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Preliminary note

Modification and enhanced photocatalytic activity of TiO_2 following exposure to non-linear irradiation sources

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Abstract

The effects of high power pulsed laser light on a TiO_2 photocatalyst (powder and 0.1% (w/v) aqueous suspension) are reported. When this material was irradiated with a laser of power over 0.8 MW peak pulse power at 355 nm wavelength a visible change in colour from white to dark blue was observed. The initial rate of change of the total colour difference is related to the laser power; the stronger the laser power the darker the colour change. The result of X-ray diffraction studies indicates that the crystal structure of the TiO_2 developed a more rutile form after laser exposure. Electron microscopic studies showed that spherical shaped particles of TiO_2 were observed after laser treatment. Preliminary results show enhanced photocatalytic activity for the destruction of methylene blue. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Laser; TiO_2; Structure change; Colour change; Photocatalytic activity

1. Introduction

The use of semiconductor photocatalysis for waste material treatment has been widely reported in recent years. When the semiconductor is illuminated with light source it generates highly active radicals, that can oxidise the organic waste materials such as dyes, pesticides, bacteria and herbicides [1–4]. TiO_2 is especially suitable for a wide range of applications compared to other semiconductors, because it is highly photoreactive, cheap, non-toxic, chemically and biologically inert, and photostable [5].

The photocatalytic activity of the TiO_2, however depends on the crystal structure, preparation method [6], annealing temperature [7] and the nature of the substrates to which it is adhered [8]. Three different crystal structures of TiO_2 exist, rutile, anatase and brookite, but commonly rutile and anatase are used in photocatalysis, with anatase showing a higher photocatalytic activity [9]. One particular form of commercial TiO_2 namely Degussa P25 titanium dioxide, a roughly 70:30 anatase/rutile mix with a surface area of 55 m^2g^{-1}, appears to be the most active readily available form of this photocatalyst [10]. The anatase form of the catalyst is usually the photoactive form of TiO_2 [11], however the presence of rutile in Degussa P25 has been cited as a reason for its notable photoactivity [12]. In this paper, we have investigated the effect of laser light on Degussa P25 TiO_2 and report an enhanced photocatalytic activity of the laser treated material for the degradation of methylene blue.

2. Experimental

A tripled Nd:YAG laser (Surlite), producing 4.5 ns pulses of up to 22 MW peak pulse power (PPP) was used for laser treatment. TiO_2 (Degussa, P25) powder or 0.1 wt% solution was illuminated with the laser set to a wavelength of 355 nm. The sample solution was agitated using a magnetic stirrer. The colour of the catalyst, which was contained in a quartz cell was measured directly, every 5 min up to 30 min after laser exposure using a chromameter (Minolta CR-200b).

Transmission electron microscope (TEM) specimens were prepared by dispersing the powder in isopropyl alcohol and depositing onto holey carbon films on nickel grids and observed using a microscope (Philips CM20, operated at 200 kV). For the photocatalytic experiments a 480 W Xenon lamp (Dr Hönle, UK) was used as a light source with the 0.1 wt% laser treated and untreated TiO_2 (Degussa, P25) suspension to degrade methylene blue (3.14×10^{-5} M) (Aldrich).

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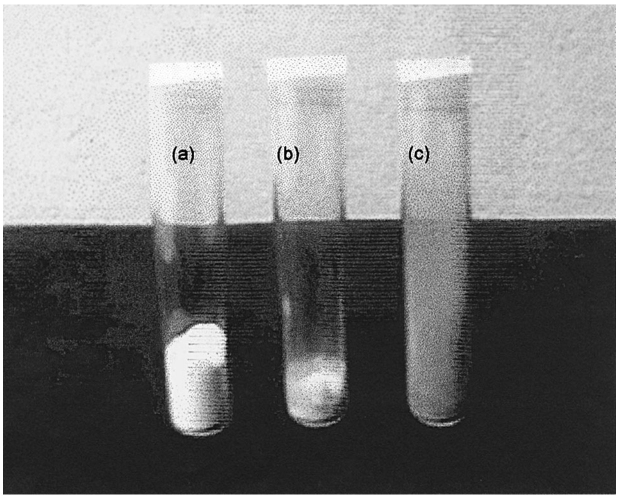

Fig. 1. Picture of Degussa P25 TiO_2 samples: (a) no laser treatment; (b) mild laser treatment (5 min at 1 MW PPP); (c) strong laser treatment (5 min at 15.2 MW PPP).

3. Results and discussion

Irradiation of TiO_2 with the laser light resulted in a visible colour change of the material from white to dark blue (Fig. 1). These changes were observed when both the dry powder and a 0.1% aqueous suspension of TiO_2 were irradiated. The colour changes were quantified using a chromameter which offers the $L^*a^*b^*$ co-ordinate which closely represents human sensitivity to colour. Equal distances in this system equal approximately perceived colour differences. L^* is the lightness variable; a^* (green to red) and b^* (blue to yellow) are chromaticity co-ordinates. The total colour difference (dE) represents a straight-line distance between co-ordinates of the sample and the target colour and is calculated using the following equation:

$$\mathrm{d}E = [(L^*)^2 + (a^*)^2 + (b^*)^2]^{1/2}. \tag{1}$$

The observed total colour difference, dE, as a function of exposure time was measured for a series of different laser powers. The results of this work are shown in Fig. 2. From these results it appears that the initial rate of change of the total colour difference is related to the laser power. At higher peak pulse powers the colour change in the TiO_2 was more pronounced. The effect of direct laser exposure on dry powder TiO_2 photocatalyst under both air and nitrogen atmospheres was also studied. In both cases the same white to dark blue colour changes were observed.

In order to elucidate what was happening to the TiO_2, the samples were examined by small angle X-ray diffraction (XRD) spectroscopy and TEM. X-ray diffraction studies indicated that the crystal structure of the TiO_2 became more rutile after strong laser treatment in air at 15.2 MW PPP as shown in Table 1. Exarhos [13] reported a phase change from anatase to rutile when investigated the damage caused to pure anatase TiO_2 optical films following irradiation by a 532 nm pulsed laser. No colour change in the TiO_2 was, however reported. It should be noted that the laser employed by Exarhos was generating laser light of sub-band gap energy (2.38 eV) while our system generates ultra band gap energy (3.5 eV). No detailed explanation for this phase change was discussed by this author.

A simple rationale for the above observation is that the intense laser light produces local heating, generating temperatures in the powder which are sufficient for the conversion of anatase to rutile TiO_2. This observation is interesting, as it provides a simple method, namely laser light irradiation, for increasing the rutile content of a TiO_2 powder. As noted earlier, anatase–rutile crystallite are noticeably more active photocatalytically, than either the individual anatase or rutile component phases [12]. This laser treatment provides a possible useful route to control and adjust the

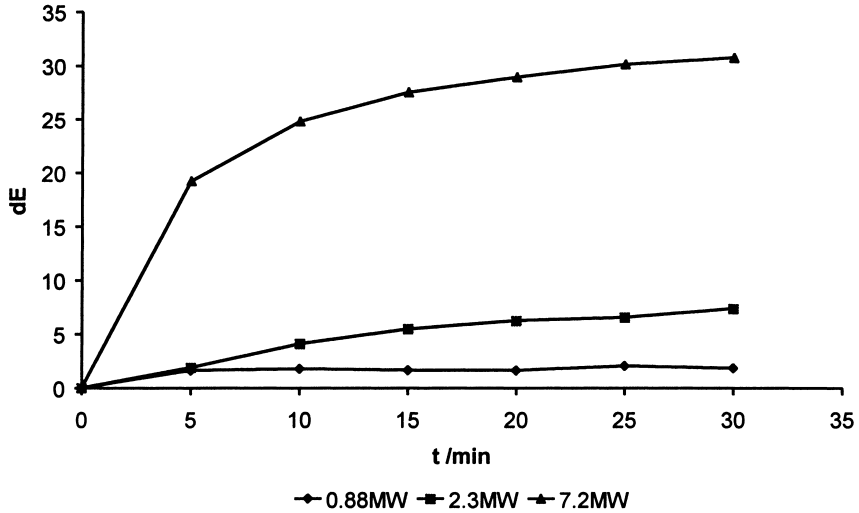

Fig. 2. Total colour difference with a laser exposure time.

Table 1
Rutile/anatase ratios for TiO_2 sample powders

TiO_2	Laser power (PPP)	XRD data		
		Rutile intensity/θ	Anatase intensity/θ	Rutile/anatase ratio
No laser treatment	0	2200/27.5	14 200/25.4	0.15
Mild laser treatment	5 min at 1 MW	3500/27.5	16 800/25.4	0.21
Strong laser treatment	5 min at 15.2 MW	9000/27.5	15 200/25.4	0.59

Table 2
The photocatalytic destruction of methylene blue using unmodified and laser modified TiO_2

TiO_2	Initial rate (μmol min^{-1})
Untreated	6.3
Strong laser treatment	10.2

anatase–rutile ratio of the micro crystallite components in a TiO_2 photocatalyst powder, without drastically affecting the overall surface area of the powder.

In addition to the conversion of anatase to rutile TiO_2, laser treatment also generates non-stoichiometric TiO_{2-x}, such as Ti_2O_3, Ti_3O_5, and Ti_nO_{2n-1} (n=4–60). These reduced forms of TiO_2 are blue-black in appearance and can be metallic to insulating in conductivity [14]. Others have also noted this colour change when a sintered rutile TiO_2 disk was laser irradiated [15] and proposed that the colour change was due to the formation of Ti(III) sites. Our work shows that the Ti(III) site responsible for the blue-black colour can be readily re-oxidised to Ti(IV), and the powder converted from grey/blue to white by annealing the laser treated TiO_2 at 773 K for 2 h.

The TEM study revealed that the TiO_2 particles were more spherical with smaller crystallites following strong laser exposure treatment. These observations are indicative of a rapid high temperature sintering process. Overall, however, although anatase to rutile conversion had taken place, the average particle size (and therefore specific surface area of the powder) remained largely unaltered (55 m^2 g^{-1}).

The oxidative mineralisation of methylene blue was examined using both untreated and strong laser treated TiO_2. Preliminary results showed a faster destruction rate with the strong laser treated TiO_2 as shown in Table 2. The presence of the Ti(III) species may be acting as a dopant in the TiO_2 which may be improving the photocatalytic activity by improving the degree of band bending within the semiconductor particles. The enhanced photocatalytic activity may also be due to the change in anatase/rutile ratio within the TiO_2 powder following laser treatment.

In conclusion changes of phase structure and pigment colour have been observed in the TiO_2 (powder and solution) photocatalyst after laser exposure. The initial rate of change of the total colour difference is related to the laser power. The photocatalytic activity of the TiO_2 was enhanced following exposure to non-linear irradiation light sources. Further work is in progress to provide a more detailed understanding of the processes involved and of the nature of the laser treated TiO_2 powders.

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