

## 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 60<sup>th</sup> birthday

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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<sub>2</sub> particles. The rate constant for interfacial electron transfer is  $9.5 \times 10^8 \text{ s}^{-1}$  at 25°C and pH 3.

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**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<sub>2</sub> 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<sub>2</sub> (particle diameter 12 nm) were prepared as described in [3]. At pH 4, the TiO<sub>2</sub> 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<sub>2</sub>O 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<sub>2</sub>O (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  $1.2 \pm 0.4$  ns. The absorption band below 460 nm is attributed to the excited singlet (S<sub>1</sub>) state of EO. This assignment is consistent with the fluorescent lifetime of EO which in alkaline water is 1.4 ns [5].

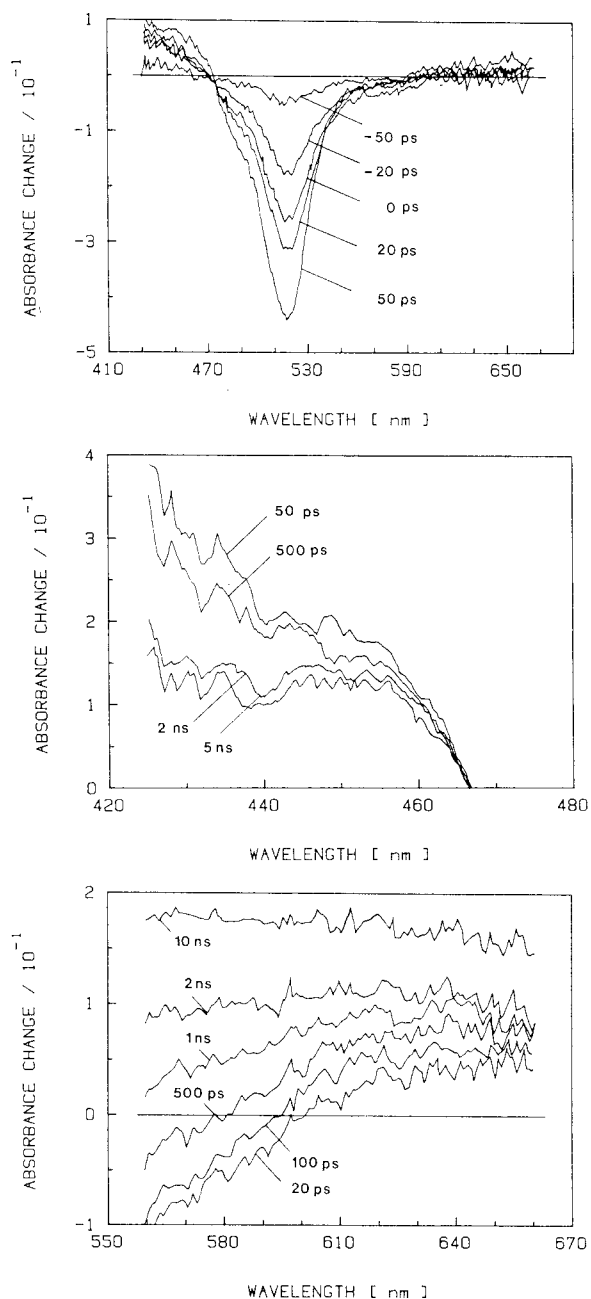
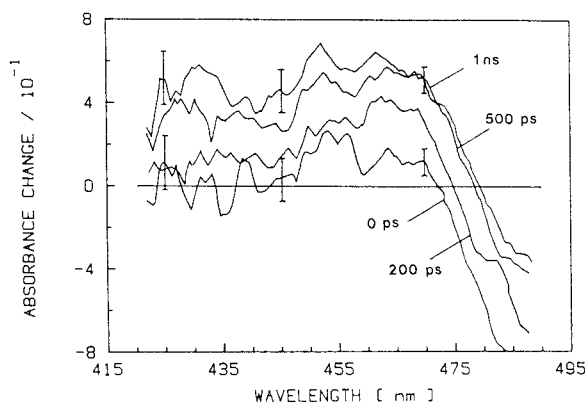


Fig. 1. Picosecond laser flash photolysis studies of EO in H<sub>2</sub>O (pH 10). Solutions saturated with Ar. The traces presented are averaged from 6 signals, time zero is the maximum of the exciting laser pulse ( $\lambda_{ex} = 355$  nm, pulse energy 1 mJ). a) Transient spectral changes within the laser pulse of  $4.1 \times 10^{-5}$  M EO; b) Spectral changes in the short-wavelength domain following laser excitation of  $1.5 \times 10^{-4}$  M EO; c) Spectral changes in the long-wavelength domain following laser excitation of  $1.5 \times 10^{-4}$  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  $1.4 \pm 0.3$  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  $3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  [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  $k_{ISC} = 5 \times 10^8 \text{ s}^{-1}$ .

In *Fig. 2*, we excite EO by the 532-nm ps laser pulse in the presence of colloidal  $\text{TiO}_2$  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  $\text{TiO}_2$ -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  $\text{TiO}_2$  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. 2.* Picosecond laser flash photolysis of  $10^{-5} \text{ M}$  EO in  $\text{H}_2\text{O}$  (pH 3) in the presence of 0.5 g/l  $\text{TiO}_2$ . Growth of the  $EO^+$  absorption following excitation at 532 nm (pulse energy 1 mJ). Signals presented are averages from 18 laser shots.

*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  $(2.5 \pm 0.5) \times 10^9 \text{ s}^{-1}$ .

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



The occurrence of such a reaction in acidic solutions of EO in the presence of colloidal  $\text{TiO}_2$  has already been ascertained in [2] [7]. In particular, the quantum yield for charge

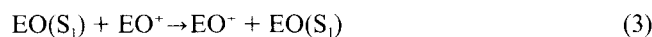
injection at pH 3 has been determined as 38% under the same conditions as employed in Fig. 2, *i.e.* at  $[\text{TiO}_2] = 0.5 \text{ g/l}$  and  $[\text{EO}] = 1 \times 10^{-5} \text{ M}$ . In such a solution, the  $\text{TiO}_2$ -particle concentration is  $3.1 \times 10^{-7} \text{ M}$  and there is an average of 32 EO molecules per particle. The contribution of concentration quenching to the deactivation of  $\text{EO}(\text{S}_1)$  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  $\text{EO}(\text{S}_1)$  into the  $\text{TiO}_2$ -conduction band. Note that both  $\text{EO}(\text{S}_1)$  and  $\text{EO}^+$  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  $\text{EO}^+$  is shifted from 475 to around 465 nm.

Using the relation  $k_{\text{inj}} = \phi(\text{EO}^+)/\tau$ , where  $\tau = 1/k_{\text{obs}} = 400 \text{ ps}$  is the time constant for the growth of the  $\text{EO}^+$  absorption in Fig. 2, one obtains for the rate constant for electron injection the value  $(9.5 \pm 1.4) \times 10^8 \text{ s}^{-1}$ . This is in good agreement with our previous estimation of  $k_{\text{inj}} = 8.5 \times 10^8 \text{ s}^{-1}$  [2] which was based on the assumption that the radiationless deactivation of  $\text{EO}(\text{S}_1)$  adsorbed onto  $\text{TiO}_2$  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

$$k_{\text{inj}} = \nu_0 \exp(-\beta(r - r^0)) \exp\left(-\frac{(\Delta G^0 + \lambda)^2}{4\lambda kT}\right) \quad (2)$$

In Eqn. 2,  $\nu_0 \approx 10^{13} \text{ s}^{-1}$  is the frequency for nuclear reorganization,  $\beta \approx 1.2 \text{ \AA}^{-1}$  is the damping coefficient and  $(r - r^0)$  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  $\text{TiO}_2$  surface. It is likely that the chemisorption of EO takes place *via* H-bonding involving its carboxylate and phenolic OH group. In this case  $r - r^0 = 3 \text{ \AA}$ . The term  $\Delta G^0$  is the free-energy change associated with charge injection. Assuming that the free energy of adsorption of  $\text{EO}(\text{S}_1)$  and desorption of  $\text{EO}^+$  are equal,  $\Delta G^0 = -0.9 \text{ eV}$  [2]. The reorganization energy for heterogeneous electron transfer  $\lambda_{\text{het}}$  is related to that for the homogeneous exchange reaction, *i.e.*



*via*

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

The inner sphere contribution to  $\lambda_{\text{ex}}$  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  $\text{EO}(\text{S}_1)$  and  $\text{EO}^+$  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  $\lambda_{\text{het}} \approx 0.4 \text{ eV}$ .

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<sub>2</sub> 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 phthalocyaninetetrasulfonate adsorbed onto TiO<sub>2</sub> 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<sub>1</sub>) into the TiO<sub>2</sub>-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<sub>2</sub> by a H<sub>2</sub>O 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<sub>2</sub> particles which have been shown to be effective in the H<sub>2</sub>O cleavage by visible light [11].

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