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On-line Monitoring of Laser Modification of Titanium Dioxide using Optical Surface Second Harmonic

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Abstract

TiO_2 Photocatalysis is a promising technology for the destruction of organic pollutants in both waste and potable waters with the mineralisation of a wide range of compounds having been reported. TiO_2 has many advantages over other semiconductors, it is highly photoreactive, cheap, non-toxic, chemically and biologically inert, and photostable. The photocatalytic activity of TiO_2 has been shown to depend upon many criteria including the ratio of anatase/rutile crystal phase, particle size and oxidation state. This paper reports the use of optical Surface Second Harmonic Generation (SSHG) to monitor modifications in TiO_2 powder induced following laser treatment. SSHG is a non-contact, non-destructive technique, which is highly sensitive to both surface chemical and physical changes. Results show that three different SSH intensities were observable as the TiO_2 samples were irradiated with the laser light. These regions were related to changes in chemical characteristics and particle size of the TiO_2 powder.

Keywords:

Photocatalysis, TiO_2, Surface Second Harmonic Generation, Laser Treatment, colour change, Structure change.

1. Introduction

The use of titanium dioxide as a photocatalyst for the destruction of polluting materials has demonstrated great potential as remediation technology for both water and gas phases [*1*]. Since TiO_2 is cheap, non-toxic, chemically and biologically inert and highly photoreactive, it is a practical material for a wide range of effluent treatment applications. The effectiveness of TiO_2 as a photocatalyst depends on a number of factors including particle size, crystal structure and surface electronic states. These properties are usually determined using surface analysis methods such as XPS, XRD or TEM, which require significant sample preparation and must be operated under vacuum. Recently Lee *et al* reported a modification of crystal structure and oxidation state of TiO_2 powders, which also changed in colour from white to blue grey, following exposure to pulsed laser light [*2, 3*]. Further work has shown that the laser induced alterations were dependent on the exposure parameters i.e. time, optical power density, and wavelength. In order to optimise the laser modification of the TiO_2 it is necessary to have a method for on-line monitoring of the changes induced in the TiO_2 during the laser treatment. Therefore there is a need for surface monitoring methods that require little sample preparation and can be operated under ambient conditions.

Surface Second Harmonic Generation (SSHG) is a technique that possesses such advantages. Second harmonic generation is the lowest order nonlinear optical process, which nonlinearly converts two incident photons of frequency ω into a single photon of twice the frequency, 2ω. In the electric dipole approximation, this phenomenon only occurs in non-centrosymmetric media or where the centre of symmetry is broken i.e. at any surface

[*4*]. The SSHG is highly sensitive to chemical and physical surface changes. It has been recently applied to study the surface characteristics of single crystals of TiO_2 under various conditions [*5-8*]. Shultz *et al* [*8*], previously reported an increase in Surface Second Harmonic (SSH) signal following the generation of Ti^{3+} defects on a (110) single crystal rutile surface on exposure to ultraband gap UV irradiation. The enhanced SSH signal together with the Ti^{3+} species disappeared following exposure of the TiO_2 surface to oxygen. Similar behaviour in the SSH signal was observed by Kobayashi [*6*] when a rutile TiO_2 (110)/H_2O interface was exposed to UV illumination. Kobayashi also reported the resonance of the SSH signal with a surface electronic excitation of the (110) rutile crystal at 3.4 eV [*5*]. All these investigations, however involved single crystals of rutile TiO_2. To date there has been no reports on studies of SSHG characteristics of TiO_2 powders, the form most commonly used in photocatalytic treatment. In this paper some initial results on the application of SSH to monitor laser-induced effects on Degussa P25 TiO_2 powders are reported.

2. Experimental

2.1.Laser Treatment of Titanium Dioxide.

The SSH response of TiO_2 was studied on Degussa P25 TiO_2 (Degussa, UK) which is roughly an 80:20 anatase:rutile mixture, rutile TiO_2 obtained from P25 and anatase TiO_2 from Aldrich. The average particle size was the same for all three powder samples. Samples were placed in rectangular plastic chambers (Hybri-well Press-Seal hybridisation chamber from Sigma, 200 μl volume). The chambers were then sealed onto microscope glass slides, which had previously been washed in ethanol. Once prepared, the samples were placed in a sample holder mounted on an XY scanner. The output beam of a tripled Nd:YAG laser was directed at the sample. In this way an area of approximately 3 cm^2 of the sample surface could be subjected to specific laser exposures using the scanner. The output wavelength of the laser system could be set to 355, 532 or 1064 nm. In all cases an iris diaphragm and appropriate optical filters controlled the beam diameter and monochromaticity. Individual samples were exposed to specific wavelength and laser power densities for a fixed scan rate.

After treatment, colour and SSH measurements were obtained for each sample. The colour measurements were carried out using a Minolta colorimeter (CR-200). The SSH measurements were taken using a laboratory developed system, as described in the following section.

2.2. Surface Second Harmonic System

A schematic of the SSH system used for the investigation is shown in figure 1. The system comprised a Q-switched, flashlamp pumped, Nd:YAG laser (Spectron, UK, model SL281) operating at 10 Hz, with an output at 1064 nm. The output beam passed through a long pass Schott-glass filter (cut-on wavelength = 695 nm) to eliminate any flashlamp light. The beam was then passed through a half wave plate and polariser in order to maintain a constant beam polarisation at the sample. 20% of the beam was removed by a beam splitter to allow monitoring of laser output power using a “reference arm”. This reference arm consisted of a cut on Schott-glass filter, a thin layer of lithium niobate powder, a 1064 nm blocker and a large area photodiode. The remaining 80% of the beam was directed, through another cut on Schott-glass filter, onto the sample mounted in the XY scanner. The laser beam was set at a fixed angle of incidence of 45° from the sample normal. A photomultipier (Thorn EMI, UK, 9956L), was positioned at 45° from the sample’s normal and collected the resultant SSH signal. A series of two short pass filters (cut off wavelength = 668 nm) and one band pass interference filter centred at 532 nm with a full width at half maximum of 10 nm were mounted in front of the photomultipier to ensure that only the second harmonic light was detected. Both the signals from the reference arm and the photomultipier were recorded on a TDS 620 Tektronix digitising oscilloscope. In order to obtain a representative measure of the effect of the laser exposure, the average SSH data from an area of 0.3 cm^2 was scanned, with readings taken every millimetre. Each SSH value shown in this work is the average of 30 readings, unless otherwise stated.

2.3. Colour measurement

The colour measurements induced in the titania samples following laser irradiation were monitored out using a Minolta colorimeter (CR-200). For each measurement three reading points were recorded, averaged and the colour difference calculated by taking a reading consisting of three parameters, L*, a* and b* which are the lightness, and chromaticity co-ordinates respectively. From two readings taken at a different points in time, the colour difference can be calculated, and this is a standard value used in colour measurement. This colour difference is defined as:

$$dE = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2}$$

Where Δ represents the difference between the original colour parameters and the sample colour parameters after a given treatment.

3. Results and discussion.

3.1. Power dependence

Irradiation of the TiO_2 specimens with laser light resulted in the distinctive colour change from white to blue/grey. This colour change for a P25 TiO_2 sample with increasing irradiation times is displayed in figure 2.

The SSH response of a variety of titanium dioxide samples as a function of the square of the incident laser peak power density was then examined. Figure 3 displays the relationship between SSH signal intensity and the Squared Peak Power (SPP) density of the probing beam. The SSH intensity of the signal generated at the titanium dioxide surface increases with the peak power density of the probing beam. In all three samples, anatase, rutile and P25 the increase is initially linear with respect to the SPP, then different relationships are observed. A careful examination of figure 3 shows that the curves are divided in two regions. The lower regions of the curves is between 5 and 20 GW^2/mm^2 for pure anatase and rutile TiO_2 while for P25, which is a mixture of the crystal phases, this region is between 5 and 40 GW^2/mm^2. The higher region suggested that for SPP density above 20 GW^2/mm^2 (40 GW^2/mm^2 for P25 TiO_2), the probing beam caused changes at the sample surface. A consistent and permanent (at room temperature) change in colour from white to dim blue was observed by the naked eye, for samples irradiated with SPP density above 20 GW^2/mm^2 (40 for P25 TiO_2). This colour change is characteristic of a slight oxygen deficiency in the material. Even a small deviation from the equilibrium stoichiometry of TiO_2 lead to a colour change from white to blue/black and is accompanied by a strong increase in the electric conductivity [*9-11*]. This observation confirmed that material changes occurred for these power densities. From these observations it is clear that there is a threshold power density above which these material changes occur. It is therefore important to work under the higher threshold power density if we want to access the changes caused by laser radiation. However if the probing beam power density is close to the lower threshold it becomes difficult to differentiate between the different forms of TiO_2. For these reasons the SPP density of the probing beam was kept at 18 GW^2/mm^2 for all the measurements in order optimise the sensitivity of the system. The SSH response of P25 titanium dioxide samples treated with different laser wavelengths, powers and times was then examined.

3.2. Laser Treatment using 355 nm

The results obtained following irradiation with a 355 nm (3.49 eV) laser beam are displayed in figure 4. With low SPP density laser irradiation (up to 20 GW^2/mm^2) the SSH intensity was relatively stable over the time period studied. At higher SPP densities, the SSH intensity increased sharply with time, reaching a maximum for around a 0.2 second exposure to the 355 nm beam. The SSH signal then decayed to the initial intensity after 1.6 seconds laser irradiation. No significant differences in the SSH signal intensity were, however, observed on increasing the SPP density. These results clearly indicate the presence of two distinct phenomena (having opposite effect on the SSH signal) occurring at the titanium dioxide surface and are in good agreement with data obtained previously in our group [*12*]. In this paper it was demonstrated that variations of the SSH signal with laser treatment time, at 355 nm, were related to changes in the oxidation state, crystal structure and particle size of the TiO_2 material. The region where the SSH intensity increases is probably due to the generation of Ti^{3+} species which was confirmed by electron spin resonance spectroscopy [*13*]. The Ti^{3+} species are also the cause of the blue colour in the titania samples. In addition transmission electron microscopy showed no variation of the crystal size of the titania, while Raman spectroscopy showed very small differences in the anatase/rutile ratio for this region [*14*]. It is therefore proposed that the observed increase in SSH signal for irradiation SPP density higher than 20 GW^2/mm^2 and for 0.2 second irradiation period results primarily from the formation of Ti^{3+} species in the TiO_2 matrix. Previous work by our group also suggested that the decrease in SSH intensity (above 0.2 second in this work) was coincident with a change in the crystal phase of the titania from anatase to rutile [*12-14*]. Similar changes have been reported by Le Mercier and co-workers when the single crystal TiO_2 materials were exposed to high power 355 nm laser [*15, 16*].

3.3 Treatment using 532 nm

A similar experiment was carried out for an irradiation wavelength of 532 nm (2.33 eV), (figure 5). Identical behaviour of the SSH intensity was observed at this wavelength with a relatively stable SSH signal for SPP density up to 110 GW^2/mm^2. It is worth noting, however that the SPP density required to produce a significant change in the SSH intensity is about 2.6 times greater than in the case of the 355 nm radiation. In addition, the exposure time required to reach the maximum SSH intensity, between 0.4 an 0.8 second, is also longer than for an irradiation at 355 nm.

3.4 Treatment using 1064 nm

In the case of an irradiation wavelength of 1064 nm (1.16 eV), the SSH intensity was stable for SPP densities up to 362 GW²/mm², as shown in figure 6. Above this SPP density threshold, the SSH intensity behaved as observed for the two other radiation wavelengths. The SPP density required to produce a change in the SSH intensity is about eight times higher than for an irradiation at 355 nm, and the time require to reach the maximum SSH intensity was also significantly longer (1 to 1.2 seconds).

3.5 Discussion.

To summarise the observations for irradiation at each wavelengths, as the irradiation wavelength increased, the threshold SPP density and exposure time required to induce changes in SSH intensity increased. An increase in the maximum SSH intensity was also observed with increasing irradiation wavelength. In addition no colour changes of the samples were observed for the SPP densities inferior or equal to the threshold detected by SSH. In order to determine a better understanding of these observations the SSH data were compared with colour measurements of the laser irradiated samples.

It is interesting to note that changes in the SSH signal were observed on irradiating the titania samples with both ultra band gap (355 nm) and sub band gap (532 and 1064 nm) laser sources. Schultz [*8*] only observed the enhanced SSH signal when the specimens were irradiated with UV light of energy greater than the TiO_2 band gap (4.7 eV, 264 nm). The enhanced SSH signal was believed to be due to the formation of Ti^{3+} species at the surface of the titania specimen. The presence of this species was confirmed by XPS. The Ti^{3+} species generated by Schultz were unstable and rapidly disappeared on introducing oxygen into the reaction vessel. Other workers have also reported the generation of Ti^{3+} sites in TiO_2 samples on irradiation with short wavelength UV light, with the TiO_2 samples changing to a characteristic blue colour [*17*]. We have also confirmed the presence of Ti^{3+} in our laser irradiated samples using ESR spectroscopy [*2*]. These species are formed following band gap excitation of the samples. The fact that similar effects were observed in our samples irradiated with 532 and 1064 laser light is probably due to a multiphoton effect.

In order to compare the relative efficiency of the three wavelengths to induce the changes in the TiO_2 the SSH and colour difference as a function of the density of energy deposited were compared (figure 7). In each case only two of the irradiation times below (or equal to) the maximum SSH intensity as observed in figures 4, 5 and 6 are shown. From figure 7 (a), the SSH data can be divided in three regions. Between 0 and 0.5 mJ/mm² the signal is constant and close to zero, which suggests that the laser radiation does not affect the sample. The second region between 0.5 and 1.5 mJ/mm², where the intensity of the SSH increases by a factor of by 2.5, suggesting alterations to the titanium dioxide specimens. Finally at energy densities above 1.5 mJ/mm² no significant change in the signal is observed. Interestingly the colour difference (dE) shows similar behaviour. The colour change, however keeps increasing, although at a slower rate, for energy density higher than 1.5 mJ/mm². For the titanium dioxide samples irradiated with 532 nm laser light, three regions were also observed (figure 7 (b)). These three regions were from

0 to 1.2 mJ/mm², 1.2 to 2.4 mJ/mm² and above 2.4 mJ/mm². Figure 7 (c) shows the results obtained for the irradiation at 1064 nm. In this case the three regions were from 0 to 2.3 mJ/mm², 2.3 to around 5 mJ/mm² and above 5 mJ/mm². This suggests that the same phenomena occur at all wavelengths although the energy densities required to induce changes increased with irradiation wavelength. The energy density at which the maximum change in SSH intensity (or colour) occurs is related to the irradiation wavelengths. Further experiments will be needed to determine the exact relationship between irradiation wavelength and maximum change in SSH intensity. However, from our data, it is possible to give a rough estimate of the amount of energy necessary to reach the maximum SSH intensity. Table 1 resumes two of the key factors influencing the SSH intensity for the three studied wavelengths, namely time and energy density. The times were the estimated time to reach the maximum SSH intensity and were deduced from figures 4 to 6. The energy density values were taken as the minimum energy density required to reach the maximum SSH intensity on figure 7 (a), (b) and (c). The total deposited energy densities were then calculated and summarised in table 1. It could be seen that 7 times more energy is required at 532 nm than at 355 nm to obtain a similar change in SSH intensity and therefore to create Ti^{3+} species. Similarly 22 times more energy is needed if the titania samples were irradiated at 1064 nm.

The fact that the SSH signal reaches a maxima in each sample while the colour change continually rises may be due one of two factors. Firstly on prolonged laser irradiation in addition to the generation of Ti^{3+} sites the crystal phase changes from anatase to rutile. The formation of the rutile phase may suppress the SSH signal. An alternative more probable reason is the fact that SSH generation is a surface phenomena. The additional colour change in the titania samples may be due to changes in the bulk of the specimens and will consequently have a reduced effect on SSH signal. Further work is on going to elucidate this observation. It should be noted that the Ti^{3+} species generated on laser irradiation are significantly more stable than those produced on irradiating with standard UV sources as the samples are stable in the open lab for several months. These species are therefore likely to predominate in the bulk of the material where they are less susceptible to attack by oxygen.

4. Conclusion.

SSH has been demonstrated to be highly sensitive to chemical/physical changes in TiO_2 powders following laser treatment. Similar trends in the SSH signal intensity were observed when TiO_2 was treated with a variety of laser wavelengths above and below the band gap energy level. The minimum threshold power densities required to induce observable changes in the specimens varied greatly and longer wavelengths were significantly less efficient. SSH provided complementary data to dE measurements obtained from the colour meter. Since the SSH is sensitive to many parameters influencing the photocatalytic activity of TiO_2 (crystal structure, oxidation state, particle size), it has therefore been demonstrated to be a powerful tool for monitoring these changes when TiO_2 was exposed to laser irradiation. So far only the enhanced photocatalytic activity of heavily treated P25 has been reported [*2,3*]. It would be interesting to study the photocatalytic activity of the TiO_2 during the different stages of modifications. In particular at the point where SSH intensity reached a maximum where the Ti^{3+} species have been generated and prior to the change in crystal phases from anatase to rutile indicated by the subsequent drop in SSH intensity.

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Legends for Figures.

Fig. 1. Schematic diagram of the Surface Second harmonic System. a) visible cutter, b) λ 1/2 plate, c) polarizer, d) iris, e) 20% beam splitter, f) reference arm, g) photodiode, h) 1064 nm absorber, i) 532 nm band pass filter.

Fig. 2. Example of P25 TiO_2 powder irradiated for 0, 0.1, 0.5, 1, 2, 4 and 6 seconds (left to right) at 355 nm, with a power of 23 mW.

Fig. 3. SSH power dependence of a variety of titanium dioxide powders.

Fig. 4. Relative SSH intensity of P25 as a function of time and squared peak power density of the treatment laser beam at 355 nm.

Fig. 5. Relative SSH intensity of P25 as a function of time and squared peak power density of the treatment laser beam at 532 nm.

Fig. 6. Relative SSH intensity of P25 as a function of time and squared peak power density of the treatment laser beam at 1064 nm.

Fig. 7. SSH intensity and colour difference (dE) as a function of the irradiation energy density for the three studied wavelengths: (a) 355 nm, (b) 532 nm, and (c) 1064 nm. The open and closed triangles and diamonds represent two irradiation times for dE and SSH respectively.

Irradiation Wavelength/ nm	**Photon Energy/ eV**	**Energy Density/ mJ mm^{-2}**	**Irradiation Time/ sec**	**Total Deposited Energy Density/ mJ mm^{-2}**
355	3.49	1.5	0.2	3
532	2.33	2.5	0.8	20
1064	1.16	5.5	1.2	66

Table 1. Total Deposited Energy Density of Different Laser Irradiation Wavelengths.