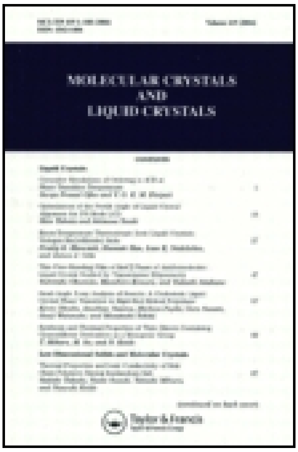

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Picosecond Time Resolved Electron Injection from Excited Cresyl Violet Monomers and Cd_3P_2 Quantum Dots into TiO_2

R. Kietzmann [a], F. Willig [a], H. Weller [a b], R. Vogel [a b], D. N. Nath [a], R. Eichberger [a b], P. Liska [a c] & J. Lehnert [a]

[a] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000, Berlin 33, W. Germany

[b] Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Glienicker Str. 100, D-1000, Berlin 39, W. Germany

[c] Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015, Lausanne, Switzerland

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PICOSECOND TIME RESOLVED ELECTRON INJECTION FROM EXCITED CRESYL VIOLET MONOMERS AND Cd_3P_2 QUANTUM DOTS INTO TiO_2

R. KIETZMANN, F. WILLIG, H. WELLER*, R. VOGEL*, D. N. NATH, R. EICHBERGER*, P. LISKA** AND J. LEHNERT
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, W. Germany
*Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Glienicker Str. 100, D-1000 Berlin 39, W. Germany
**Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

Abstract Picosecond time resolved luminescence was employed for monitoring the decay of electronic excited reactants on the surface of oxide semiconductors. Decay of cresyl violet monomers was determined on TiO_2 and on α-Al_2O_3 by measuring decay curves over a wide range of very low coverages. The decay curves showed a characteristic opposite dependence on coverage on the oxide semiconductor with a low conduction band edge, i.e. TiO_2, compared to the oxide semiconductor with a high conduction band edge, i.e. α-Al_2O_3. The dominating time constant for cresyl violet monomer decay was in the range of 280 ps on TiO_2 and 560 ps on α-Al_2O_3. In both cases quenching was attributed to electron transfer.

At room temperature the decay of excited Cd_3P_2 quantum dot luminescence was faster than 1 ps when the dots were attached to TiO_2 colloidal particles in solution. The ultrafast decay was ascribed to electron injection.

Keywords: Electron transfer, picosecond time resolved luminescence, adsorbed dye molecules, Cd_3P_2 *quantum dots,* TiO_2, α-Al_2O_3

INTRODUCTION

Electron-injection from excited dye molecules into certain polycrystalline TiO_2 electrodes has recently received considerable attention since Grätzel et al. reported high photocurrent yields in the range of 40 to 80 percent electrons per incident photons and open circuit voltages of 400 mV /1/. Obviously the excited dye molecules decay in this case with high yield via electron transfer into TiO_2. This is a remarkable observation. Earlier and recent studies of dye sensitized injection into single crystal oxide semiconductor electrodes resulted in much lower injection yields of the order of 10^{-2} injected electrons per absorbed photon /2/.

It is well known that oxide semiconductors can show large time dependent shifts of their ionisation energy even in UHV and can release e.g. oxygen from the lattice /3/. Metastable oxides, e.g. of Al_2O_3, develop acceptor states deep in the band gap that abstract electrons from e.g. perylene molecules already in the dark /4/. Thus, we have to consider two modifications of the surface that can affect the decay of an excited molecule via electron transfer to an oxide surface. Firstly, a layer of different chemical composition from the bulk and of finite thickness can be formed at the surface that decreases or even prevents the overlap of bulk electronic wavefunctions with orbitals of adsorbed molecules. Secondly, electrons can be transferred from adsorbed molecules to surface acceptor sites in the band gap of the oxide material. The latter reaction should be even more effective for molecules in the excited state since the donor orbital of an excited molecule lies much higher than that of the ground state and the density of acceptor sites in the band gap often increases towards the edge of the conduction band.

In this paper we present picosecond time resolved luminescence measurements of the quenching of firstly, excited cresyl violet monomers and secondly, of excited Cd_3P_2 quantum dots attached to TiO_2. For comparison fluorescence decay of cresyl violet monomers was measured on an oxide ceramic, i.e. transparent platelets of α-Al_2O_3, whose surface reactivity is expected to be small in comparison with metastable phases of Al_2O_3 and with most other oxide materials. We removed the ambiguity in the interpretation of decay curves measured at one given surface coverage by measuring decay curves over a wide range of small coverages. This reveals a characteristic opposite concentration dependence of the fluorescence decay curves on TiO_2, where electron injection into the conduction band takes place, from that observed on α-Al_2O_3, where the electron injection channel is not available. This way we identified unambiguously the decay behavior of excited monomer dyes and separated it from the well known complicated concentration quenching effects /5,6/.

Extremely fast luminescence quenching was found when TiO_2 was attached with a chemical preparation method to Cd_3P_2 colloids. The diameter of the latter was prepared sufficiently small to obtain a quantum dot where the excited electron was lifted high enough to reach the conduction band of TiO_2. Thus, it was established that extremely fast electron injection with a time constant <1 ps can be achieved even when the interface is prepared by applying wet chemistry methods.

EXPERIMENTAL

Aqueous solutions of cresyl violet (λ-Physik) were prepared at pH 3.5 with triple quartz distilled water. The pH was chosen in accordance with recommendations for dye molecule adsorption at TiO_2 electrodes /1,7/.

Polycrystalline TiO_2 electrodes were prepared on Ti sheets as described before /1/. For each dye solution a new spot on the sheet electrode was chosen to measure the decay curve. Transparent platelets of α-Al_2O_3 (Cerac) were dipped into the dye solution for 15 min and then removed for the measurement of the decay curves.

TiO_2 colloids were attached to small Cd_3P_2 colloids applying the wet chemistry method described elsewhere /8/.

The light source for the measurements of the fluorescence decay curves was a cavity dumped rhodamine 6 G dye laser (344S, 375 Spectraphysics) pumped by a mode-locked Argon ion laser (342, 171 Spectraphysics) to yield 6 ps wide (409 Spectraphysics autocorrelator) pulses at 591 nm at a repetition frequency chosen in the kHz range. The laser beam passed through a 591 nm interference filter before reaching the sample. Fluorescence was detected at 90 degrees to the incident laser beam and was time resolved with either the single photon counting method applying a proximity focussed microchannel photomultiplier (Hammamatsu R 1564 U-01) or with a Synchroscan Streak Camera (Imacon 500, Hadland) /9/. The fluorescence light passed through 3 RG 630 filters (Schott) before reaching the detector.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Fluorescence decay of adsorbed dye molecules

a) without electron injection

Fig. 1 shows the fluorescence decay of rigid cresyl violet molecules adsorbed from a pH 3.5 aqueous solution onto transparent platelets of

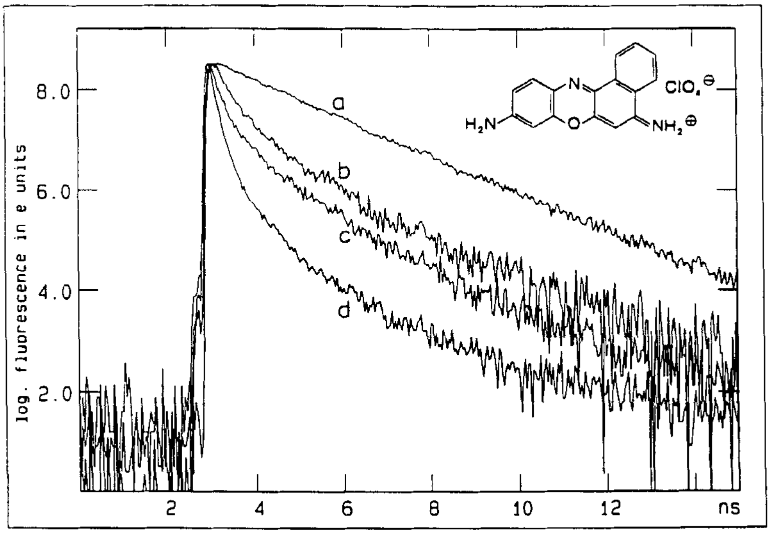

FIGURE 1 Coverage dependence of decay curves of cresyl violet on α-Al_2O_3 in the range of increasing low coverages (b-d).

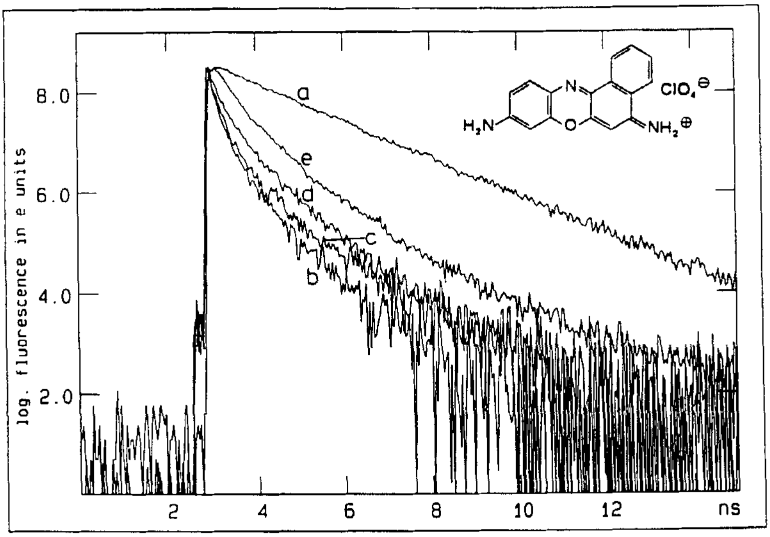

FIGURE 2 Coverage dependence of decay curves of cresyl violet on polycrystalline TiO_2 electrodes in the range of increasing low coverages (b-e)

the wide band gap ceramic insulator α-Al_2O_3. The conduction band edge of this oxide lies well above the excited donor orbital of the cresyl violet molecules /10/.

Before each measurements a new platelet was dropped into the respective dye solution for 15 min and then removed. The fluorescence decay curves were measured immediately after removal of the platelet from the dye solution ("wet" sample) and later after storage for one day in the dark ("dry" sample). The "wet" samples often showed a slightly slower decay than the "dry" samples but these differences were much smaller than those between the decay curves of the different concentrations shown in Fig. 1. The dye concentrations were 10^{-8} M (curve b), 10^{-7} M (curve c), and $3x10^{-7}$ M (curve d). The decay curve of a 10^{-9} M aqueous solution (pH 3) is shown (curve a) for comparison. The decay was the faster and the more non-exponential the higher the dye concentration, i.e. the higher the dye coverage. Such a concentration dependent family of decay curves is already well known for dye adsorption on glass and quartz /6,11/ and also for dye molecules with alkane chains attached that were incorporated into 2-dimensional Langmuir-Blodgett films /12/. The non-exponential decay is caused by direct Förster-type energy transfer to non-fluorescent or spectrally shifted weakly fluorescent dye aggregates at lower dye coverages /5/ and to energy hopping to the aggregates at higher dye coverages /6/. It is important to notice the influence of the dye coverage on the decay curve and in particular that the slowest decay curve is observed at the lowest dye coverage. A multi-exponential fit gave a dominant decay time of 560 ps with 79 percent weight at the lowest dye coverage (10^{-8} M solution, curve b).

b) with electron injection

Fig. 2 shows the fluorescence decay curves of the same dye cresyl violet adsorbed from aqueous solution (pH 3) onto the porous TiO_2 electrodes. In this case the droplet of the dye solution always disappeared in the porous electrodes. Again "wet" and "dry" samples were measured as described above. The decay curves of the "wet" samples were generally slightly slower than those of the"dry" samples shown in Fig. 2. The decay curves correspond to the following dye concentrations: curve b (10^{-9} M), curve c (10^{-8} M), curve d (10^{-7} M) and curve e ($3x10^{-7}$ M). Curve a is again the decay curve of 10^{-9} M cresyl violet in aqueous solution (pH 3) for comparison. It should be noticed that the influence of the dye coverage on the speed of the decay is reversed in Fig. 2 with respect to that seen in Fig.1. At still higher dye coverages ($>3\times10^{-7}$ M solution concentration) the decay on TiO_2 became faster again and followed for even higher coverages the reverse trend similar to that shown for low coverages in Fig. 1. At these higher dye coverages concentration quenching dominates the decay curve of cresyl violet also on TiO_2. We observed this type of reversed concentration dependence at high concentration with many different dyes on surfaces allowing for electron injection /10,13/. In a multi-exponential fit to the fastest decay curve at the lowest dye coverage the dominating time constant was 280 ps with 81 percent contribution. This decay constant is very close to the 210 ps value reported by Hashimoto et al. /14/ for the decay of rhodamine B on TiO_2 powder. The non-exponential decay curve is attributed to electron injection with a distribution of decay times for dye monomers adsorbed at different distances from the TiO_2 surface.

Grätzel and coworkers have suggested /1/ that anchoring of dye molecules on the surface of TiO_2 via a carboxylic group could be important for fast electron injection. Therefore we carried out similar measurements as shown in Figs. 1 and 2 with the rigid dye molecule rhodamine 101 that has a carboxylic acid group. With pH 3.5 dye solution we found almost identical families of curves as shown here in Figs. 1 and 2 for cresyl violet. In particular the fastest decay curve at the lowest dye coverage (10^{-8} M) had a dominant decay constant of 390 ps with 84 percent contribution. Thus we did not find a noticeable influence of the carboxylic group on the speed of electron injection in our measurements.

It is difficult to attribute absolute values to the dye coverages corresponding to the decay curves in Figs. 1 and 2. However very similar shapes and signal heights of decay curves were measured with related dye molecules where alkane chains were attached to the chromophore and a 2-dimensional layer was assembled with the Langmuir-Blodgett technique /15/. From a comparison with these systems we infer that the dye coverages must be very small approaching 10^{-3} at the lowest dye concentrations in Figs. 1 and 2 (10^{-9} to 10^{-8} M). Curves b in Figs. 1 and 2 approach the decay curve of isolated cresyl violet monomers adsorbed on α-Al_2O_3 and on TiO_2 respectively. The non-exponential shape of the decay curves b suggests in both cases a distribution of decay constants that can be attributed to a distribution of different sites on the surface. The conduction band edge of α-Al_2O_3 is out of reach for the donor orbitals of the excited cresyl violet monomer whereas it can reach empty states in the conduction band of TiO_2. We have shown elsewhere /13/ that Franck-Condon limitations do not arise for electron transfer in the latter case as long as the donor orbital lies sufficiently high in the conduction band above the band edge. The fairly slow dominant time constant of only 280 ps in the present system, cresyl violet on TiO_2, suggests that electronic overlap is fairly weak with a distribution of distances and that e.g. vibrations of the adsorbed molecules towards the surface could enhance the speed of electron transfer. Structural details of the adsorption sites are not known. In view of the very low coverage that can be attributed also to curve b in Fig. 1 we interpret the difference between curve a and curve b in Fig. 1 as due to slow electron tranfer quenching of cresyl violet on α-Al_2O_3 involving local acceptor sites in the band gap. The energy and rate constants scheme in Fig. 3 summarizes the results. A fairly high density of shallow and deep electrons traps was found in time resolved photocurrent measurements at the TiO_2 electrodes /15/.

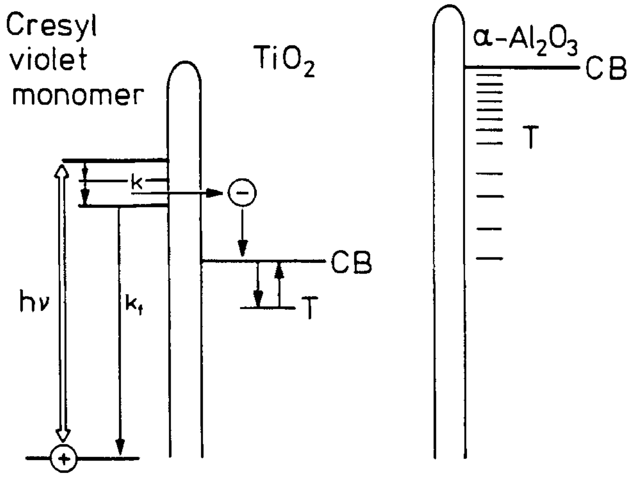

FIGURE 3 Illustration of cresyl violet monomer decay via electron transfer to TiO_2 and α-Al_2O_3 respectively. T=localized electron traps.

2. Luminescence decay of attached Cd_3P_2 quantum dots

Colloids of small band gap semiconductors like CdS and Cd_3P_2 can be prepared with wet chemistry resulting in fairly narrow size distributions /16/. A quantum size effect arises when the particle size is samller than the spatial extension of the exciton in the bulk material /17/. Decreasing the mean diameter of the colloid one can shift the energy of the optically excited electrons in the Cd_3P_2 quantum dots above the conduction band edge of TiO_2. This is similar to choosing a molecule with a donor orbital above the edge of the conduction band. Hetero-colloids can be prepared in solution where TiO_2 colloids are attached to CdS or Cd_3P_2 quantum dots /8/. Luminescence of the Cd_3P_2 particles is virtually not affected by the attached TiO_2 particles as long as the diameter of the former remains large enough to keep the excited eletrons below the conduction band of TiO_2. Luminescence of small diameter e.g. 40 Å Cd_3P_2 or CdS quantum dots is strongly quenched when TiO_2 is attached. It is well known that fast fluorescence quenching of molecules attached to TiO_2 colloids occurs via electron transfer /18/.

Fig. 4 shows the absorption edge and emission spectrum of the Cd_3P_2 particles (uncorrected) used for the experiments presented here. The wavelength of the exciting laser pulse and the detection window for lu-

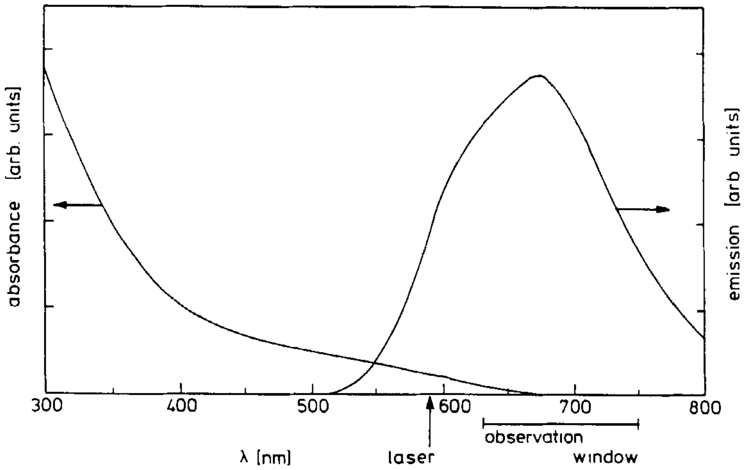

FIGURE 4 Absorption and emission spectra (uncorrected) of Cd_3P_2 colloidal particles in solution. Excitation wavelength (591 nm) and observation window for time resolved luminescence measurements are indicated.

minescence decay measurements are indicated in Fig. 4. In this window the sensitivity decreased steeply towards longer wavelengths (not shown).

Fig. 5 shows the influence of an increasing concentration of TiO_2 particles added to the solution on the luminescence decay of Cd_3P_2 colloids at room temperature. The instrumental response was much faster than the initial decay of curves a and b. The luminescence peak was strongly quenched and the slow emission extending to µs (almost horizontal in Fig. 5) had disappeared in curve c when every Cd_3P_2 quantum dot was attached to at least one TiO_2 particle in the solution. The time scale for electron injection can be estimated as faster than 10 ps from the measurements shown in Fig. 5.

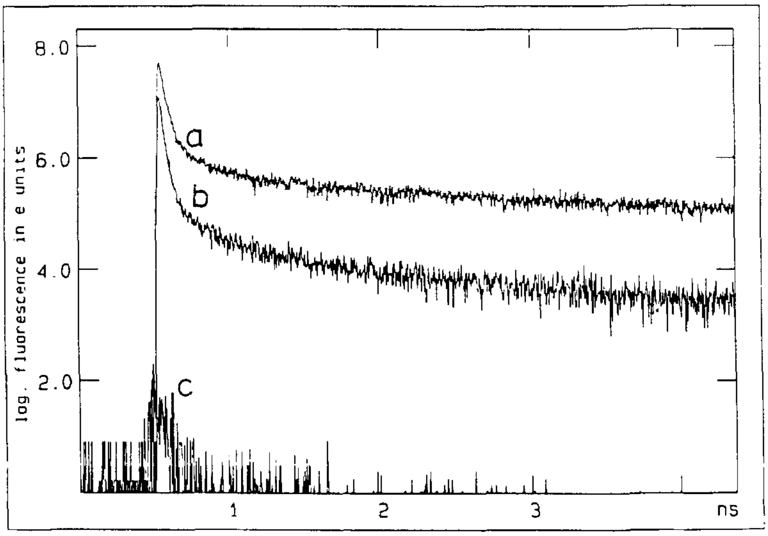

FIGURE 5 Luminescence decay of Cd_3P_2 colloidal particles. a = absence of TiO_2; b = small concentration of TiO_2 colloidal particles added; c = excess of TiO_2 added.

To obtain a more precise time scale of the electron injection process the measurement corresponding to curve c of Fig. 5 was carried out with a synchroscan streak camera. The noisy curve in Fig. 6 is the experimental result. Using a careful measurement of the instrumental response to the laser pulse under identical experimental conditions we calculated the influence of various electron injection time constants assuming a simple exponential decay. Two results of such fits are represented in Fig. 6 by the two smooth curves corresponding to 4 ps and 0.5 ps electron injection time constant respectively. Thus, we established that a time constant in the range of 500 fs gave an upper limit to the electron injection time at room temperature. This measurement (Fig. 6) also shows that the emitting state that facilitated electron injection was formed within 1 ps. At 77 K the injection reaction slowed down to at least 400 ps decay time. The temperature dependence of the system will be described in detail elsewhere.

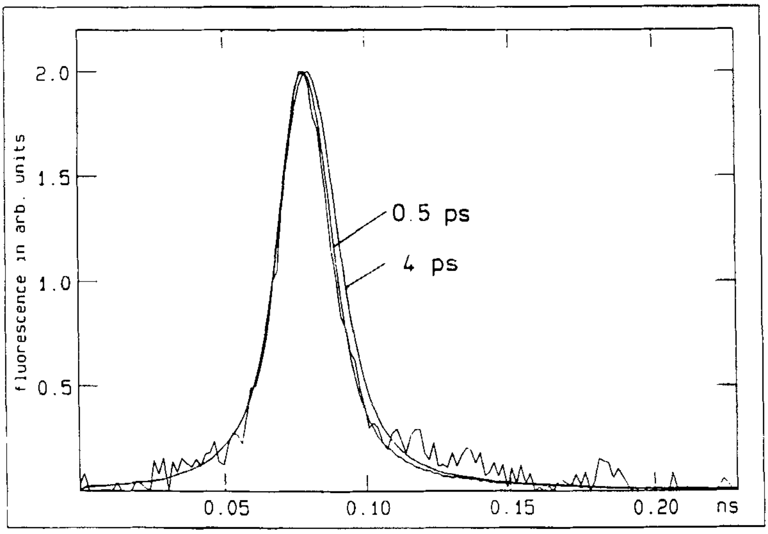

FIGURE 6 Experimental (noisy curve) and calculated luminescence decay of Cd_3P_2 particles attached to TiO_2 particles in solution. The calculated smooth curves correspond to an exponential decay with 4 ps and 0.5 ps time constant respectively.

It is remarkable that ultrafast electron injection can be achieved with less than 1 ps time constant at room temperature across this interface prepared with wet chemistry techniques.

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