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Journal of Photochemistry and Photobiology A: Chemistry 127 (1999) 111–115

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Microwave photodielectric and photoconductivity studies on titanium dioxide exposed to continuous polychromatic irradiation; Part II: Correlation of the microwave response with changes in sample microstructure during milling

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Received 15 March 1999; received in revised form 29 May 1999; accepted 1 June 1999

Abstract

Microwave photoconductivity and photodielectric measurements using a tuned microwave cavity method, operating in real time, were carried out for a series of commercial titanium dioxide (TiO_2) pigments. Changes in attenuation of microwave power and resonant frequency were shown to be sensitive to changes in particle size and composition. The data was interpreted by consideration of the relative contribution of excess carriers following saturation of traps during exposure, and the formation of long-lived states that persist during dark storage. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanium dioxide; Photoactivity; Pigment

1. Introduction

Microwave methods, in particular photodielectric measurements have been widely employed for the study of photochemistry and kinetic processes in photographic materials and semiconductors [1]. The effect serves as an informative non-contact approach to the measurement of photoconductivity in an alternating electric field, and can be applied to complex semiconductors for which growth of monocrystals of sufficient size and orientation is problematic.

In our previous paper [2] we exploited a real-time microwave cavity perturbation method as a gauge of photoactivity in titanium dioxide (TiO_2) pigments. This, we believe, is a novel application, which could form the basis of an effective characterisation technique for commercial systems. By this method a photoconductor may be continuously irradiated and the resulting changes to the electric susceptibility of the sample monitored in terms of its microwave response. This approach provides an extended timescale probe of charge carrier dynamics in photoconductors, complementary to the numerous time-resolved studies published to date [3–6]. The methodology offers the potential for a predictive tool of photoactivity in TiO_2 commercial pigments and photocatalytic applications where commercial applications are now becoming a reality [7,8]. This would be of particular value to the paint industry, where in the presence of TiO_2 coatings exposed to light suffer yellowing and loss of integrity which is manifested by erosion and deposition of loose surface pigment (‘chalking’) [9]. In this regard, all our measurements reported to date have used polychromatic light as the excitation source [2]. This mimics the conditions where the pigment would be employed in a real system, as well as standard natural weathering measurements.

Real-time microwave measurements facilitate observation of both changes in conductivity and dielectric constant during irradiation of photoconductors [1,2]. In essence, the apparatus consists of a tuned microwave cavity, which concentrates the microwave field at the sample, with shifts in resonant frequency and Quality (Q) factor being monitored during ultra band-gap exposure. Unlike time-resolved microwave conductivity (TRMC) measurements, which monitor decay of conductivity following a high intensity pulse of radiation, the real-time method adopted here is able to probe charge carrier dynamics over extended periods. The link between cavity parameters and the photophysics of

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PII: S1010-6030(99)00127-6

the samples applied here, was developed from the work of Hartwig and Hinds [10]. These workers demonstrated that the cavity resonant frequency decreases due to trapped carriers which increase the dielectric constant, and increases due to the decreased dielectric constant of delocalised carriers. Attenuation of microwave power may be attributed to delocalised carriers, which reduce the Q-factor of the loaded cavity. Furthermore, it was concluded that shallow-trapped carriers (with trap depths $\leq$100 meV) perturb both the cavity Q and resonant frequency.

A qualitative interpretation of the photoactivity of a pigment, on the basis of the microwave response requires a consideration of the interplay between charge carrier recombination, trapping and interfacial charge transfer. In this work we report real time microwave cavity perturbation measurements on a series of commercially produced TiO_2 samples, with controlled crystallite size and morphology, both being factors fundamental to the control of pigment photoactivity. During industrial production, treatment of base pigment, both sulphate and chloride derived, includes milling and micronising steps. The latter take place subsequent to coating and may involve the addition of surface coatings such as polyols and alkanolamines [11]. The effect of these treatments on the behaviour of electronic carriers, and the subsequent photocatalytic mechanism is clearly of interest in a commercial context.

2. Experimental

Full details of the construction of the instrumentation, irradiation configuration and light source are given in our previous work [2], thus, only the briefest details will be given here.

Microwave measurements were undertaken using a Marconi (6310) 2–20 GHz programmable sweep generator and Marconi (6500) scalar, automatic amplitude analyser, coupled to a rectangular waveguide and cylindrical cavity. Powdered samples (2.00 g) were packed in the cavity using a vibrator (to ensure reproducibility), all measurements were carried out in triplicate, and at 25°C. The uncertainty in the values of ‘shift in microwave cavity resonant frequency’ is of the order ±0.0004 GHz; while that for ‘attenuated power’ is ±0.05 dBm. Here dBm is $10\log_{10}(W_1/W_0)$, where W_0 = reference power level and W_1 = sample power level. Changes in microwave cavity resonant frequency and attenuation of microwave power were monitored during 1800 s of irradiation and for 1800 s after switching off the light source (unless stated otherwise).

Samples were irradiated with polychromatic light from a Rank Aldis projector lamp tungsten source, 250 W.

Commercial pigment samples were obtained from Millenium Inorganic Chemicals, Grimsby, UK. Selected samples were sand-milled on site and size distribution data supplied.

A Cambridge 250 stereo-scanning electron microscope was used to obtain electron micrographs of unmilled and milled rutile powders. Particle size data (Malvern Particle Analyser) as a function of milling time were supplied by Millenium Inorganic Chemicals.

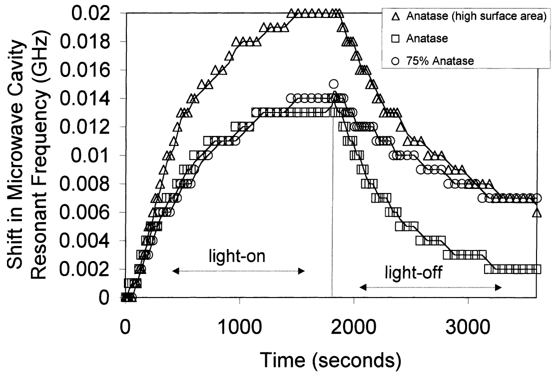


Fig. 1. Shift in the microwave cavity resonant frequency (GHz) during successive periods of exposure to polychromatic light (30 min) and dark storage (30 min) for anatase powders; of high surface area (△), anatase consisting of 0.15 μm (□), and 75% anatase (○).

3. Results and discussion

To initiate photocatalytic process occurring in real systems polychromatic light was chosen to irradiate the samples. It is important to stress that, given the wavelength distribution of the source, in addition to bandgap excitation, sub-band gap effects, including detrapping of localised electronic states would be expected to contribute to the overall response.

Fig. 1 shows the shift in microwave cavity resonance frequency for successive periods of exposure and dark storage for three pigments. These were a high surface area anatase sample consisting of 1 μm aggregates of 30 nm crystallites (specifically formulated as a catalyst support), anatase consisting of 0. 15 μm particles, and Degussa P25 (75% anatase, with the other 25% being predominantly rutile). It should be pointed out that data was collected for a similar series of rutile derived pigments. The trends in microwave response were very similar to the anatase pigments, and for the sake of brevity will not be considered in detail here.

The general appearance of the frequency curve was similar in each case. The largest resonant frequency shift was observed for the catalytic support material, which can be attributed to a higher photocarrier concentration, a consequence of its high surface area which optimises absorption of incident light.

Published photoconductivity measurements, carried out over a similar timescale to that used here, reveal an S-shaped response characteristic of initial electron trapping; followed by a further increase in conductivity resulting from excess carrier formation on prolonged exposure [12,13]. The high initial frequency shift for the catalytic support material reflects the greater contribution of excess carriers following

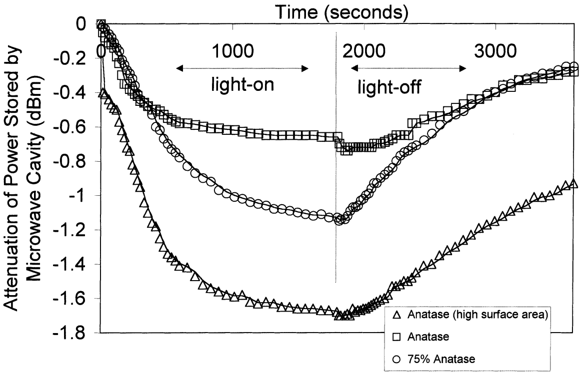


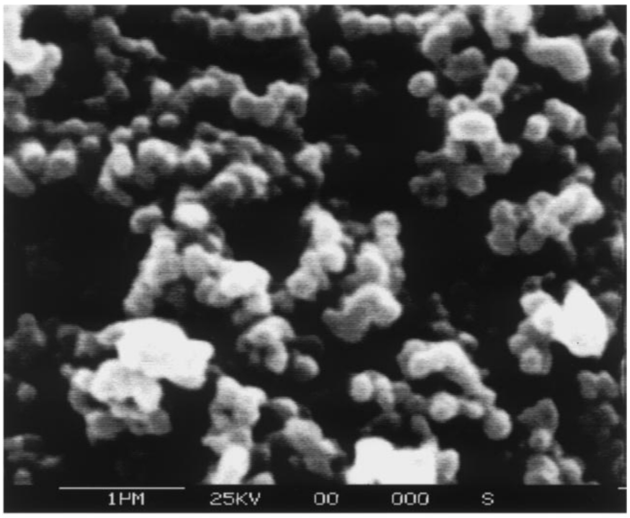
Fig. 2. Attenuation of power stored by the microwave cavity (dBm) during successive periods of exposure to polychromatic light (30 min) and dark storage (30 min) for anatase powders; of high surface area (△), anatase consisting of 0.15 μm (□), and 75% anatase (○).

saturation of traps during exposure. The relatively smaller contribution from excess carriers in P25 and 0.15 μm anatase was reflected in a smaller maximum frequency shift.

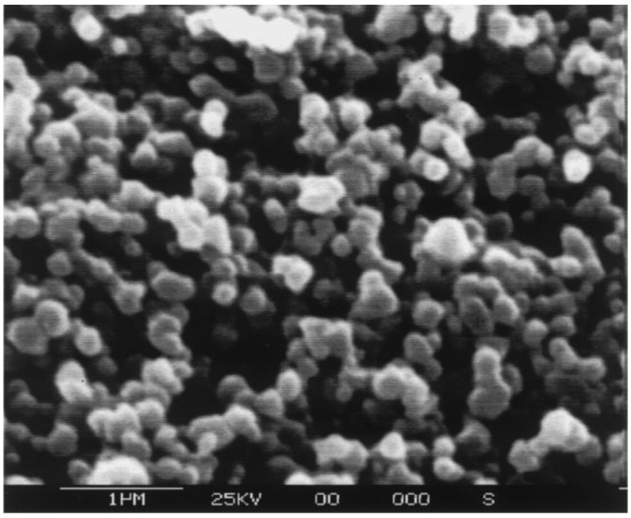
A further insight into the dynamics of photocarriers may be gleaned from a consideration of the frequency shift following an extended period of darkness. For all samples, on cessation of excitation, the cavity resonant frequency followed an apparently complex decay process, though not to its value prior to exposure. The catalytic grade material showed a value of residual frequency following dark storage, which was approximately equal to the P25. This would seem reasonable, given that the rate of trap related recombination increases linearly with surface area. In this regard, the focus of much current heterogeneous photocatalytic research using TiO_2, employs nanometer size particles which maximise the surface area to volume ratio and produce the highest quantum yield for photoreactions [14], the photocatalytic behaviour being further modified by size quantisation effects [15]. Furthermore, in commercial coatings, photodurability measurements of pigments demonstrated that the higher the surface area, the greater their photoactivity [16].

The data reported here suggests excess carriers are trapped in deep lying states giving rise to the long-lived residual frequency component of the decay process. This is not unreasonable considering the thermally stimulated current data reported by Addiss and co-workers which revealed trap depths for photoelectrons of up to 0.87 eV below the conduction band. It is anticipated that the presence of residual carriers would play a key role in photocatalytic processes over extended periods of exposure and dark storage.

On comparing P25 with 0.15 μm anatase, it can be seen that the existence of long lived states was significantly more pronounced in the former even though their initial frequency shifts were comparable. This is evidence for localisation of electrons in rutile regions of the mixed morphology material, the spatial inhibition of carrier recombination resulting in a higher residual frequency. Segregation of carriers in this manner has been proposed on the basis of time-resolved microwave measurements [17,18] and luminescence data



(a) unmilled



(b) milled for 30 minutes

Fig. 3. Electron micrographs (×25 000) of rutile powders; unmilled (a) and sand milled for 30 min (b).

[19] and arises from the conduction band in rutile being 0.1–0.2 eV lower than that for anatase (the valence band energies being approximately the same for both polymorphs).

The time dependence of attenuation of microwave power provides a profile of the production and the fate of excess free-carriers in the sample, during and after exposure. The response for the same set of samples, shown in Fig. 2 clearly mirrored the frequency shift. Here the catalytic grade anatase showed the highest concentration of free carriers thus corroborating the interpretation of the frequency data.

To further probe the effect of particle size on the microwave response, a sample of rutile was sand-milled for periods up to 30 min. The scanning electron micrographs in Fig. 3(a,b) revealed a breaking up of agglomerates on milling for 30 min. Particle size analysis revealed the per-

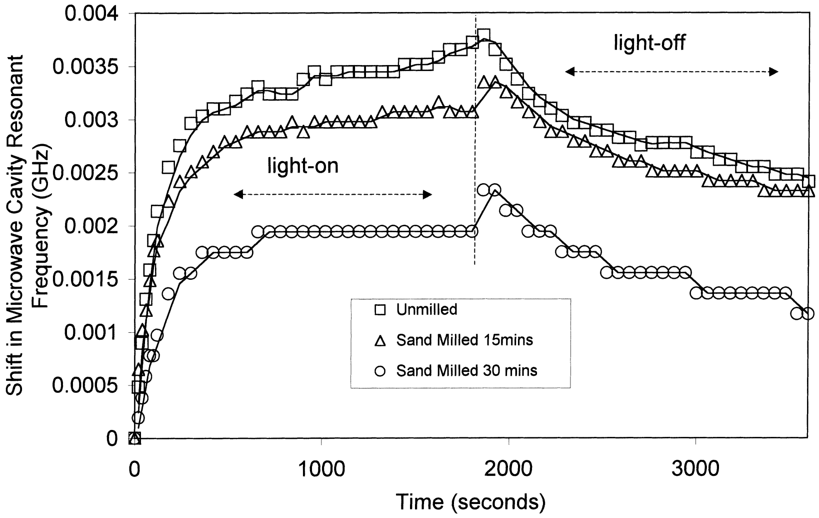


Fig. 4. Shift in the microwave cavity resonant frequency (GHz) during successive periods of exposure to polychromatic light (30 min) and dark storage (30 min) for rutile powders; unmilled (□), milled for 15 min (△), and milled for 30 min (○).

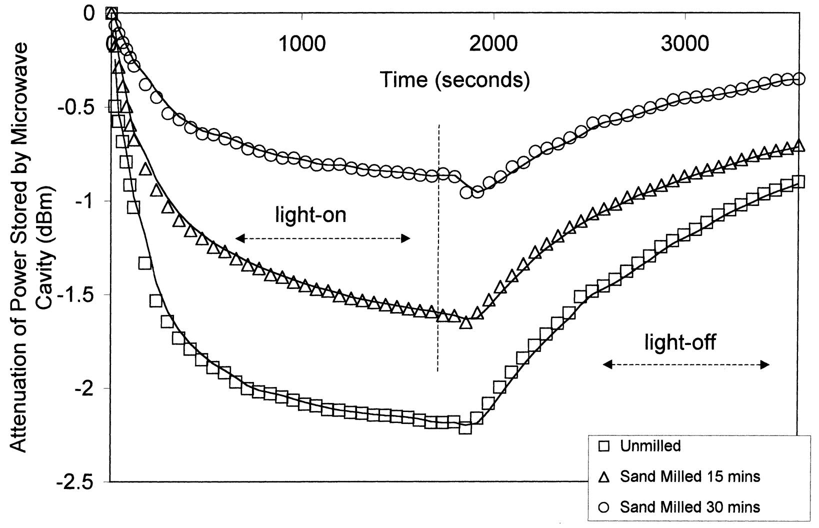


Fig. 5. Attenuation of power stored by the microwave cavity (dBm) during successive periods of exposure to polychromatic light (30 min) and dark storage (30 min) for rutile powders: unmilled (□), milled for 15 min (△), and milled for 30 min (○).

Table 1
The effect of sand milling on rutile particle size

Milling time (min)	Percentage particles with size > 0.5 μm	Standard deviation
0.00	22.885	0.260
15.00	9.569	0.124
30.00	6.786	0.120

centage of particles with size greater than 0.5 μm decreased dramatically during this process (Table 1). The microwave frequency data in Fig. 4 showed a shift towards greater carrier localisation on milling; manifested by the suppression of overall frequency shift during irradiation. This is indicative of the mechanically induced defects at the surface, which act as trapping centres. These new singularities would be expected to promote recombination, thus accounting for the lower residual frequency. Once again, these conclusions are supported by the power response (Fig. 5), where enhanced trapping and recombination are manifested by a smaller attenuation on exposure and after 30 min dark storage, respectively. Hence, a lower photoactivity for the milled samples is predicted here. In this regard, Heller and co-workers reported a decrease in photoactivity for ball-milled rutile samples where average particle size dropped from 0.2 to 0.1 μm [20]. Indeed, it is generally accepted by manufacturers that milling TiO_2 pigments, reduces their photo activity in polymeric systems [21,22].

The existence of a significant concentration of long lived trapped states is clearly of some importance, and must be viewed in the light of published work detailing the fate of photogenerated carriers in TiO_2. Time-resolved measurements, which have been reported on the picosecond or sub-picosecond timescales detail the primary photoevents occurring on irradiation. From time-resolved laser flash photolysis experiments, Bahnerman et al. have reported electron trapping in less than 20 ns, with both deep and shallowly trapped hole centres being detected [23]. The optical transitions observed were interpreted as arising from electronic excitation within localised states, such as the d–d transition within hydrated Ti^{3+} species. Serpone and co-workers [24] and Colombo et al. [25] have demonstrated extremely rapid electron and hole trapping at surface states. Microwave photoconductivity experiments carried out over similar timescale reveal conductivity transients indicative of rapid recombination. For P25, Schindler and Kunst report a half-life conductivity decay of 2.0 μs [17] and Martin and co-workers report 1.1 μs [5,6].

Clearly transients of this nature are not directly relevant to our experiments, however longer-lived states in irradiated TiO_2 have also received attention. ESR experimental parameters, *g*-values hyperfine splitting and linewidths (a consequence of electron spin relaxation) would be expected to provide microscopic information about trapped centres. Spectra from photoexcited anatase have been interpreted in terms of electron trapping at bulk Ti^{4+} centres. Surface hydroxide ions have been shown to act as deep hole traps, photogenerated holes reacting to form ESR active centres of the type $[Ti^{4+}O^{\bullet-}\ Ti^{4+}OH^{-}]$ [26,27]. The extent to which these centres participate in photocatalytic degradation and their relevance to degradation of polymer is currently unresolved and provides an impetus for future investigation. It is however, apparent that the real time microwave measurements reported here provide information on dynamics of photocarriers in TiO_2 pigments and the nature and extent of carrier trapping in centres such as these.

4. Conclusions

Real-time microwave photoconductivity and photodielectric measurements were shown to be a probe of free-carrier production, trapping and recombination in commercial TiO_2 pigments of differing particle size and composition. The cavity resonant frequency shift and attenuation of microwave power following exposure to ultra-bandgap light were sensitive to the concentration of free carriers and carrier localisation in deep lying states within the bandgap. A correlation between the microwave response and the concentration of mechanically induced singularities was observed. Given the inextricable link between charge carrier dynamics and photoactivity, the technique described here holds the promise of application as an effective predictive tool for commercial pigments and photocatalysts. With this in mind, in Part III of this paper we have extended this study to examine the real-time microwave response arising from TiO_2 powders coated with silica and/or alumina.

Acknowledgements

The authors would like to thank Millenium Chemicals, UK, for useful discussions and financial support.

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