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Excitation-Wavelength Dependence of Photoinduced Charge Injection at the Semiconductor-Dye Interface: Evidence for Electron Transfer from Vibrationally Hot Excited States[a]

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Abstract. Heterodyad systems composed of a redox photosensitizer adsorbed on the surface of a wide band gap semiconductor were designed in a way that the $\upsilon' = 0$ energy level of the electronically excited state of the dye lies below the bottom of the conduction band of the solid. Under these conditions, the quantum yield of the charge injection from the sensitizer into the conduction band of the solid was found to depend upon the excitation photon energy. This observation provides an evidence that interfacial charge transfer is occurring prior to nuclear relaxation of the sensitizer's excited state. It allows the use of a simplified kinetic model and offers an easy experimental path to the determination of the electronic coupling that controls the rate of the ultrafast injection process.

Introduction

Dye sensitization of wide band gap semiconductors *via* photoinduced interfacial electron transfer is at the basis of technologically important processes in photography and xerography. In the last decade, redox sensitization of oxide nanoparticles has found additional applications in photoelectrochemical solar-energy conversion [1].

Charge injection from an electronically excited molecular state S* into a wide continuum of acceptor levels constituting the conduction band of a semiconductor (SC) is one of the simplest photochemical surface reactions (*Eqn. 1*). It is, however, a rather special process, where no defined free energy is associated with the electron transfer. The reaction can, in fact, choose its energetic path to yield electrons within the band that are characterized by various kinetic energies.

Absorption of photons, whose energy $h\nu$ is larger than the electronic excitation energy $\Delta E_{0,0}$ of the dye, leads to the population of higher vibronic levels $S^*(\upsilon' > 0)$. Relaxation of those vibrationally excited intramolecular states (*Eqn. 2*) and of the whole system along the classical reaction coordinate are expected to compete with the electron-transfer process [2]. Under these conditions, the occurrence of the charge transfer from undefined donor energy levels prevents the description of the reaction by a general kinetic model.

Results and Discussion

cis-[Bis(4,4'-dicarboxy-2,2'-bipyridyl)bis(thiocyanato)]ruthenium(II) (**1**) is an efficient redox sensitizer of titanium dioxide, a 3.2-eV-bandgap semiconductor. Carboxylic groups carried by the ligands provide a good anchoring of the dye on the acidic surface of TiO_2. Absorption of visible light by the complex is due to a d-π^* metal-to-ligand charge-transfer (MLCT) transition that causes in the excited state an increase of the electronic population of the ligand that is linked to the surface. An optimum electronic coupling is thus ensured between the dye excited state and the acceptor levels manifold of the semiconductor. Upon irradiation, the adsorbed dye has been found to inject an electron into the solid with a quantum yield approaching unity [3]. Recently, ultrafast laser flash photolysis was applied to dye-sensitized, transparent, nanocrystalline TiO_2 films. Experimental results showed that electron injection from the MLCT excited state of **1** into the conduction band of TiO_2 occurs within 130 fs ($k_{inj} = 8 \cdot 10^{1}$ s^{-1}) [4]. The lifetime of the dye excited state in solution being $\tau \cong 50$ ns, the charge-separation reaction (*Eqn. 1*) appeared to be more than five orders of magnitude faster than the competing natural decay of S* (*Eqn. 3*).

$$S \mid SC + h\nu \rightarrow S^* \mid SC \xrightarrow{k_{inj}} S^+ \mid (e^-)\,SC \qquad (1)$$

$$S^*(\upsilon' > 0) \mid SC \xrightarrow{k_r} S^*(\upsilon' = 0) \mid SC + \text{heat} \qquad (2)$$

$$S^* \mid SC \xrightarrow{k_d} S \mid SC + \text{energy} \qquad (3)$$

$$S^+ \mid (e^-)\,SC \xrightarrow{k_b} S \mid SC \qquad (4)$$

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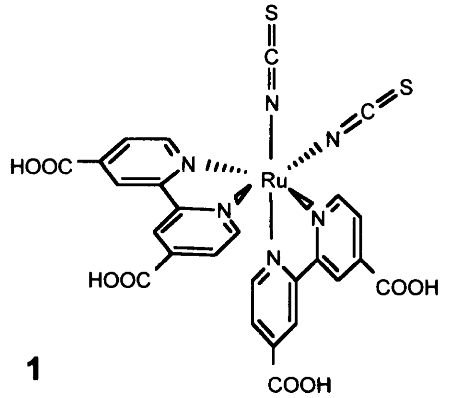
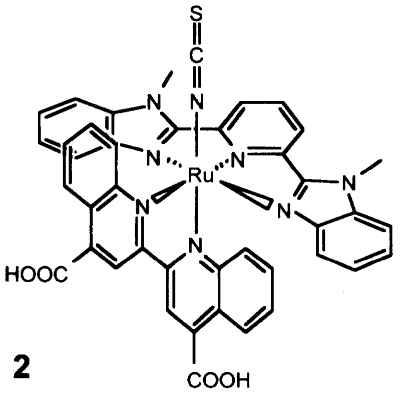


1

$\Delta E_{0,0}$ = 1.75 eV
ϕ^0 (S^+/ S) = + 1.10 V / NHE



2

$\Delta E_{0,0}$ = 1.60 eV
ϕ^0 (S^+/ S) = + 1.60 V / NHE

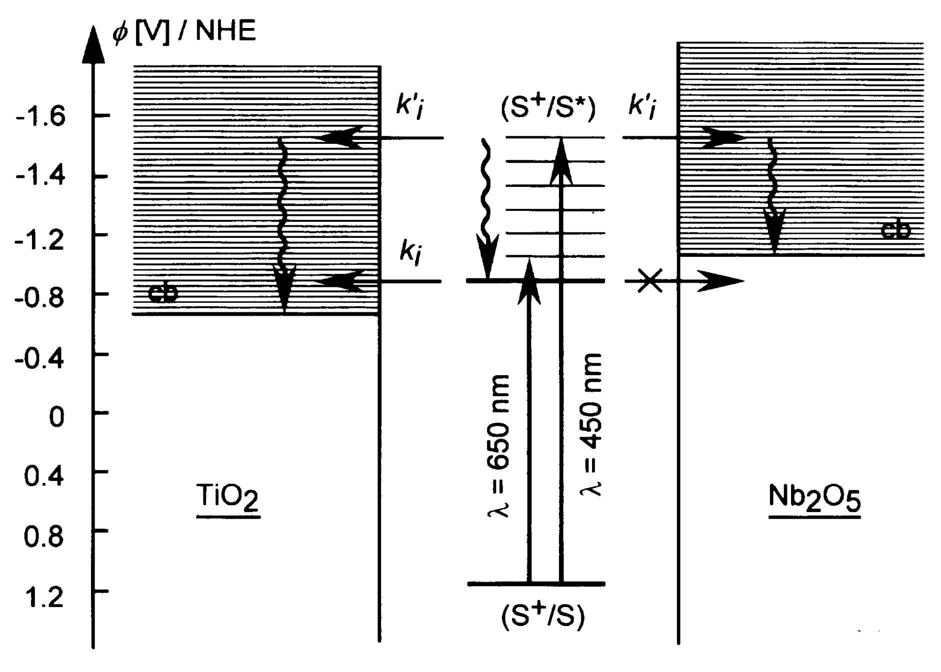


Fig. 1. *Energetics of photoinduced electron transfer from the excited state of dye sensitizer 1 to the conduction-band acceptor levels of* TiO_2 *and* Nb_2O_5. On Nb_2O_5, only hot vibronically excited states formed upon excitation at wavelengths $\lambda \leq 650$ nm should be thermodynamically able to inject electrons in the solid.

Similar very high rate constants for interfacial electron-transfer processes were observed for other efficient redox sensitizers of TiO_2 [5]. In all cases, the absorption spectrum of the dye was not affected by surface adsorption onto the semiconductor. Formation of a ground-state charge-transfer complex and resonant electron injection upon light excitation could therefore be ruled out. In complex **1**, vibrational relaxation of the excited state is expected to take place within a few picoseconds ($k_r \cong 10^{12}\,s^{-1}$). The observed ultrafast kinetics for interfacial electron transfer would thus preclude complete nuclear relaxation of the dye excited state prior to reaction.

In the same medium, the conduction band of niobium pentoxide (Nb_2O_5) is *ca.* 0.2–0.3 eV higher in energy than that of TiO_2 [6]. As a consequence, the $\upsilon' = 0$ level of the MLCT excited state of compound **1** lies below the bottom edge of the conduction band of this material. On Nb_2O_5, no electron transfer to the solid can thus take place from the vibrationally relaxed excited state of the dye. However, if electron injection from a hot vibronic excited state of the sensitizer is able to compete successfully with its vibrational relaxation ($k_{inj} \geq k_r$), charge injection should become possible for $\lambda < 650$ nm (*Fig. 1*). An excitation-wavelength dependence of the quantum yield for charge injection would be expected in this case.

Monitoring of the sensitizer's ground state bleaching signal upon nanosecond laser flash photolysis of the Ru^{II} complex clearly showed biphasic kinetic behavior. Excited dye molecules that do not inject in the solid produce a recovery of the ground-state absorption within a few tens of nanoseconds (*Eqn. 3*). On the other hand, the dye cation S^+, produced by the photoinduced electron-transfer process, recaptures the injected electron (*Eqn. 4*) in the microsecond time domain. Both kinetic steps are easily separated. Quantitative evaluation of their respective amplitudes allows for the determination of the injection quantum yield Φ_{inj} at any wavelength, independently of the absorption spectrum of the dye. Results reported in *Fig. 2, a* show a strong excitation-wavelength dependence of Φ_{inj} between $\lambda = 650$ nm, the onset of injection, and $\lambda = 500$ nm, where the charge-transfer quantum yield reached a plateau value of 50%. This yield reflects the kinetic competition between electron transfer and vibrational relaxation of the excited state: $\Phi_{inj} = k_{inj} / (k_{inj} + k_r)$. The maximum value obtained thus indicates that the injection rate constant k_{inj} in this case is at most comparable to k_r. Measurements conducted under identical conditions with dye **1** adsorbed on TiO_2 gave an injection quantum yield close to unity that was independent of the excitation wavelength (*Fig. 2, b*).

Another ruthenium complex, [(4,4'-dicarboxy-2,2'-biquinoline)(2,6-bis(1'-methylbenzimidazol-2'-yl)pyridine)(thiocyanato)]ruthenium(II) (**2**) is characterized by an oxidation potential 0.5 V higher compared to that of the $Ru^{II}(dcbpy)_2(NCS)_2$ (**1**) dye [7]. Upon adsorption onto TiO_2, carboxylic groups provide a good coupling between the biquinoline ligand that carries the LUMO of the molecule and the empty acceptor levels of the solid. The thermodynamic situation prevailing in this case is similar to that of **1**|Nb_2O_5, in as much as the $\upsilon' = 0$ level of the sensitizer's excited state lies lower than the bottom of the semiconductor conduction band. Comparable results were indeed obtained with the **2**|TiO_2 system: Although light absorption of the dye extends well above 700 nm, charge injection decreases at excitation photon energy below 1.8 eV. Above that threshold, Φ_{inj} increases steeply to reach unity at 2.1 eV ($\lambda = 580$ nm). The subsequent decrease of the injection quantum yield at shorter wavelengths is probably due to the excitation of a differ

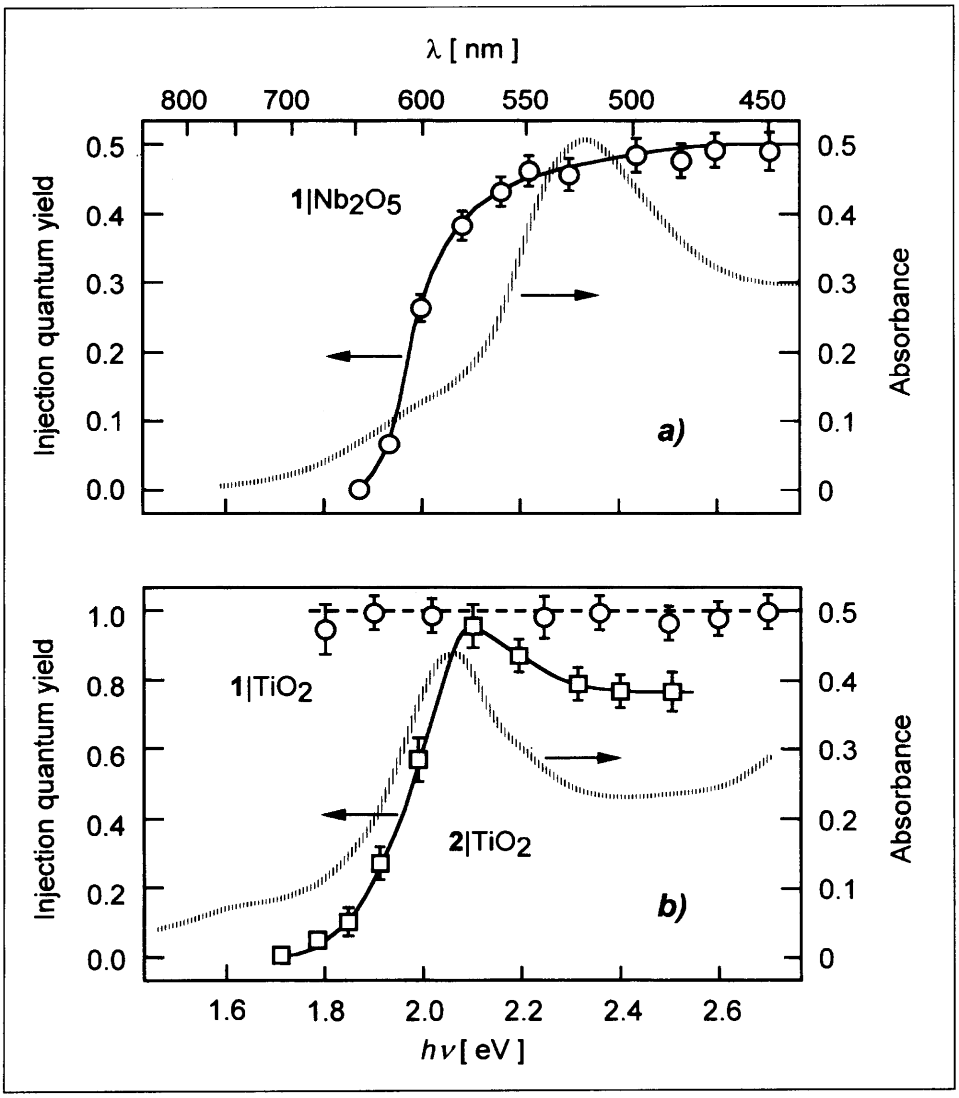


Fig. 2. *Dependence of electron-injection quantum yield upon excitation photon energy. a)* Results obtained for Nb_2O_5 nanocrystalline films sensitized by adsorption of complex **1**. *b)* Yields obtained for TiO_2 layers dyed by sensitizers **1** (--○--) and **2** (–□–), respectively. Ground-state absorption spectra of sensitizers **1** (*a*) and **2** (*b*) are displayed for direct comparison. In all cases, propylene carbonate was used as a solvent. 0.1 M Trifluoro-methanesulfonic acid was added in system **2**|TiO_2.

ent MLCT state involving electron transfer from Ru^{II} to the benzimidazol-pyridine ligand.

These observations of an excitation-wavelength dependence of the charge-injection process are the first reported evidence that photoinduced electron transfer from a molecular excited state to a continuum of acceptor levels can take place prior to vibrational relaxation. The occurrence of the electron-transfer process from a single prepared state allows in these present cases the use of a simplified model of the rate constant k_{inj} for charge injection derived from *Fermi*'s golden rule [8]:

$$k_{\mathrm{inj}} = \frac{2\pi}{\hbar} |\mathrm{H}|^2 \frac{1}{h\omega} \qquad (5)$$

In *Eqn. 5*, the actual density of acceptor states is approximated by the reciprocal energy level spacing $1/h\omega$ of the S^+ product oscillator. By admitting $\bar{\omega} = 1500$ cm^{-1}, an electronic coupling matrix element $|H| = 100\ cm^{-1}$ is estimated from the value of the injection rate constant $k_{\mathrm{inj}} = 8 \cdot 10^{12}\ s^{-1}$ obtained for **1***|TiO_2. This rather modest number calculated for the electron coupling (*ca.* 0.5 *kT*) justifies the use of the *Fermi* golden rule that implies a nonadiabatic charge-transfer process.

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