OPTICAL DETECTION OF A PHOTOINDUCED THERMAL TRANSIENT IN TITANIUM DIOXIDE POWDER BY DIFFUSE REFLECTANCE LASER FLASH PHOTOLYSIS

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Summary

It is shown that the transient absorption detected in a sample of TiO_2 (anatase) powder following intense ultra-band gap pulsed laser excitation can be assigned as a photoinduced thermal phenomenon caused by rapid heating and cooling of the sample. The transient difference spectrum of the absorption has a maximum that is slightly red shifted from the ground state absorption edge of TiO_2 at room temperature, and a faster decay is observed at long wavelengths than at shorter ones.

1. Introduction

The extension of the flash photolysis technique to optically dense substances by employing diffusely reflected monitoring light has permitted the direct observation of the absorptions of transient species in a variety of opaque samples, including microcrystalline ketones [1, 2], dyes in different heterogeneous environments [3, 4] and hydrocarbons adsorbed on a catalytic surface [5, 6]. The transients in these particular samples were assigned to triplet states, the evidence being the similarity between the spectra of the transient absorptions and those published for the triplet–triplet absorptions in a fluid medium, and, for the ketone and hydrocarbon samples, a close correlation in decay kinetics between laser-induced luminescence of the samples and the transient absorption decay. The luminescences were assigned as phosphorescences by their spectral distribution. We recently reported on transient absorptions in powdered semiconductors [4] and suggested that trapped minority carriers could give rise to the observed absorption, noting that other workers had obtained a similar transient absorption in colloidal TiO_2 using transmission flash photolysis, and reasoned that trapped positive

holes were responsible [7]. There is an enormous amount of interest in TiO_2, which has been generated following the report by Fujishima and Honda in 1972 that a single crystal of the material could act as a photoanode in the photoassisted electrolysis of water [8]. Since that time, photoelectro-chemical cells have been developed using polycrystalline forms of TiO_2 [9 - 11], and it was later discovered that when TiO_2 powder is suspended in the appropriate solution, chemical reactions can be initiated photocatalytically [12, 13]. Work on powder suspensions has developed more recently into studies of "microdisperse" and colloidal samples, in which, for example, transmission laser flash photolysis [14 - 16] and transient Raman spectros-copy [17] have been employed to probe electron transfer reactions between redox couples in solution and the semiconductor. In this paper, we wish to discuss the transient absorption in dry powdered TiO_2 in terms of a photo-induced thermal effect and to draw attention to the fact that significant heat generation in a sample must be expected for laser excitation of materials which have a high optical absorption coefficient at the exciting wavelength, and this may play a part in transient generation and decay in such samples.

2. Experimental details

The flash photolysis apparatus has been described in detail previously [1]. Excitation was achieved with the 354 nm harmonic of a pulsed Nd–YAG laser (pulse width, about 20 ns; intensity, 50 mJ pulse^{-1}), and a pulsed 250 W xenon arc lamp (pulse width, about 0.5 ms) was used as the monitor-ing light. A variety of TiO_2 samples were employed in the flash photolysis experiments; all showed essentially the same transient absorption spectrum, but slight differences in decay constants were noted. Ground state spectra of TiO_2 at low temperatures were recorded employing a Cary 14 spectrometer using an integrating sphere. The TiO_2 was cooled down to 20 K in a closed-cycle helium cryostat (CTI, model 21). Spectra at ambient and elevated temperatures were recorded using a Spex Fluorolog 222 spectrometer in the S1–S2 mode. Details of this procedure will be given in another paper [18]. An air thermostat in the sample compartment of the spectrometer was used for the measurements up to 600 K.

3. Results and discussion

A substantial transient absorption is observed in TiO_2; its time-resolved spectrum is given for an anatase sample (Fisons Ltd., which had a particle size of the order of 1 μm) in Fig. 1 and the decay at 380 nm as a function of time is shown in Fig. 2. It is evident from Fig. 1 that a more rapid decay of the transient occurs at longer wavelengths than at shorter ones. For example, at 380 nm the initial half-life is approximately 3 μs, whereas at 440 nm this value has decreased to about 0.5 μs. The transient difference spectrum shows
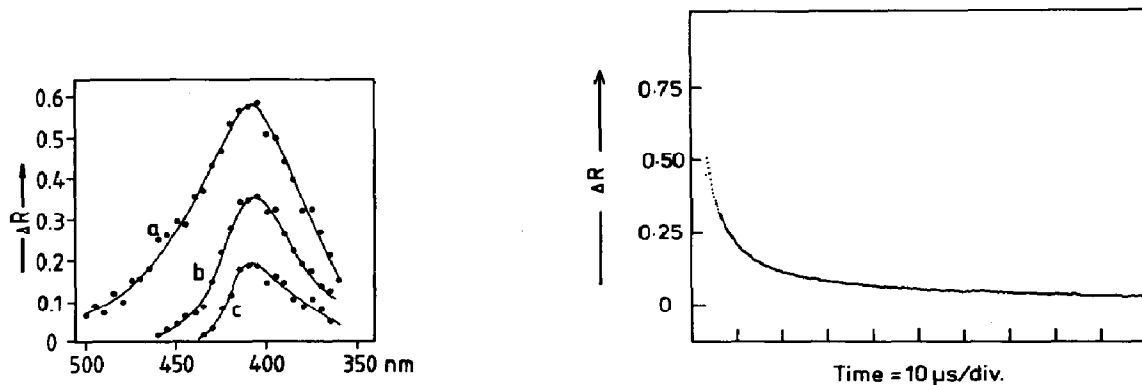
Fig. 1. Photoinduced changes in diffuse reflection of powdered TiO_2 (anatase) excited by 50 mJ pulse^{-1} (over a sample area of 0.78 cm^2) (a) at the laser pulse, (b) after 2 μs and (c) after 8 μs.

Fig. 2. Decay of transient absorption in powdered TiO_2 (anatase) monitored at 380 nm.

a maximum that is slightly red shifted from the absorption edge of TiO_2 at room temperature (which has a value of 3 eV [19], corresponding to a wavelength of 410 nm) and could therefore be assigned as an absorption across the band gap which has been decreased in energy by the heat generated within the semiconductor by the exciting pulse.

To verify the assignment as a photoinduced thermal effect, the position of the absorption edge of TiO_2 at temperatures between 20 K and 600 K was measured. This is shown in Fig. 3 for a sample of anatase. The spectra obtained by plotting the difference between each ground state spectrum and that obtained at 295 K are given in Fig. 4. The difference spectrum for a given pair of absorption edges represents the detectable distribution of
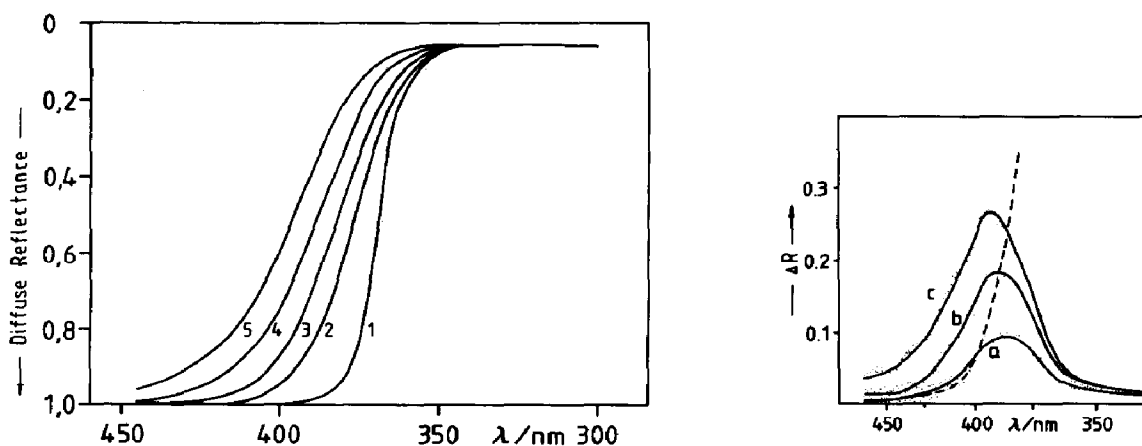

Fig. 3. Absorption edge of TiO_2 (anatase) at 20 K (curve 1), 295 K (curve 2), 385 K (curve 3), 485 K (curve 4) and 585 K (curve 5).

Fig. 4. Difference spectra from Fig. 3. ΔR is the difference between the reflectance of TiO_2 measured at 295 K and that at 385 K (curve a), 485 K (curve b) and 585 K (curve c). In addition, the absorption edge at 295 K is shown (— — —).

band-gap energies existing between the given temperature limits. The three difference spectra in Fig. 4 are similar to the time-resolved spectrum in Fig. 1 and provide evidence for assigning the transient as a valence-to-conduction band absorption in a rapidly heated sample which decays by cooling.

The temperature rise in the semiconductor can be calculated according to the following equation [20]

$$Q_0 = \frac{E_0 \alpha}{\rho C} \tag{1}$$

where Q_0 is the temperature rise at the semiconductor surface before significant heat flow into the sample has occurred, E_0 is the incident energy per unit area, C is the specific heat capacity of the material and ρ is its density, and α is the absorption coefficient. The above equation can be used to predict that an initial temperature rise of about 1100 K will occur at the surface of TiO_2, using the values $E_0 = 0.064$ J cm^{-2}, $\alpha = 1.2 \times 10^4$ cm^{-1}, $C = 0.69$ J g^{-1} K^{-1} and $\rho = 1$ g cm^{-3}. This value of ρ is used instead of the published value of 3.9 g cm^{-3} for solid anatase [22] because in the form employed in the experiments, i.e. as a powder, the anatase has an "apparent density" of 1 g cm^{-3}. Values of the other variables inserted in eqn. (1) to calculate Q_0 are either measured on or are directly applicable to the powder sample. The value of α was measured for a sample of TiO_2 (anatase, Merck) as well as for samples in which the absorption had been reduced by diluting the TiO_2 with an excess (tenfold to 50-fold) of $BaSO_4$. The initial temperature profile (i.e. before any significant heat flow has occurred) can be calculated from the equation [20]

$$Q_x = Q_0 \exp(-\alpha x) \tag{2}$$

where Q_x is the temperature at a distance x into the sample. From this equation, a temperature gradient extends over a distance of about 10^{-4} cm. Since the band gap of a semiconductor decreases with increasing temperature by about (5×10^{-4}) - 10^{-5} eV K^{-1} [23], the monitoring light will probe a "spectrum" of band gaps of different energies. Thus the decay of the transient absorption at any one wavelength will follow the cooling of the material, and the spectral variation in decay rates, as shown by the transient at longer wavelength decaying more rapidly than that at shorter wavelengths, will result from the "hottest" bands (i.e. those with the smallest energy transition) cooling more rapidly. The slight variation in decay parameters between different types of TiO_2 is probably a result of the differing particle sizes, optical absorption coefficients, heat conduction properties etc. resulting in different thermal properties.

Materials which have a large optical absorption coefficient (i.e. with $\alpha >$ 10^4 cm^{-1}) are likely to experience a large temperature rise following pulsed excitation, and this should be borne in mind when considering such experiments. Calculations have shown for the other materials we have studied by diffuse reflectance laser flash photolysis (for which α does not exceed 10^2 cm^{-1}) that the temperature rise is of the order of a few degrees, and any

photoinduced thermal processes will not contribute significantly to the transient behaviour. With regard to the spectra published by Bahnemann *et al.* of the transient absorptions of holes and excess electrons in colloidal TiO_2 [7], it is interesting to note that these transients do not directly represent a photoinduced thermal effect, but it must be pointed out that a rapid temperature jump has to be expected upon laser excitation of a highly absorbing colloid. Equation (1) cannot be applied directly to colloidal semiconductor materials for which the particle diameter is of the order of 10 nm, although other models still predict a substantial temperature rise. We have observed a quenching of the photoinduced thermal transient when TiO_2 powder is suspended in water, in which the heat can be dissipated rapidly into the aqueous medium, and the same process probably occurs for colloidal TiO_2. We are hopeful that the absorption of positive holes and excess electrons can be detected in TiO_2 and other semiconductor powders without significant interference from and domination by the photoinduced thermal effect, and current developments in the diffuse reflectance laser flash photolysis technique should permit this to be achieved.

Acknowledgments

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