Detection of Transient Absorption in a Dyed Cotton Fabric and in Semiconductor Powders by Diffuse Reflectance Laser Flash Photolysis

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Transient absorption spectra for aluminium sulphonated phthalocyanine dyed into water-saturated cotton fabric and for powdered samples of titanium dioxide and cadmium sulphide have been obtained by the technique of diffuse reflectance laser flash photolysis.

The successful extension of laser flash photolysis to heterogeneous[1] and opaque[2] samples by using diffusely reflected analysing light to monitor transient absorptions has meant that time-dependent absorption properties of optically dense materials are now amenable to study. Hitherto the powerful technique of flash photolysis has been restricted to homogeneous or at least transparent samples since spectral and temporal information has been obtained from measurements of changes of intensity of transmitted analysing light at various wavelengths as a function of time resulting from pulsed excitation. We report here on the variety of samples which can now be studied directly by monitoring changes in diffusely reflected monitoring light following pulsed excitation, and the breadth of possible applications. To this end we present results from diverse samples, namely semiconductor powders (including TiO_2 which finds many commercial applications) as well as the first results of direct flash photolysis studies on a dyed cotton fabric.

The spectra of the transient absorptions in powder samples of undoped TiO_2 (anatase) and CdS are depicted in Figure 1. The maximum of each spectrum lies to the red of the fundamental absorption edge (also depicted), which is a common phenomenon in other n-type semiconductors we have studied[3] and implies that a general assignment of this behaviour could be possible. Indeed, the absorption spectrum of trapped holes in colloidal TiO_2 has been detected by transmission laser flash photolysis[4] and that spectrum is quite similar to ours; this leads us to suggest that we may be observing the absorption of minority carriers from deep traps. At the maximum absorption, the decays have half-lives of 2.5 and 17 μs for TiO_2 and CdS respectively.

Figure 2 shows the transient absorption difference spectrum of water-saturated non-fluorescent cotton dyed with aluminium sulphonated phthalocyanine (ALPCS) and its ground state diffuse reflectance spectrum. Methods have not yet been evaluated to permit accurate evaluation of the extinction coefficients of photo-induced species detected in the diffuse

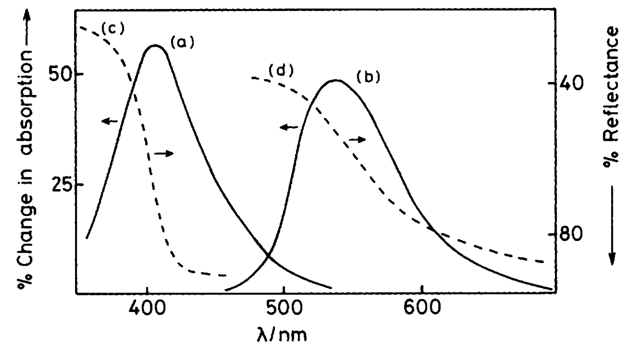

Figure 1. Photoinduced changes in absorption for (a) TiO_2, and (b) CdS, following pulsed excitation at 354 nm (40 mJ/pulse; pulse duration 20 ns). Ground-state diffuse reflectance spectra of TiO_2 and CdS are shown in (c) and (d), respectively.

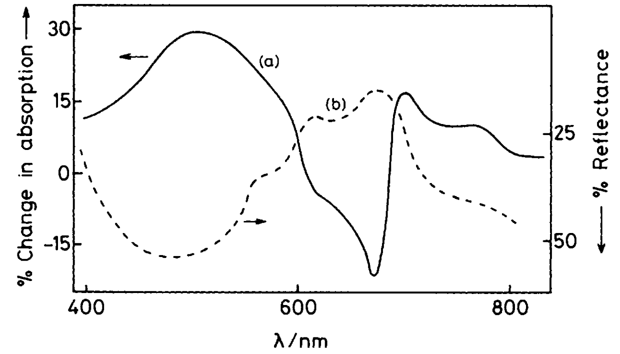

Figure 2. (a) Transient difference spectrum following pulsed excitation at 354 nm for water-saturated cotton fabric dyed with aluminium phthalocyanine and (b) ground-state diffuse reflectance spectrum.

reflectance mode, and thus we cannot accurately correct the transient absorption spectrum for ground-state effects. A published triplet–triplet absorption spectrum of ALPCS in aqueous solution maximises at 480 nm,[5] while the radical anion in dimethylformamide has maxima at 575 and 618 nm.[6] The 490—500 nm maximum in our difference spectrum lies close to the aforementioned 480 nm peak, and leads us to believe that the triplet–triplet absorption of ALPCS is being observed. Other species, such as the radical anion, may contribute to the spectrum at longer wavelengths. The half-life of the absorption at 500 nm is about 0.34 ms.

The results presented here together with our previous studies using this technique to study photo-induced transient absorptions in aromatic hydrocarbons adsorbed as fractions of a monolayer on catalytic, highly scattering γ-alumina surfaces,[1] and organic microcrystals,[2] and including the successful development of diffuse reflectance pulse radiolysis[7] demonstrate the wide potential application when diffuse reflectance is used as an analysing probe following pulsed excitation.

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References

1 R. W. Kessler and F. Wilkinson, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 309.
2 F. Wilkinson and C. J. Willsher, *Chem. Phys. Lett.*, 1984, **104**, 272.
3 F. Wilkinson and C. J. Willsher, in preparation.
4 D. Bahnemann, A. Henglein, J. Lilie, and L. Spanhel, *J. Phys. Chem.*, 1984, **88**, 709.
5 J. R. Darwent, I. McCubbin, and D. Phillips, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, 347.
6 L. R. Rollman and R. T. Iwamoto, *J. Am. Chem. Soc.*, 1968, **90**, 1455.
7 F. Wilkinson, C. J. Willsher, P. Warwick, E. J. Land, and F. P. Rushton, *Nature (London)*, 1984, **311**, 40.