the quantum efficiency for heterogeneous regeneration of the dye can be increased.

In summary, photoelectrochemical responses featuring TiO_2 nanoparticles electrostatically assembled at polarisable liquid|liquid interfaces can be extended into the visible region by dye sensitisation. Photocurrent responses associated with the photooxidation of ferrocene in DCE were observed in the presence of TiO_2 colloids sensitised with chlorin e-6, catechol and alizarin in the aqueous phase. Interfacial sensitisation was also observed by introducing the hydrophobic dye alizarin in the DCE phase. For the TiO_2 -alizarin and TiO_2 -catechol systems, the photocurrent spectra showed the characteristic metal-to-ligand charge transfer spectroscopic signatures, indicating that the photoelectrochemical process is initiated by an ultrafast electron injection from the dye into the conduction band of the particle. The lifetime of the charge separated state is comparable to the transient time for electron tunnelling from ferrocene across the liquid|liquid boundary. The interfacial cosensitisation step manifests itself as photocurrent responses under potentiostatic control. The steady state condition is determined by the matching of the electron flux across the interface with the diffusion of redox species in the organic phase and the capture of injected electrons from the particle surface by species in the aqueous electrolyte.

Experimental Section

TiO_2 nanoparticles with an average radius of 56 Å were prepared by hydrolysis of TiCl_4 at low temperature (0 °C) followed by dialysis, as described elsewhere.^[21] This method yields spherical particles, mostly anatase, which are electrostatically stabilised in aqueous solution at pH lower than the point of zero zeta potential ($\text{zpp} = 4.7$).^[21–23] The aqueous and organic supporting electrolytes were LiCl (pH 3.5) and bis(triphenylphosphoranylidene) ammonium tetrakis(pentafluorophenyl)borate (BTTPATPFB), respectively. Details on the preparation of BTTPATPFB have previously been reported.^[24] All reagents were analytical grade or higher.

The electrochemical experiments were performed using a home-made four-electrode potentiostat connected to a PPR1 waveform generator (HI-TEK instruments). The Galvani potential difference was estimated from the formal transfer potential of tetramethylammonium ($\Delta_0^W \phi^{\circ} = 0.160$ V). Photocurrent spectra were measured using polychromatic light from an arc Xe lamp (Oriel) in conjunction with a grating monochromator. The spectral resolution in this set-up was typically 5 to 10 nm. Light intensity was normalised by a high voltage photomultiplier tube. Alternatively, photocurrent-potential curves were measured at 442 nm, using a He–Cd laser (Omnichrome series 74) with a photon flux of approximately $1 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$ (not corrected for reflection losses and organic phase absorption). The laser illumination was performed in total internal reflection from the organic phase. The photocurrent signal was obtained using chopped illumination and lock-in detection (Stanford Research System SR830).

Cyclic voltammograms as well as impedance measurements show that particles are reversibly assembled at the liquid|liquid boundary upon applying a positive Galvani potential difference (see Figure 3 a).^[17] The excess charge associated with the TiO_2 assembly was not affected upon consecutive cycling, suggesting that the particles are stable at the liquid|liquid boundary and that no significant aggregation takes place.

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Transient Optical Studies of Interfacial Energetic Disorder at Nanostructured Dye-Sensitised Inorganic/Organic Semiconductor Heterojunctions

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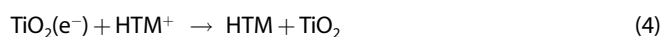
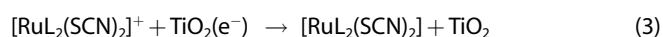
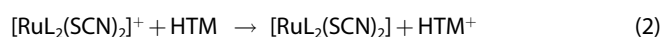
KEYWORDS:

charge transfer · interfaces · semiconductors · sensitizers · time-resolved spectroscopy

The process of charge transfer at the contact between two semiconductors or between a metal and a semiconductor plays an important role in many areas of technology. For example,

light-induced charge separation at p–n semiconductor heterojunctions and charge injection at metal/organic semiconductor interfaces form the basis of inorganic photovoltaics and organic light-emitting diodes, respectively.^[1, 2] The optimisation of such devices requires a good theoretical description of the interfaces involved. This, in turn, has motivated detailed mechanistic studies of interfacial charge-transfer reactions at metal/organic, organic/organic, and organic/inorganic semiconductor heterojunctions.^[3–5] Despite considerable progress, there remain some fundamental aspects of interfacial charge-transfer processes that have received less attention. In particular, early models of charge injection from metal contacts into semiconductors considered the semiconductor as a homogeneous material.^[6] Such models did not take into account the disordered nature of the materials involved. Although recent models of charge injection at metal/organic semiconductor interfaces have indeed considered the role of inhomogeneous broadening of the interfacial energetics,^[7, 8] such disorder has not been considered in charge-transfer models of dye-sensitised inorganic/organic semiconductor heterojunctions. Herein, we report on the influence of energetic inhomogeneity upon the charge-transfer kinetics at such an inorganic/organic semiconductor interface.

A configuration of particular interest is the dye-sensitised nanocrystalline solar cell (DSSC). Over the last decade, DSSCs have emerged as an attractive alternative to conventional p–n junction based photovoltaic devices.^[9] More recently, there has been heightened interest in solid-state versions of DSSCs, where the liquid based I₃[−]/I[−] electrolyte system is replaced by an organic p-type semiconductor, referred to as a hole-transporting material (HTM).^[10] Here, the HTM forms a large surface area interface with the dye-sensitised nanocrystalline TiO₂ film. The charge-transfer reactions at the dye-sensitised nanocrystalline TiO₂/HTM interface play a key role in the determination of the overall efficiency of the solar cell device. The main charge-transfer events, which take place at such an interface, are depicted in Figure 1. Visible light is absorbed by the sensitizer dye, typically [RuL₂(SCN)₂] (L = 4,4'-dicarboxy-2,2'-bipyridyl). Electron injection from the excited state of the ruthenium dye into the conduction band of the TiO₂, Reaction (1), is followed by the subsequent regeneration of the dye by hole transfer from the dye cation to the HTM, Reaction (2). In a functioning device, the resulting charge carriers (electrons in the TiO₂ and holes in the HTM) are transported through their respective phases to external contacts. Interfacial recombination pathways act as a loss mechanism in competition with these transport processes. The photoinjected electrons in the TiO₂ have two possible recombination pathways: Direct recombination with cations of the dye, Reaction (3), or with the HTM, Reaction (4).



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