ELSEVIER

Dyes and Pigments 48 (2001) 29–34

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

The effect of sample treatment and composition on the photoluminescence of anatase pigments

R. Janes *, M. Edge, J. Rigby, D. Mourelatou, N.S. Allen

Department of Chemistry and Materials, Manchester Metropolitan University, John Dalton Building, Chester Street, Manchester M1 5GD, UK

Received 5 May 2000; accepted 13 July 2000

Abstract

We report low temperature luminescence studies of a series of pure and treated anatase pigments. The intensity of the green excitonic emission correlated with the photoactivity of the pigment, recombination being enhanced in milled and coated samples. Weak emission was also detected from amorphous titania gels and the photocatalytically active Degussa P25 pigment. The latter gave no evidence for segregation of photocarriers because of the multiphasic nature of the material. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Pigment; Titanium dioxide; Anatase; Recombination; Luminescence; Photocatalysis

1. Introduction

The commercial applications of titanium dioxide pigments are widespread. These pigments constitute the whitest and brightest of industrial pigments, a consequence of an exceptionally high refractive index in the visible region of the spectrum. This stems from a high optical dielectric constant and high relectivity, a prerequisite for a finely divided material to scatter light efficiently. Indeed, commercial titania pigments are produced to tight tolerances to optimise this property [1]. It has long been recognised that an inherent drawback in the application of TiO_2 in coatings, is the "chalking" effect resulting from photoredox processes at the pigment surface [2]. Interestingly, these same reactions have stimulated a vast research effort into applications of titania in such areas as photoelectrochemical cells and as photocatalysts for the destruction of organic and inorganic pollutants [3]. The latter process arises due to the creation of active radical centres following generation of photocarriers and subsequent interfacial redox processes.

An understanding of the fundamental bulk and surface charge carrier dynamics in irradiated titania particles is essential to the underpinning of effective chemical control of pigment photoactivity. This will generally centre around manipulating the efficiency of electon-hole recombination. In our earlier work we used real-time microwave cavity perturbation techniques to gauge the photoactivity of commercial TiO_2 pigments that had been subjected to a variety of

---

* Corresponding author at present address: Department of Chemistry, The Open University, Walton Hall, Milton Keynes MK7 6AA. Tel.: +44-20-7794-0575; fax: +44-20-7556-6196.

PII: S0143-7208(00)00081-4

standard treatments [4] and doping with d-block ions [5]. Given that the primary electronic processes and interfacial charge transfer in TiO_2 photocatalysts typically occur on very rapid timescales [3], this approach facilitated measurement of both the accumulation of charge carriers during irradiation and their decay during dark storage. These measurements demonstrated the existence of excess carriers trapped in deep lying states, that may potentially contribute to the photocatalytic processes over extended periods of exposure and dark storage. In this regard, a correlation between the microwave response and the photoactivity of treated pigments was observed [4]. Given the nature of these photoelectronic processes, a correlation between the microwave response and conventional photoluminescence spectroscopy, (a technique widely applied to photoconducting solids [6]) would be anticipated.

The low-temperature photoluminescence from the two common titania polymorphs is markedly different. In the case of anatase TiO_2, a broad green emission has been attributed to localised (self-trapped) exciton recombination by Tang and coworkers [7]. For the rutile form, Addiss et al. [8] observed a broad emission band at 850 nm and 77 K, which was tentatively assigned to recombination at interstitial Ti^{3+} ions. A subsequent study by Grabner and coworkers [9] confirmed the existence of the broad band but, under high resolution, vibronic structure was revealed. These workers proposed the origin of the emission, even in nominally pure samples, to be Cr^{3+} (d^3) ions. Allen et al. reported an additional band at 1015 nm [10], with the 815 nm emission only being detected from rutile prepared by the sulfate [1] route. Interestingly, the infrared component was also observed from anatase TiO_2, and was stable to room temperature for both polymorphs [10]. Room temperature luminescence has also been reported from recent investigations into nanostructured titanias. During studies into optical non-linearlities in ultrafine TiO_2, Zhu and Ding reported emissions assigned to surface TiOH and $TiOC_2H_5$ centres [11]. A similar band was also detected from a hydrothermally prepared, layered TiO_2 mesostructucture [12]. Studies of transition metal ion-doped titania revealed emission bands having wavelengths that were characteristic of the host lattice, the energy of recombination being independent of the dopant ion [5]. This somewhat intriguing result was in contrast to a system such as ZnS, where doping with copper ions, silver ions and manganese ions produced different Stokes' shifts [6].

Motivated by a desire to investigate the dynamics of photocarriers in practical systems and their relevance to the durability of pigmented polymers, we report emission spectra of a series of industrially prepared materials. Commercial pigments for specialist applications are frequently sand-milled and coated with inorganic oxides (usually alumina, silica or zirconia) and often organic compounds such as polyols and amines [1]. Such treatments would be expected to temper the behaviour of photocarriers. In addition, we consider the nature of the emission from Degussa P25 (approximately 75% anatase TiO_2, 25% rutile TiO_2) and from alkoxide derived amorphous titania. The former compound is commonly used as a standard reference material in the field of semiconductor photocatalysis [3].

2. Experimental

Titanium dioxide (anatase) powders were supplied by Millenium Inorganic Chemicals, Grimsby UK. Selected samples were sand-milled on-site. Two types of coatings were examined; a general purpose surface treatment of alumina, and a mixed alumina–zirconia coating. The mixed coating produced a more durable pigment [13]. Anatase was also prepared by acid-catalysed hydrolysis of titanium (IV) isopropoxide to form a gel [14]. Drying the gel at ca.110°C yielded a xerogel which was then fired in a muffle furnace at temperatures between 500 and 800°C for 12 h to yield a crystalline product.

Luminescence spectra were recored using a Perkin–Elmer LS50-B spectrometer operating between 77 K and room temperature. The instrument was operated in phosphorescence mode, with careful optimisation of parameters, including spectral bandwidths of the illuminating and emission beams, and scan speed. X-ray powder diffraction was carried out using a Philips PW3020 diffractometer employing CuK_α radiation. Scanning Electron Microscopy was carried out using a Cambridge 250 SEM.

3. Results and discussion

Photoluminescence spectra from a series of anatase TiO_2 pigments under near band gap excitation at 77 K, are shown in Fig. 1. All the samples gave rise to a low intensity Stokes' shifted, green emission band in the range ca. 450 to 650 nm. This reached a maximum intensity at about 580 nm. The spectral shape and position were not influenced by the excitation wavelength, although the intensity of the band increased as the excitation wavelength was decreased between 370 and 240 nm. This followed the increase in absorption coefficient for the optical absorption edge [15], a similar variation being reported for mesostructured TiO_2 [12]. Given that charge carrier recombination for electrons and holes occurs in the 10–100 ns time domain [3], the luminescence centres observed here, are analogues of the long-lived states described by Addiss et al. from rutile TiO_2, (trap depths of up to 0.87 eV below the conduction band were reported) [8] and the centres inferred from real-time microwave photoconductivity data and photodielectric data [4].

Fig. 1 shows the emission band recorded under identical instrumental conditions for the milled and coated pigments, a direct comparison is justified as all materials are derived from the same base pigment. Scanning electron microscopy indicated no appreciable reduction in particle size, (or any other microstructural modification) on milling. Thus the increase in intensity may be attributable to the introduction of mechanically induced defects within the grains that act as trapping centres, hence promoting recombination. It should be emphasised that, as photoluminescence is not a bulk characterisation technique, only the near surface region, defined roughly by the minority carrier diffusion length and the incident radiation penetration depth, is sampled. The signal intensity recorded here probably represents a lower limit for the sample. Given the increased recombination,

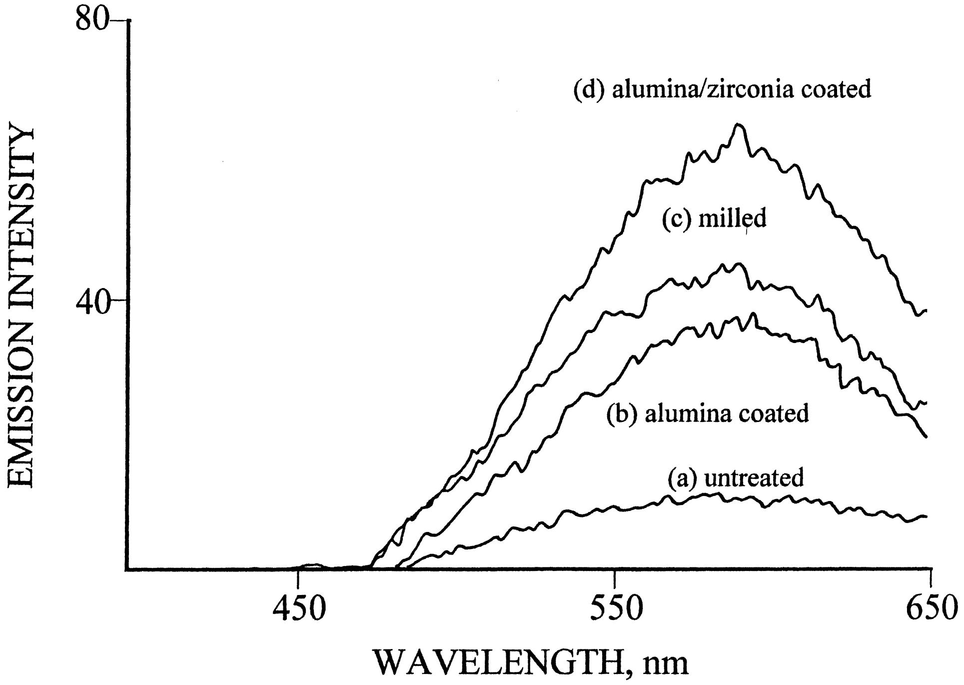

Fig. 1. Photoluminescence emission spectra for anatase powders measured at 77 K. Excitation wavelength = 370 nm.

one might anticipate that the photoactivity of milled pigments would be reduced relative to the photoreactivity of the unmilled parent material. Indeed, it is generally accepted by manufacturers that milling TiO_2 pigments reduces their photoactivity in polymeric systems [16]. Indeed a detailed study by Heller and coworkers demonstrated a decrease in photoactivity of TiO_2 following milling [17]. We have previously reported real-time microwave cavity perturbation measurements for milled pigments [4]. Measurements of the resonant frequency of a tuned microwave cavity also revealed greater carrier localisation on milling, which was manifested by the supression of overall frequency shift during irradiation.

A similar effect was observed in the coated samples. In a practical sense, coating enhances pigmentary characteristics including durability, gloss and dispersibility in a polymeric system, where the inert surface oxide provides a physical barrier to photoredox reactions. The increased green emission intensity, indicates that the coating process has introduced recombination centres into the material, possibly at the interface between the coating and the parent material. Notably, the most intense emission was detected from the more durable alumina/zirconia-coated material. One may speculate that the increased, evident carrier recombination, also contributes to the reduction of overall photoactivity of pigments treated in this way. Furthermore, on an atomic level, any substitutional aluminium atoms would be expected to provide negatively ionised centres, that would also promote excitonic recombination. Indeed, Tang and coworkers proposed the formation of acceptor states in aluminium doped anatase, TiO_2 single crystals [7].

Prompted by literature reports of photoactivity in amorphous-anatase TiO_2 compositions [18], photoluminescence in sol-gel derived anatase TiO_2 and a precursor xerogel was examined. The formation of crystalline anatase TiO_2 on firing, was confirmed by X-ray powder diffraction (Fig. 2). For the xerogel, a weak green emission was detected. This finding was somewhat reminiscent of the observations of Deb [19] who reported a similar emission from amorphous TiO_2 thin films, which was attributed to localised exciton recombination.

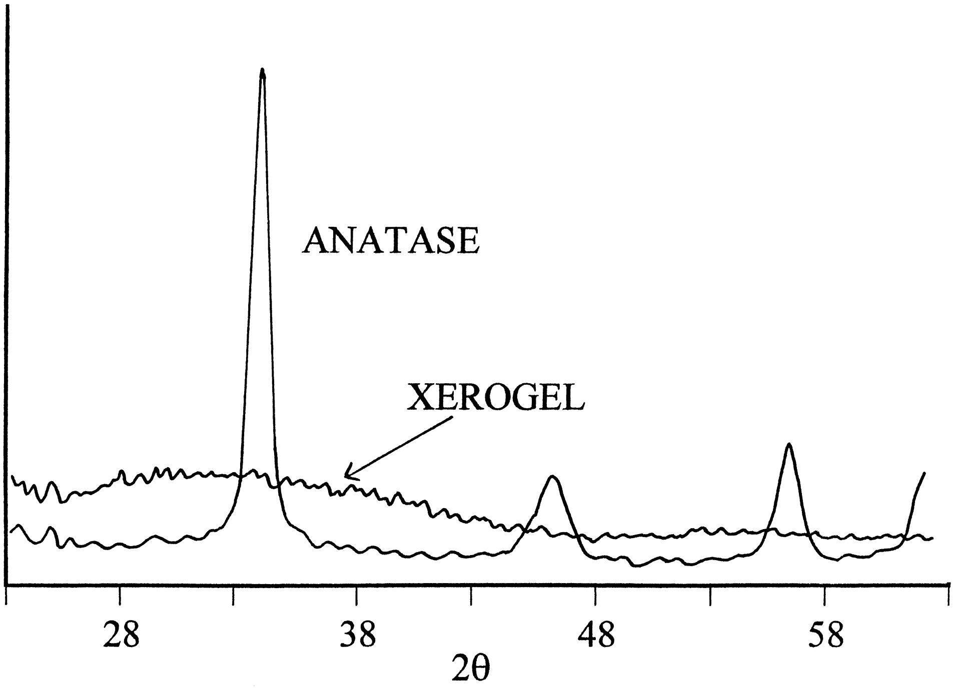

Fig. 2. Powder X-ray diffraction (CuK_α radiation) pattern of sol-gel derived anatase and intermediate xerogel.

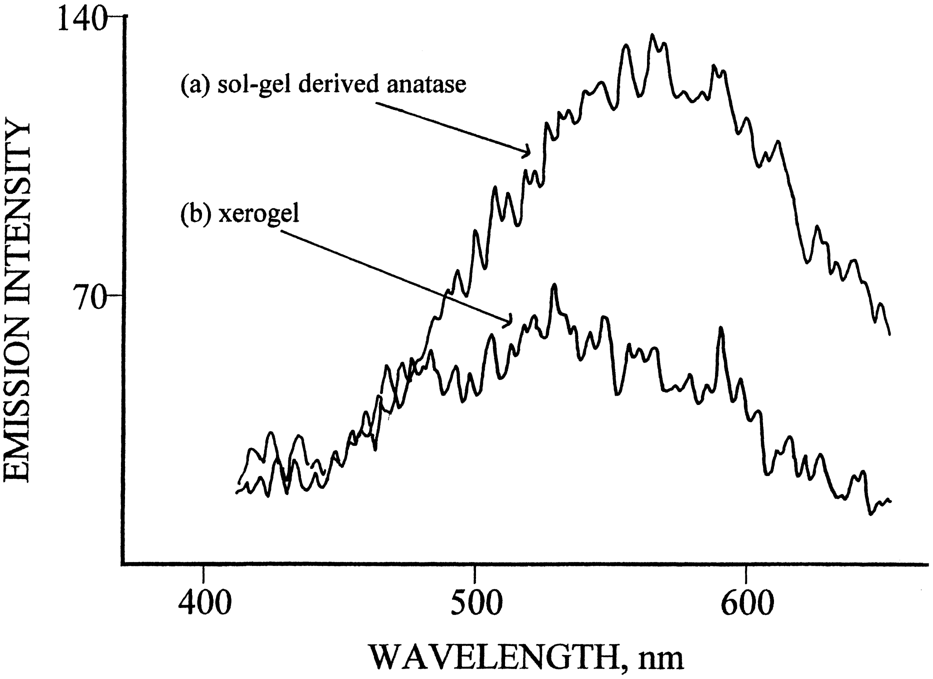

Fig. 3. Photoluminescence emission spectra measured at 77 K for: sol-gel derived anatase, (b) xerogel.

The intensity of the green emission from the xerogel grew in intensity as the material crystallised on firing (Fig. 3). Amorphous anatase has been shown to be photocatalytically inactive [18], a feature attributed to high levels of surface and bulk trapping centres which facilitate recombination. The weak emission band that was detected suggested that rapid recombination channels dominate, leaving few long-lived states. However, one cannot rule out the possibility that the emission originates from crystalline anatase TiO_2 present at levels below the X-ray diffraction detection limits.

Photoluminescence spectra of Degussa P25, a highly active photocatalyst, were again characterised by a weak green emission, identical in form to the spectra shown in Fig. 1. From time resolved microwave conductivity measurements, Warman and coworkers [20] proposed the spatial segregation of electrons and holes, given that the rutile TiO_2 conduction band lies 0.1–0.2 eV lower in energy than anatase TiO_2. Shallow electron localisation was thought to occur in rutile-like outer layers of the P25 particles, hence reducing recombination ineffeciencies. From real-time microwave measurements, an enhancement of the lifetime of localised states relative to single phase anatase TiO_2 was observed [4]. The presence of rutile TiO_2 and amorphous titania regions within P25, clearly did not modify the phosphorescence response over an extended timescale. Recombination, indicative of long-lived deep states in anatase regions was observed. Furthermore, there was no evidence of emission in the 800–900 nm range, characteristic of the rutile polymorph [8–10].

4. Conclusions

The low temperature photoluminescence measurements of anatase TiO_2 pigments, show a sensitivity to prior mechanical treatment, particularly milling and coating, and revealed a propensity for carrier localisation at structural defects or dislocations within the lattice. It is clear that, although a description of the nature of the recombination centres is certainly not clear-cut, the detection of the long-lived states reported here, is analogous to, and must be viewed alongside, published work detailing the fate of photocarriers in TiO_2 using complementary techniques.

Acknowledgements

The authors would like to thank Millenium Chemicals, Grimsby, UK for financial support and supplying many of the treated pigments used in this study.

References

[1] Egerton TA, Tetlow A. In: Thompson, R, editor. Industrial inorganic chemicals: production and uses. Royal Society of Chemistry, 1995. Chapter 13.

[2] Allen NS. Photofading and light stability of dyed and pigmented polymers. Polym Degrad Stab 1994;44:357–74.

[3] Mills A, Le Hunte S. An overview of semiconductor photocatalysis. J Photochem Photobiol A: Chemistry 1997;108:1–35.

[4] Janes R, Edge M, Robinson J, Rigby J, Allen NS. 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. J Photochem Photobiol A: Chemistry 1999;127:111–5.

[5] Janes R, Edge M, Robinson J, Rigby J, Allen NS. Microwave photodielectric and photoconductivity studies on commercial titanium dioxide pigments: the influence of transition metal dopants. J Mater Sci 1998;33:3031–6.

[6] Bube RH. Photoelectronic properties of semiconductors. Cambridge: Cambridge University Press, 1992.

[7] Tang H, Berger H, Schmid PE, Levy F, Burri G. Photoluminescence in TiO_2 anatase single crystals. Solid State Commun 1993;87(9):847–50.

[8] Addiss RR, Ghosh AK, Watkim FG. Thermally stimulated currents and luminescence in rutile (TiO_2). Appl Phys Lett 1968;12(11):397–400.

[9] Grabner L, Stokowski SE, Brower WS. No phonon ${}^4T_{2g}$–${}^4A_{2g}$ transitions of Cr^{3+} in TiO_2. PhysRev 1970;B2(3):590–7.

[10] Allen NS, Bullen DJ, McKellar JF. Luminescence and manufacturing history of titanium dioxide pigments. 1978; Chemistry and Industry 629–30.

[11] Zhu YC, Ding CX. Investigation on the surface state of TiO_2 ultrafine particles by luminescence. Solid State Chem 1999;145:711–5.

[12] Lin W, Pang W, Sun J, Shen J. Lamellar TiO_2 mesophase with an unusual room temperature photoluminescence. J Mat Chem 1999;9:641–2.

[13] Janes R, Edge M, Rigby J, Allen NS, Internal report to Millenium Inorganic Chemicals, UK. September 1999.

[14] Yoldas BE. Hydrolysis of titanium alkoxide and effects of hydrolytic polycondensation parameters. J Mat Sci 1986;21:1087–92.

[15] Cox PA. Transition metal oxides, an introduction to their electronic structure and properties. Oxford: Oxford University Press, 1992 (Chapter 3).

[16] Braun JH. Titanium Dioxide-A Review. J Coatings Technol 1997;69(868):59–72.

[17] Heller A, Degani Y, Johnson DW, Gallagher PK. Controlled suppression and enhancement of the photoactivity of titanium dioxide pigment. J Phys Chem 1987;91:5987–91.

[18] Ohtani B, Ogawa Y, Nishimoto S. Photocatalytic activity of amorphous-anatase mixture of titanium (IV) oxide particles suspended in aqueous solutions. J Phys Chem 1997;B101:3746–52.

[19] Deb SK. Photoconductivity and photoluminescence in amorphous titanium dioxide. Solid State Commun 1972;11:713–5.

[20] Warman JM, de Haas MP, Pichat P, Koster TMP, van der Zouwen-Assink EA, Mackor A, Cooper R. Electronic processes in semiconductor materials studied by nanosecond time-resolved microwave conductivity—III. Al_2O_3, MgO and TiO_2 powders. Radiat Phys Chem 1991;37(3):433–42.