Sub-nanosecond Processes in the Quenching of a Copper Phthalocyanine Dye Adsorbed on TiO_2

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An excited copper phthalocyanine adsorbed on TiO_2 injects an electron in *ca.* 20—50 ps; the conduction band electron is trapped in TiO_2 localized sites in an average time of *ca.* 500 ps.

A recent observation by Kirk[1] on the transients observed following excitation of a water soluble sodium salt of copper phthalocyanine tetrasulphonate (CuPc-TS) (Eastman, purified by recrystallization) suggested that this might prove a suitable compound for exploration of the interfacial electron transfer between an adsorbed sensitizing dye molecule and a colloidal semiconductor such as the hydrous oxide of titanium(IV). The advantage of the dye CuPc-TS is that a transient excited state absorption at 480 nm appears promptly with the leading edge of a 30 ps third harmonic (355 nm) pulse from a mode locked Nd/YAG laser. Bleaching and a negative absorbance change at the absorption maximum of the ground state of the dye at 606 nm is prominent. In homogeneous aqueous solution, both the excited state absorption maximum and the bleaching persist to beyond the limit of the instrument (10 ns).[1]

The dye CuPc-TS may be adsorbed onto a TiO_2 colloid prepared by the methods used in Graetzel's laboratory for photocatalytic systems.[2] The completeness of adsorption of a dye concentration of 6.65×10^{-5} M onto a dispersion of 1000 mg l^{-1} of titanium dioxide in aqueous acid at pH 2 is established by the complete removal of the dye spectrum when the TiO_2 is removed by an ultrafilter. The consistency of particle size with the range reported[2] is established by the capacity of the dispersion with dye adsorbed to pass a filter of nominal pore size of 1 micron. However, the anionic dye does induce the coagulation of the colloid over a period of 2—4 days and the particle size almost surely grows during the time required for the experiments described. Fortunately the spectroscopic results show very little sensitivity to ageing of the colloid over 24 h and beyond.

When the fresh colloid with adsorbed dye is excited with a third harmonic pulse from the laser system, which is like that described elsewhere,[3] (355 nm, pulse energy 2.5—3.0 J, width 30 ps) and then probed with a continuum pulse (400—650 nm delayed between 20 ps and 10 ns), the spectral sequence shown by the typical experiment recorded in Figure 1 is obtained. In Figure 1, at a delay time of 20 ps, we see evidence of the excited state absorbance centred at 510 nm which is known for the dye in homogeneous solution, and also a dip corresponding to the bleaching of the ground state at 605 nm. However, this absorbance does not persist. By a delay time of 100 ps the 510 nm band is negligible but some broad underlying absorbance is apparent. The initial excited state of the dye has a lifetime on the colloid surface of the order of 20 to 50 ps. Following the decay of the initial transient absorbance, a second very broad band is seen to grow. Examining the 500 ps delay spectrum in Figure 1 shows that this broad band develops while evidence of the bleaching of the dye ground state persists. (Note the local minimum near 600 nm.) By a delay time of 10 ns, the broad band is fully developed and is comparatively intense. Three features of this sequence deserve note. First, the dye is quenched rapidly compared to its decay in solution. Second, the state initially produced by quenching leaves the ground state substantially bleached but does not produce any large transient absorbance in the visible region probed by the 'continuum' available. Third, the final state reached less rapidly gives an extremely broad absorption envelope not characteristic of molecular species.

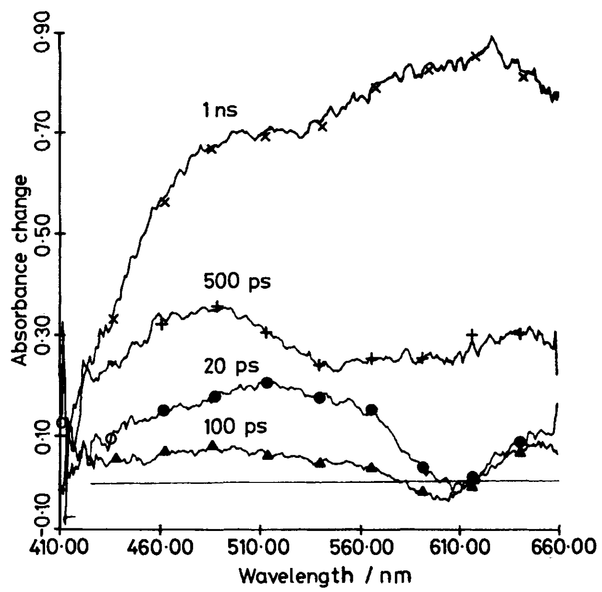

Figure 1. Transient spectra of the system CuPc-TS on TiO_2. The spectra were recorded with the probe delay times shown. (Note: the 10 ns spectrum resembles the 1 ns spectrum.)

Two other experimental observations are significant. Steady state irradiation over several hours does not produce any net spectral changes in the dye in the absence of added solution reagents. The dye eventually recovers its ground state. Additionally, a careful search revealed no luminescence from either the dye or the supporting colloid. Addition of benzoquinone leads to net reduction to hydroquinone. The system does accomplish electron transfer.

Since the first excited state absorption rises on the leading edge of the pulse (<20 ps grown in), we tentatively assign it as originating in the lowest spin allowed state: a doublet in this Cu^{II} complex. (It would make little difference to the remainder of the present argument if intersystem crossing to the quartet occurs in this short time domain.)

The quenching by TiO_2 is attributed to electron injection into the semiconducting colloid with no more than a small barrier to this interfacial electron transfer. The non-absorbing intermediate state is probably one in which the electron is in the conduction band of the semi-conductor. The final state associated with the broad intense absorption is assigned to a transition from a trap state in the semiconductor band. It is, in fact, reminiscent of the absorption band which gives a blue colour to n doped TiO_2.[4] The competition between trapping

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and 'back electron transfer' to the dye appears to favour trapping thereby giving the oxidized dye the lifetime necessary for reaction with a solution species.

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