

## Adsorption processes on semiconductor colloids studied by pulsed-laser-induced electron-transfer reactions

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**Abstract.** A method is presented to study adsorption of electron-transfer reagents on colloidal semiconductors by laser pulse energy-dependent transient absorption measurements.

**Keywords.** Semiconductor colloids; pulsed lasers; adsorption; electron transfer.

### 1. Introduction

In the field of photochemistry, one of the applications of lasers has been the measurement of properties of metastable species, such as quantum yields and extinction coefficients of triplet states of organic molecules (Bensasson and Land 1978; Carmichael and Hug 1986). One of the methods used to that effect takes advantage of the depletion of the molecular states originally present in the system due to absorption of a high fluence of photons from a pulsed laser. In this communication, we present a different application of this same method, aimed at gaining information about adsorption of electron-transfer reagents on colloidal semiconductors. A more detailed account of this work, including discussion of the validity of the model presented here and of its results, will be published elsewhere (Grabner and Quint, to be published).

### 2. Results and discussion

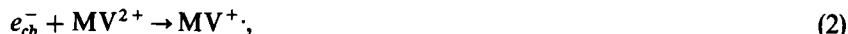
The systems studied consisted of colloidal  $\text{TiO}_2$  in aqueous solution, prepared by hydrolysis of Ti(IV) tetraisopropylate following the method of Bahnmann *et al* (1984). The colloid consists of particles of 40 nm average diameter (Duonghong *et al* 1982) and is transparent to visible and near UV light so as to allow measurement of photoinduced transient absorptions.

Conduction band electrons and valence band holes are separated when the semiconductor absorbs photons whose energy exceeds its band gap (3.2 eV for anatase  $\text{TiO}_2$ ). The charges can either recombine or react with donors or acceptors present at the particle surface. For this purpose, either methyl viologen ( $\text{MV}^{2+}$ ) was added to an alkaline sol, or  $\text{I}^-$  to an acid one. In these cases, the following reactions will lead to transients whose extinction coefficients are known (Duonghong *et al* 1982;

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Henglein 1982; Moser and Grätzel 1982):



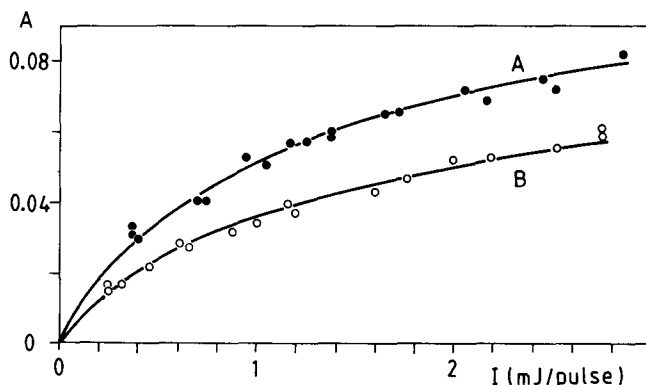
In the experimental set-up used in this work, details of which can be found elsewhere (Grabner *et al* 1990), the third harmonic of a Q-switched Nd:YAG laser (pulse duration 10 ns,  $\lambda = 355$  nm) was used as the exciting light source. Transient absorptions were detected at pulse end at 606 nm ( $\text{MV}^+$ ) or 385 nm ( $\text{I}_2\cdot$ ). The absorption of these species was always fully developed by the end of the laser pulse.

Figure 1 shows the dependence of the transient absorbance due to  $\text{MV}^+$  (curve A) and  $\text{I}_2\cdot$  (curve B) on the energy of the laser pulse, i.e. on photon fluence. The observed behaviour is strongly nonlinear, reminiscent of a saturation curve as it is frequently encountered in pulsed-laser-irradiated systems in which the photon-absorbing state is depleted. In the case of figure 1, nonlinearity can however not originate from depletion of  $\text{TiO}_2$  which would require pulse energies exceeding 100 mJ. On the other hand, it is generally assumed, and demonstrated by prompt formation of the transients, that adsorption of the reagents on the particle surface is required for reaction. This could introduce a further depletion mechanism, since the order of magnitude of the number of adsorbed molecules could be the same as that of photons absorbed by the semiconductor. A rough evaluation illustrates this: assuming 1.6 g  $\text{TiO}_2$ /l with particle diameter 40 nm, complete coverage with ions of radius 0.215 nm (the value for  $\text{I}^-$ ) gives a number of ions equivalent to 1.7 mJ per pulse of 355 nm photons absorbed in the reaction volume. It thus seems quite reasonable to take depletion of adsorbed species into account.

On the basis of reactions (1) to (3), we describe the data of figure 1 by the following equation:

$$c_t = c_{\text{ads}} \times (1 - \exp(-\varepsilon \times \phi \times I)), \quad (4)$$

where  $c_t$  is the concentration of transients,  $c_{\text{ads}}$  the concentration of adsorbed reagents,  $\varepsilon$  the extinction coefficient for absorption at 355 nm,  $\phi$  the quantum yield of transient



**Figure 1.** Dependence of transient absorbance at pulse end on laser pulse energy: (A)  $10^{-4}$  M  $\text{MV}^{2+}$ , 0.8 g/l  $\text{TiO}_2$ , pH 10. Absorbance measured at 606 nm. Values for both axes multiplied by a factor of 10; (B) 0.1 M  $\text{I}^-$ , 1.6 g/l  $\text{TiO}_2$ , pH 1. Absorbance measured at 385 nm. Solid lines are fits according to (4).

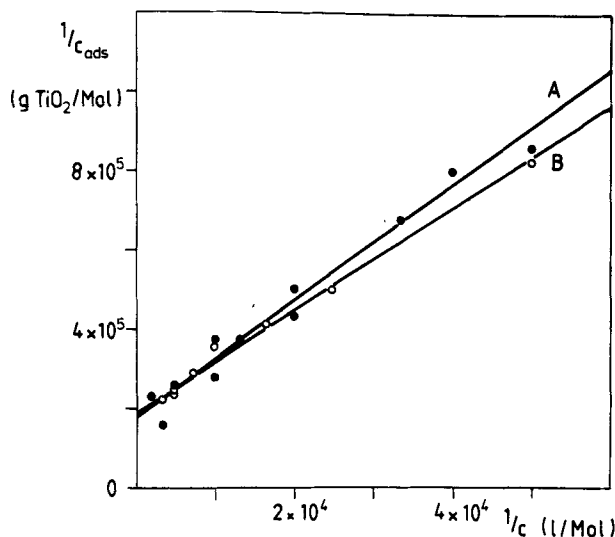


Figure 2. Inverse of adsorbed concentration, obtained from fit by (4), vs. inverse of bulk concentration, (A)  $MV^{2+}$ , 0.8 g/l  $TiO_2$ , pH 10; (B)  $I^-$ , 1.6 g/l  $TiO_2$ , pH 1. x axis values multiplied by factor 500, y axis values multiplied by a factor of 5.

formation, and  $I$  the photon fluence, proportional to pulse energy. Equation (4) is fitted to the data of figure 1, free parameters being  $\phi$  and  $c_{ads}$ . The procedure is analogous to the 'partial saturation' method to determine triplet-triplet extinction coefficients (Carmichael and Hug 1986). The results of the simulation for the data of figure 1 are: for the  $MV^{2+}$  system,  $c_{ads} = 2.86 \times 10^{-6}$  mol/g  $TiO_2$ ,  $\phi = 0.148$ ; for the  $I^-$  system,  $c_{ads} = 2 \times 10^{-5}$  mol/g  $TiO_2$ ,  $\phi = 0.204$ .

A test of the validity of the proposed model consists in studying the dependence of the obtained values of  $c_{ads}$  on the bulk reagent concentration,  $c$ . To that effect, families of curves according to (4) are computed for different values of  $c$ . Two examples are shown in figure 2, again for  $MV^{2+}$  and  $I^-$ .

The form of the plot of figure 2 is that of a Langmuir adsorption isotherm:

$$c_{ads} = c_{ads}^{max} \times (k_A c) / (1 + k_A c), \quad (5)$$

$k_A$  being the apparent adsorption coefficient for the species under consideration. Figure 2 shows that the data obtained from the fits according to (4) indeed conform to (5). The numerical results are  $k_A = 1.2 \times 10^4 M^{-1}$  and  $c_{ads}^{max} = 5.55 \times 10^{-6}$  Mol/g  $TiO_2$  for  $MV^{2+}$ , and  $k_A = 30.9 M^{-1}$  and  $c_{ads}^{max} = 2.6 \times 10^{-5}$  Mol/g  $TiO_2$  for  $I^-$ . This latter value corresponds to a coverage of about 6% of the colloid particles by  $I^-$  assuming an ion radius of 0.215 nm.

### 3. Conclusions

The results presented here show that a Langmuir adsorption isotherm formalism can be applied to data obtained from pulse energy-dependent measurements of surface electron-transfer processes in  $TiO_2$  sols. This represents a first test of the depletion model used to treat the data. Further experiments are in progress to assess the validity

of this approach, which, if successful, can provide quantitative information about adsorption processes on semiconductor colloids.

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### **References**

- Bahnemann D, Henglein A, Lilie J and Spanhel L 1984 *J. Phys. Chem.* **88** 709  
Carmichael I and Hug G L 1986 *J. Phys. Chem. Ref. Data* **15** 1  
Duonghong D, Ramsden J and Grätzel M 1982 *J. Am. Chem. Soc.* **104** 2977  
Grabner G, Köhler G, Marconi G, Monti S and Venuti E 1990 *J. Phys. Chem.* **94** 3609  
Grabner G and Quint R M *Langmuir* (in press)  
Henglein A 1982 *Ber. Bunsenges. Phys. Chem.* **86** 241  
Land E J and Bensasson R 1978 *Photochem. Photobiol. Rev.* **3** 163  
Moser J and Grätzel M 1982 *Helv. Chim. Acta* **65** 1436