

**REDUCTION OF ACCEPTOR RELAY SPECIES
BY CONDUCTION BAND ELECTRONS OF COLLOIDAL TITANIUM DIOXIDE:
LIGHT-INDUCED CHARGE SEPARATION IN THE PICOSECOND TIME DOMAIN**

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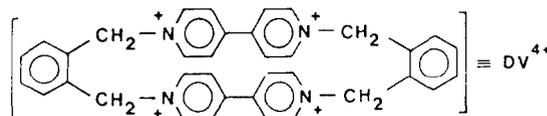
Photoinduced interfacial electron transfer from the conduction band of colloidal TiO₂ semiconductor particles to the cofacial dimeric viologen DV⁴⁺, an electron acceptor, occurs in the picosecond time domain. The interfacial electron-transfer rate constant is about $2 \times 10^{10} \text{ s}^{-1}$ at *pH* 7.8. The reaction involves consecutive one-electron transfer to give the monoreduced DV³⁺ initially, followed by formation of DV²⁺. In acidic aqueous media (*pH* 3.5) transient picosecond absorption spectra show the formation of the monoreduced species only.

1. Introduction

The mapping of primary events in light-induced phenomena is important in the understanding of processes that occur in photocatalysis with semiconductor-based catalysts [1]. The utilization of semiconductor particles of colloidal dimensions ($\approx 100 \text{ \AA}$) allow investigations to be pursued with laser flash photolysis techniques because Rayleigh scattering is minimized. The excite-and-probe technique of picosecond transient absorption spectroscopy has been widely used to unravel fast events in many homogeneous phase photoinduced phenomena; the technique has only recently been applied to probe events in heterogeneous media [1-4]. Particularly important have been the studies of electron injection from a dye (eosin Y) excited state to the conduction band of TiO₂ and studies of primary events in "naked" TiO₂ colloidal sols [4]. These have provided direct measurement of rates of charge injection [3] and information on the fate of the photogenerated electrons and holes [4].

We have recently investigated [5] interfacial elec-

tron transfer from the conduction band of colloidal TiO₂ particles to cofacial dimeric viologen DV⁴⁺.



DV⁴⁺ is a four-electron acceptor, the first two reduction steps occurring at almost the same potential [5,6], $E^0(\text{DV}^{4+/3+}) = 0 \text{ V}$ and $E^0(\text{DV}^{3+/2+}) = -0.07 \text{ V}$ versus NHE. The earlier investigation [5] employed nanosecond laser photolysis to excite the colloidal TiO₂ particles. The time resolution of these experiments was insufficient to allow for an analysis of the primary charge transfer events, leading to the formation of DV³⁺ and DV²⁺, which occurred concomitantly and within the time interval of the 15 ns light pulse. In the present communication we apply picosecond excitation in order to directly monitor, for the first time, this ultrafast interfacial electron transfer from a colloidal TiO₂ particle to an acceptor species.

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2. Experimental

Colloidal solutions of TiO_2 (consisting of both anatase and an amorphous phase; mean particle diameter ≈ 10 nm) were prepared and characterized as described earlier; the point of zero zeta potential (PZZP) is 4.7 [5]. The sol shows an absorption which rises sharply towards the UV below 380–390 nm, the onset corresponding to a bandgap of 3.2 eV [7]. At *pH* 3.5, TiO_2 sols are stable for several days (even months). At *pH* 7.8, pre-treated polyvinyl alcohol (PVA) [8] was added as a stabilizer to TiO_2 sols to prevent flocculation. The *o*-xylene-bridged viologen dimer DV^{4+} was a generous gift of Professor Sigfried Hünig, Institute of Organic Chemistry, University of Würzburg, West Germany. Water was doubly distilled from a quartz still. Other conditions are indicated in the figure captions.

Nanosecond laser flash-photolysis experiments were carried out on a frequency-doubled (347.1 nm pulses of 15 ns duration) JK 2000 ruby laser combined with a fast kinetic spectroscopic technique to detect transient species [9]. Picosecond laser photolysis experiments employed a frequency-tripled (355 nm pulses with *fwhm* ≈ 30 ps duration; average energy ≈ 2.3 mJ pulse), double-beam and passively mode-locked Nd:YAG laser system coupled to a fast detection system comprised of a SIT Vidicon and an EG & G optical multichannel analyser OMA-2 [10]. An outline of our laser system at the Canadian Centre for Picosecond Laser Flash Photolysis (Concordia University) is shown in fig. 1.

The picosecond absorbance-change (ΔA) spectra at a designated time after excitation at 355 nm represent the average of 10 pairs of laser shots. One laser shot of each pair recorded the double-beam ratios at 250 wavelengths in the 425–675 nm range when the sample was not excited. The other shot repeated the measurements when the sample (in a 2 nm quartz cell) was excited. The logarithm of the ratio of these double-beam ratios gave the reported ΔA values. The standard deviation of the mean ΔA value is the calculated error (≈ 0.010 in ΔA) of the measurement and parallels the noise illustrated in figs. 2 and 4 (see below). A 0.25 m double monochromator (M_o in fig. 1) in the subtractive dispersion mode was placed after the sample but before the final spectrograph to reject stray excitation light. It was equipped with two 150

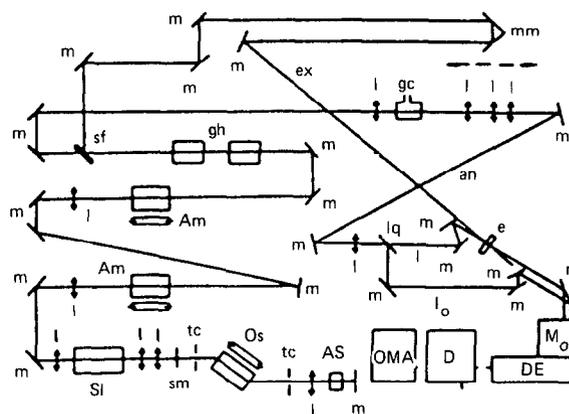


Fig. 1. Schematic illustration of the passively mode-locked Nd:YAG picosecond laser system. Description: m, mirror; AS, saturable absorber dye (Eastman Kodak 9740 in chlorobenzene); l, lens; tc, diaphragm; Os, laser head (Nd:YAG) placed at the Brewster angle in the oscillator cavity; SI, pulse selector (pockels cell); Am, amplifier (Nd:YAG); gh, harmonic generating crystals; sf, dichroic mirrors; mm, mirrors mounted on an optical delay stage; gc, continuum generation (deuterated phosphoric acid); ex, excitation beam; an, analyzing probe beam; lq, 50%/50% double prism; e, sample; Mo, double monochromator, DE, monochromator coupled to a SIT-Vidicon; D, analog-to-digital converter; OMA, optical multichannel analyzer.

grooves/mm gratings and a 10 mm intermediate slit which passed about 300 nm of spectral information. The white probe light was generated by focusing the 1064 nm laser light into a 5 cm cell containing a solution of H_3PO_4 in D_2O . The duration of the weak probe pulse was ≈ 35 ps (*fwhm*). After passing through the double monochromator, the white probe light was dispersed by a 150 grooves/mm holographic grating in a second 0.25 m monochromator. The spectral resolution of our apparatus is ≈ 10 –15 nm depending on the size of the entrance slit in the final spectrograph. The response time of the Nd:YAG system was 35 ± 5 ps due to convolution of the excitation and probe pulses. The measurement times in the spectral plots refer to optical delay times determined by the position of a translation stage in the excitation beam. The error in locating the translation stage corresponded to an error in measurement time of < 0.1 ps which was negligible in our studies. Also negligible were the effects of time dispersion in the white probe pulse which may be important when transient events are very short [11,12]. These effects arise because light of shorter wavelengths travels

more slowly in dense media (e.g. H₂O and glass) than does light of longer wavelengths.

3. Results and discussions

Fig. 2 shows the transient absorption spectra at three delay times of 50 ps, 500 ps, and 5 ns for argon-purged TiO₂ sols (0.5 g/l) containing 2 × 10⁻⁴ M DV⁴⁺ and 0.25 g/l PVA at pH 7.8. The lower dashed line represents the transient absorption spectrum obtained with a DV⁴⁺ free TiO₂/PVA sol. The weak signal observed for the latter solution arises from light absorption by conduction band electrons [4]. In the presence of DV⁴⁺, one observes the formation of a much stronger absorption at 630 nm which can be unambiguously assigned [5] to the monoreduced acceptor, i.e. DV³⁺. More than 50% of this signal is formed during the 30 ps duration of the Nd:YAG laser pulse, the 630 nm absorption reaching a plateau after ≈ 500 ns. From this analysis, the rate constant for the interfacial electron transfer from the conduction band of colloidal TiO₂ to the DV⁴⁺,



is estimated to be 2 × 10¹⁰ s⁻¹.

While the 630 nm band leaves no doubt as to the

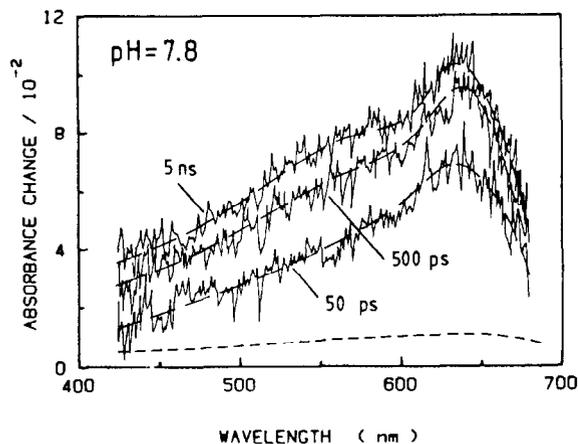


Fig. 2. Transient absorption spectra (absorbance change versus wavelength) at three delay times of 50 ps, 500 ps, and 5 ns for argon-purged TiO₂ sols (0.5 g/l) containing 2 × 10⁻⁴ M DV⁴⁺, PVA (0.25 g/l); pH 7.8; pathlength 2 mm. The lower dashed line represents the transient absorption spectrum of a TiO₂/PVA sol under identical conditions but containing no DV⁴⁺

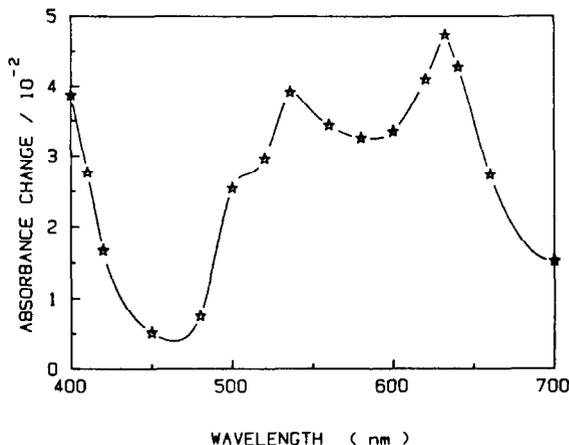


Fig. 3. Transient absorption spectrum taken 20 ns after the laser pulse from a frequency-doubled, Q-switched ruby laser (347.1 nm). TiO₂, 0.5 g/l; PVA, 1 g/l; DV⁴⁺, 10⁻⁴ M; argon-purged aqueous solutions; pH 7.0.

predominant presence of the monoreduced DV³⁺ substrate, a spectral deformation in the 450–550 nm region can be seen in fig. 2 which increases with increasing delay time. This is confirmed by the transient spectrum of fig. 3 which was taken 20 ns after ruby laser excitation of a 10⁻⁴ M argon purged aqueous solution of DV⁴⁺ (pH 7) containing TiO₂ (0.5 g/l) and PVA (1 g/l). Two main features are noteworthy: (i) a peak at 630 nm corresponding to DV³⁺, and (ii) a peak at 530 nm corresponding to DV²⁺. The latter is identified by analogy with the results from continuous photolysis experiments [5]. Clearly, both species are formed within the 15 ns laser pulse. From our observations in the picosecond time domain, it can be inferred that the formation of DV²⁺ occurs via a sequential one-electron transfer from the conduction band of the colloidal semiconductor to the dimeric viologen. The mono reduced species is formed first and this is followed by the addition of a second electron to yield the DV²⁺ species,



Thus, the picosecond results rule out the formation of a significant part of the DV²⁺ via a truly concerted two-electron transfer process. The data in fig. 2 are such that only a rough estimate of the rate constant k_2 – which is 3 to 10 times slower than the first electron transfer step – can be made.

Picosecond laser experiments were also conducted

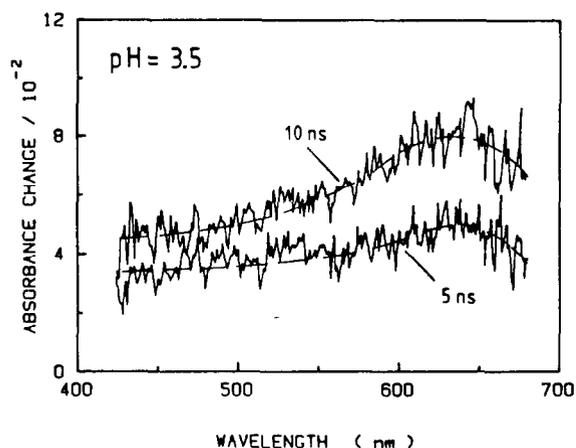


Fig. 4. Transient absorption spectra at two delay times (5 and 10 ns) for argon-purged TiO_2 sols (4.5 g/l) containing DV^{4+} (5×10^{-4} M); pH 3.5; no PVA was used here.

at pH 3.6 which is below the point of zero zeta potential (4.7) for the TiO_2 sols used here. Under these conditions the Coulombic attraction between the highly charged DV^{4+} and the semiconductor surface is suppressed. This results in a drastic decrease in the rate of formation of DV^{3+} which occurs here in the nanosecond time domain. Even after a 10 ns delay, no DV^{2+} transient absorption is detectable under these conditions (fig. 4). The broadness of the absorption throughout the visible range monitored (425–675 nm) does not preclude its formation, but the quantity must be small.

Our observations in the picosecond time domain confirm the extreme rapidity [5] of the reduction of DV^{4+} under pH conditions where it is adsorbed on the surface of TiO_2 . For further interpretation of these results we evoke the current theory of non-adiabatic electron-transfer reactions [13]. The overall electron transfer is comprised of two individual steps: (i) diffusion of the electric charge carrier to the particle surface and (ii) interfacial electron transfer. In colloidal semiconductors the diffusion event requires at most a few picoseconds [14] and the heterogeneous charge transfer at the interface is therefore rate determining. The rate constant for interfacial electron transfer may be approximated by the expression

$$k_1 = \nu_0 \exp[-\beta(r-r^0)] \times \exp[-(\Delta G^0 + \lambda)^2 / 4\lambda kT], \quad (3)$$

where $\nu_0 \approx 10^{13} \text{ s}^{-1}$ is the frequency for nuclear reor-

ganisation, $\beta \approx 1.2 \text{ \AA}^{-1}$ is the damping coefficient and $r-r^0$ is the electron tunneling distance. The latter is assumed to be equal to the distance between the center of the DV^{4+} molecule and the first layer of titanium lattice ions at the TiO_2 surface, $r-r^0 \approx 5 \text{ \AA}$. ΔG^0 is the standard free energy change associated with the electron transfer. At pH 7.6, the conduction band edge of the colloidal TiO_2 particle is at a potential of -0.55 V (NHE) and ΔG^0 is therefore -0.55 eV , if the free energies of adsorption of DV^{4+} and desorption of DV^{3+} are equal. Agreement between the predictions of eq. (3) and the experimentally determined k_1 value can only be obtained if it is assumed that the driving force for the interfacial electron transfer is optimal, i.e. $-\Delta G^0$ is equal to the reorganization energy λ . In this case one derives from eq. (3) a k_1 value of $2.5 \times 10^{10} \text{ s}^{-1}$.

In conclusion, we have succeeded in directly monitoring the electron transfer from the conduction band of colloidal TiO_2 to a viologen dimer present at the particle surface which takes place in the picosecond time domain. The charge transfer process occurs extremely rapidly under neutral pH conditions where the intimate contact between the acceptor and the semiconductor favours efficient coupling between the $3d^1$ wavefunction manifold of the Ti lattice ions and the DV^{4+} acceptor orbitals. The reaction is essentially barrierless, the energetic requirements for the reorganisation of the reactants being compensated for by the thermodynamic driving force.

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