Kinetics of Electron Build-up in TiO_2 Colloids Probed by Hole Scavenging after Picosecond Excitation

Claude Arbour, Devendra K. Sharma, and Cooper H. Langford*

Canadian Centre for Picosecond Laser Flash Photolysis, Department of Chemistry, Concordia University, 1455 de Maisonneuve W. Montreal (Quebec), Canada H3G 1M8

Excess electrons generated in the conduction band of colloidal TiO_2 are trapped into n-type sites with a time constant of *ca.* 2 ns; this process is significantly slower than recombination of electrons and holes in the surface layer of the colloid at the concentrations of the experiment.

In our recent paper,[1] the kinetics of the build-up of a broad absorption band following excitation with a 20 ps, 355 nm pulse absorbed by a Cu–phthalocyanine dye adsorbed on the surface of colloidal TiO_2 was reported. The broad band was assigned to a transition to the conduction band of electrons which had been trapped in the localized sites occupied in n-doped TiO_2. This assignment referred to a band very similar to one seen after prolonged irradition of the oxide,[2] one produced by the reaction with radiolytically produced electrons,[3] and one observed using polyvinyl alcohol (PVA) as a hole scavenger.[4] All workers agreed that the bands reflect excitation of electrons accumulated in the colloid. The novel feature of the flash study was the recognition of a delay between the delivery of the electron to the colloid and the appearance of the absorption. The exact band shapes depend on the detailed mode of preparation of the colloids, but two limiting features define the range. In ref. 2, a peak at 475 nm was assigned to a t_{2g} to e_g d–d transition of Ti^{III}. This corresponds to a monomer (localized) equivalent of the band transition from n-trap states to the conduction band which is

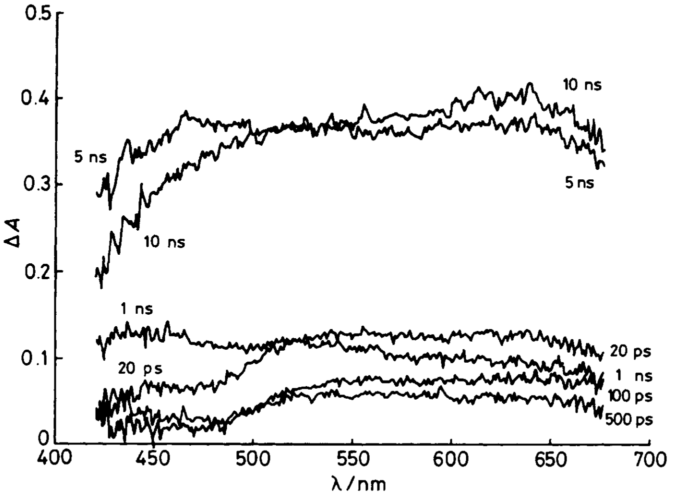

Figure 1. Typical transient spectra showing change in absorbance from a probe delay of 20 ps to one of 10 ns. Notice that the 20 ps curve and the 1 ns curve cross near 500 nm. Intensity is decreasing from 20 ps to 500 ps and increasing subsequently.

assigned to the broad feature more to the red. Thus, it is not surprising that the band shape can vary as colloids vary in the ratio of surface monomer-like groupings to bulk hydrous oxide. What is interesting is that the band is uniformly assigned as a $\mathrm{Ti^{III}}$-like trapped electron transition.

Since ref. 1 appeared, a report has been published[5] concerning the broad transient observed from picosecond flash excitation of TiO_2 alone. In agreement with the weak blanks reported in ref. 1, this feature is of much lower intensity than the feature under discussion here. Also, hole–electron recombination in TiO_2 flashed in the absence of scavengers leads to the decay of transients in 200 ps. We have confirmed the report in ref. 5 using our colloid preparations. According to the assignment in ref. 5 of the weaker short lived transient as an electron spectrum, we are required to conclude that at least two different types of electron absorption transients exist in TiO_2 since the prompt production of the spectrum reported in ref. 5 precedes the growth of the stronger transient described in ref. 1 even though changes in the dye spectrum imply fast electron transfer to the colloid. The present communication confirms this two trapping site interpretation using hole scavenging rather than electron injection.

In the present experiments, TiO_2 hydrous colloids were prepared by the slow hydrolysis of $TiCl_4$ in water[6] to give TiO_2 concentrations ranging from 4 to 6 g dm^{-3}. The pH was adjusted to 3 by dialysis and no protective agent was added. (It is interesting that the use of polyvinyl alcohol as a 'protective' agent can lead to the development of the broad absorption band described here). These particles have a radius between 50 and 200 Å.[7] These colloids have an absorbance of *ca.* 0.5 at 355 nm in the 2 mm cell used for irradiation with a 2.5 mJ 20 ps third harmonic pulse from the Nd/YAG mode locked system in the Canadian Centre.[6] After irradiation with the pulse, the evolution of the spectrum to 10 ns was followed by probing with continuum pulses spanning the range from 450 to 675 nm which were delayed with respect to the exciting pulse.

The new feature we report is that experiments were conducted with tris[bis-4,7-(4-sulphophenyl)-1,10-phenanthroline]ruthenium(II) tetra-anion adsorbed onto the colloid. Static quenching of the $\mathrm{Ru^{II}}$ charge-transfer luminescence when the dispersion is irradiated at wavelengths in the absorption band of the $\mathrm{Ru^{II}}$ complex confirms the surface adsorption. When a concentration of 2—25 µM of the anion is added to the dispersion the electron band grows in to give a final electron concentration of up to 4×10^{-9} M electrons. The $\mathrm{Ru^{II}}$ complex itself has an absorption minimum at 355 nm and contributes <0.1 to the total absorbance of $\geqslant 0.5$ in the 2 mm cell at 355 nm. More than 80% of the excitation is absorbed by the TiO_2 colloid.

The electron excess is produced by the thermodynamically very favourable hole capture by the $\mathrm{Ru^{II}}$ species adsorbed on the positive surface, giving $\mathrm{Ru^{III}}$ and preventing recombination, thereby leaving the electron to relax into the trap site. The kinetics of this relaxation process are revealed in Figure 1.

Several colloid preparations with some variation of particle size around the average values reveal minor variation in the shape of the excess electron band reflecting a variation in the fraction of trap sites associated with the surface as compared to bulk.

The interesting observation is that the rate constant for trapping varied by less than a factor of two. Formation of a local '$\mathrm{Ti^{III}}$' from the conduction band electrons occurs at essentially the same rate whether it is associated with a nearly monomeric complex at the surface or with an interior location structure. The rate constant obtained here after hole trapping to produce excess electrons is in excellent agreement with the value obtained earlier from injection of the electron after photon absorption by the dye adsorbed on the TiO_2 surface.[1]

Flashing TiO_2 produces a prompt broad weak transient in <20 ps which was described in ref. 5 as a surface trapped electron. These experiments and those in ref. 1 show the growth of a stronger transient when hole scavenging or electron injection produces an excess electron population. This stronger transient is not prompt, but requires 2 ns to develop. It may reflect deeper trapping at sites which exist initially in the colloid but are not populated promptly, or it may reflect reorganization within the colloid.

Since hole–electron recombination in the absence of scavenger is quite rapid, but the formation of the stronger electron signal is faster than diffusional encounter times in moderately dilute solution, the electron spectrum reported here may characterize an important species in photocatalytic reductions involving TiO_2. We are attempting to explore the energetics of this state by photothermal spectroscopy.

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References

1 A. D. Kirk, C. H. Langford, C. Saint Joly, R. Lesage, and D. K. Sharma, *J. Chem. Soc., Chem. Commun.*, 1984, 961.

2 D. Duonghong, J. Ramsden, and M. Grätzel, *J. Am. Chem. Soc.*, 1982, **104**, 2977.

3 A. Henglein, *Ber. Bunsenges Phys Chem.*, 1982, **86**, 241.

4 U. Kolle, J. Moser, and M. Grätzel, *Inorg. Chem.*, 1985, **24**,2253.

5 G. Rothenberger, J. Moser, M. Gratzel, N. Serpone, and D. K. Sharma, *J. Am. Chem. Soc.*, 1985, **26**, 8054.

6 N. Serpone and D. K. Sharma, to be published.

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