175. Picosecond Time Resolved Studies of Photosensitized Electron Injection in Colloidal Semiconductors

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Dedicated to Prof. *Tino Gäumann* on the occasion of his 60th birthday

(11.VI.85)

Using a single picosecond pulse from a frequency-doubled Nd:YAG-mode-locked laser for excitation, we measured directly the rate of electron injection from the excited singlet state of eosin in the conduction band of colloidal TiO_2 particles. The rate constant for interfacial electron transfer is $9.5 \times 10^8 s^{-1}$ at 25°C and pH 3.

Introduction. – Several years ago, we initiated photochemical investigations with colloidal semiconductor dispersions [1]. One advantage of these systems is their transparent nature allowing for the application of laser photolysis to probe the dynamics of interfacial charge transfer reactions. Recently, we have applied this technique to investigate the sensitization of colloidal TiO_2 by eosin (EO) [2]. However, the time resolution of these experiments was insufficient to unravel the dynamics of charge injection from the excited chromophore in the conduction band of the semiconductor. Using ps laser excitation, we have now succeeded to directly monitor this interfacial electron-transfer reaction.

Experimental. – Colloidal solns. of TiO_2 (particle diameter 12 nm) were prepared as described in [3]. At pH 4, the TiO_2 soln. is stable over at least several days in the absence of protective agent. Eosin Y disodium salt *(Fluka)*, was purified as described in [2]. Deionized H_2O was distilled twice from a quartz still.

The second or third harmonic of a double beam, passively mode-locked Nd:YAG laser was used to excite the EO. The full width at half maximum amplitude of the pulse at 355 and 532 nm was 35 and 40 ps, resp. Details concerning the fast detection system used to monitor absorbance changes have been given in [4].

Results and Discussion. – *Fig. 1* shows transient absorption spectra obtained from the 355-nm ps laser photolysis of EO in H_2O (pH 10). In *Fig. 1a,* we record the absorbance change in the 420- to 650-nm region during and immediately after the light pulse. Concomitantly with the bleaching of the ground state at 515 nm, one observes the formation of a broad absorption below 460 nm. In *Fig. 1b,* we examine the behavior of this absorption on a longer time scale. Most of the signal decays within a few ns. The kinetic evaluation yields a lifetime of 1.2 ± 0.4 ns. The absorption band below 460 nm is attributed to the excited singlet (S_1) state of EO. This assignment is consistent with the fluorescent lifetime of EO which in alkaline water is 1.4 ns [5].

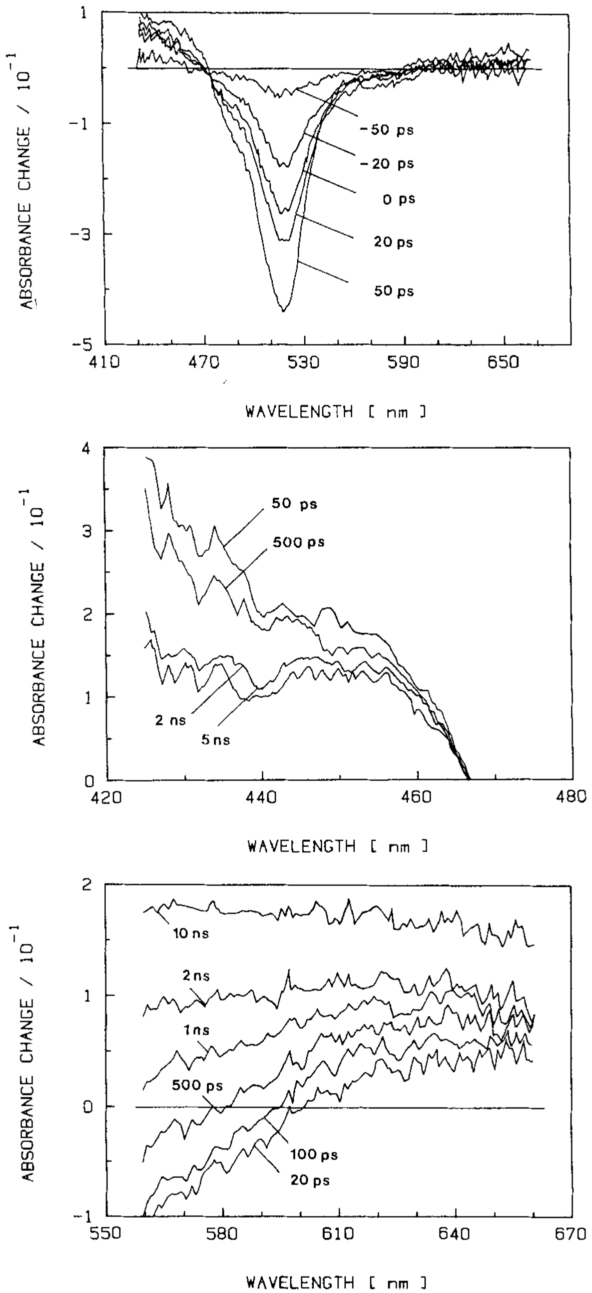

Fig. 1. *Picosecond laser flash photolysis studies of EO in H_2O* (pH 10). Solutions saturated with Ar. The traces presented are averaged from 6 signals, time zero is the maximum of the exciting laser pulse (λ_{ex} = 355 nm, pulse energy 1 mJ). *a*) Transient spectral changes within the laser pulse of 4.1 × 10^{-5} M EO; *b*) Spectral changes in the short-wavelength domain following laser excitation of 1.5 × 10^{-4} M EO; *c*) Spectral changes in the long-wavelength domain following laser excitation of 1.5 × 10^{-4} M EO.

The temporal behavior of the absorption in the red part of the spectrum is shown in *Fig. 1c.* One observes here the gradual build up of a broad peak which grows with a time constant of 1.4 ± 0.3 ns and is stable in the ns domain. This spectrum is assigned to the EO triplet state EO(T_1) which is formed *via* intersystem crossing from EO(S_1). EO(T_1) has an absorption maximum around 520 nm with an extinction coefficient of $3 \times 10^4 \mathrm{M}^{-1}\mathrm{cm}^{-1}$ [2]. As expected, the triplet growth kinetics are identical with that observed in *Fig. 1b* for the EO(S_1) decay within the accuracy of our measurements. Using $\phi_T = 0.76$ [6], one obtains for the rate constant of intersystem crossing the value $k_{ISC} = 5 \times 10^8 \mathrm{s}^{-1}$.

In *Fig. 2,* we excite EO by the 532-nm ps laser pulse in the presence of colloidal TiO_2 and observe the spectral changes in the 415- to 495-nm domain. This wavelength region was selected, since it was known from earlier studies [2] [7] employing ns time-resolved laser technique, that, under the experimental conditions chosen, the radical cation of eosin (EO^+) is formed which has a characteristic maximum at 470 nm. Indeed, *Fig. 2* shows that there is a pronounced increase of the absorbance in this region following excitation of EO. In contrast to TiO_2-free solutions, where the appearance of the EO(S_1) absorption followed the leading edge of the laser pulse, the increase occurs more slowly and, in fact, is clearly discernable on a time scale of several hundred ps, reaching a plateau after *ca.* 1 ns. The transient absorption in the 430–490-nm region observed in the presence of TiO_2 is much stronger than that of the EO(S_1) in *Fig. 1b.* (When comparing these signals, it should be noted that the EO concentration in *Fig. 2* is 15 times smaller than in *Fig. 1b.*) The kinetics of the growth process were analyzed at 430 and 490 nm, and were found to obey a first-order law. The rate constant derived from semilogarithmic absorbance *vs.* time plots at these two wavelengths is $(2.5 \pm 0.5) \times 10^9 \mathrm{s}^{-1}$.

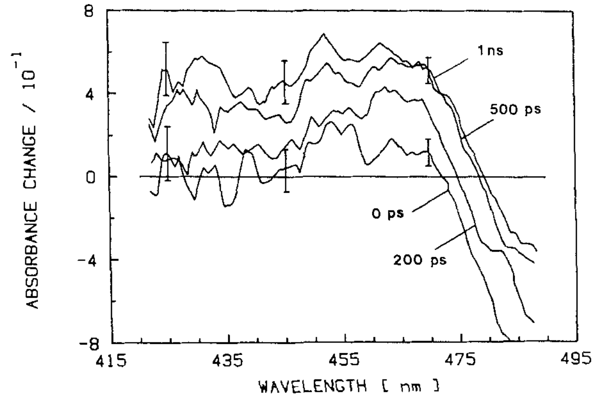

Fig. 2. *Picosecond laser flash photolysis of 10^{-5} M EO in H_2O* (pH 3) *in the presence of 0.5 g/l TiO_2.* Growth of the EO^+ absorption following excitation at 532 nm (pulse energy 1 mJ). Signals presented are averages from 18 laser shots.

The observations in *Fig. 2* are interpreted in terms of electron injection from EO(S_1) in the conduction band of the semiconductor particles.

$$\mathrm{EO(S_1)} \rightarrow \mathrm{EO^+} + e^-_{cb}(\mathrm{TiO_2}) \qquad (1)$$

The occurrence of such a reaction in acidic solutions of EO in the presence of colloidal TiO_2 has already been ascertained in [2] [7]. In particular, the quantum yield for charge injection at pH 3 has been determined as 38% under the same conditions as employed in *Fig. 2, i.e.* at $[TiO_2] = 0.5$ g/l and $[EO] = 1 \times 10^{-5}$ M. In such a solution, the TiO_2-particle concentration is 3.1×10^{-7} M and there is an average of 32 EO molecules per particle. The contribution of concentration quenching to the deactivation of $EO(S_1)$ is not significant under these conditions. The growth of the absorbance in the ps time domain observed in *Fig. 2* reflects, therefore, directly the rate of electron transfer from $EO(S_1)$ into the TiO_2-conduction band. Note that both $EO(S_1)$ and EO^+ contribute to the transient spectrum. However, between 420 and 470 nm the extinction coefficient of the former is much smaller than that of the latter since the charge injection is associated with a net absorption growth in this wavelength region. The spectral data in *Fig. 2* are not corrected for ground-state bleaching. This explains why the apparent absorption maximum for EO^+ is shifted from 475 to around 465 nm.

Using the relation $k_{inj} = \phi(EO^+)/\tau$, where $\tau = 1/k_{obs} = 400$ ps is the time constant for the growth of the EO^+ absorption in *Fig. 2*, one obtains for the rate constant for electron injection the value $(9.5 \pm 1.4) \times 10^8 s^{-1}$. This is in good agreement with our previous estimation of $k_{inj} = 8.5 \times 10^8 s^{-1}$ [2] which was based on the assumption that the radiationless deactivation of $EO(S_1)$ adsorbed onto TiO_2 occurs at the same rate as in MeOH. The present results confirm this hypothesis.

For further interpretation of these results, we evoke the current theory of nonadiabatic electron-transfer reactions [8]. The rate constant for interfacial electron transfer may be approximated by the expression

$$k_{inj} = \nu_o \exp(-\beta(r - r^o)) \exp\left(-\frac{(\Delta G^o + \lambda)^2}{4\lambda kT}\right) \quad (2)$$

In *Eqn. 2*, $\nu_o \simeq 10^{13} s^{-1}$ is the frequency for nuclear reorganization, $\beta \approx 1.2$ Å^{-1} is the damping coefficient and $(r - r^o)$ is the tunneling distance of the electron, which we assume to be equal to the distance between the center of the EO molecule and the first layer of oxygen lattice ions at the TiO_2 surface. It is likely that the chemisorption of EO takes place *via* H-bonding involving its carboxylate and phenolic OH group. In this case $r - r^o = 3$ Å. The term ΔG^o is the free-energy change associated with charge injection. Assuming that the free energy of adsorption of $EO(S_1)$ and desorption of EO^+ are equal, $\Delta G^o = -0.9$ eV [2]. The reorganization energy for heterogeneous electron transfer λ_{het} is related to that for the homogeneous exchange reaction, *i.e.*

$$EO(S_1) + EO^+ \rightarrow EO^+ + EO(S_1) \quad (3)$$

via

$$\lambda_{het} > \tfrac{1}{2} \lambda_{ex} \quad (4)$$

The inner sphere contribution to λ_{ex} is not known while the outer sphere part is estimated to be between 0.4 and 1.1 eV. The uncertainty arises from the lack of precise knowledge of the activated complex configuration. EO has a disk-like shape and the two values are calculated for a distance between the center of $EO(S_1)$ and EO^+ in the activated complex of 6 Å (sandwich configuration) and an edge-to-edge distance of 14 Å, respectively. Using *Eqn. 2*, one obtains from the experimentally observed injection rate $\lambda_{het} \simeq 0.4$ eV.

In conclusion, we have presented here the first ps time-resolved observations of a photosensitized charge injection process in semiconductor particles. EO monolayers adsorbed on SnO_2 glass have been previously examined by ps laser technique [5]. However, only concentration quenching and no charge injection was observed. Very recently, sub-nanosecond processes in the quenching of copper phtalocyaninetetrasulfonate adsorbed onto TiO_2 have been reported by *Kirk et al.* [9]. In this case, since a 355-nm light pulse was used, it is probable that the semiconductor particle instead of the dye was excited.

Our results confirm that electron transfer from EO(S_1) into the TiO_2-conduction band is a very rapid reaction. Undoubtedly, the intimate contact between dye and semiconductor surface favors charge injection. Similar effects have been observed recently in the sensitization of colloidal TiO_2 by a H_2O cleavage sensitizer, *i.e.* ruthenium tris(2,2′-bipyridyl-4,4′-dicarboxylate) [10]. A particularly interesting future field for application of the ps laser technique should be the newly discovered surface-derivatized TiO_2 particles which have been shown to be effective in the H_2O cleavage by visible light [11].

This work has been generously supported by the *Natural Sciences and Engineering Research Council of Canada* and by the *Swiss National Science Foundation*, to whom we are very grateful.

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