Section B: Applications 1
Paper presented at Sensors and their Applications X, 5–8 September 1999

The application of surface second harmonic sensor to probe laser induced modification of titanium dioxide

Soo-Keun Lee, Guerric Vrillet, Ala H.R. Al-Obaidi, Peter K. J. Robertson and Daniel McStay

The Optoelectronics Research Centre, School of Applied Sciences, The Robert Gordon University, Blackfrairs Street building, Schoolhill, Aberdeen, AB25 1FR, UK

Abstract. The effects of high power pulsed laser light on a TiO_2 photocatalyst have been investigated using a surface second harmonic generation (SSHG) sensor. When TiO_2 is irradiated with a laser at 355nm a visible change in colour from white to dark blue crystals was observed. X-ray diffraction studies indicate that the crystal structure of the TiO_2 developed a more rutile form following laser exposure.

1. Introduction

TiO_2 photocatalysis is a promising technology for the destruction of organic pollutants and is especially suitable for wide range applications, when compared to other semiconductors.

It is highly photoreactive, cheap, non-toxic, chemically and biologically inert, and photostable [1]. There is however, scope for enhancing the photocatalytic activity of TiO_2. There has been little progress in the development of materials which display a better photocatalytic activity compared to Degussa P25. 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 [2]. One particular form of commercial TiO_2 namely Degussa P25 titanium dioxide, a roughly 80:20 anatase/rutile mix with a surface area of $55m^2g^{-1}$, appears to be the most active readily available form of this photocatalyst [3]. Recently, we have reported the enhanced photocatalytic activity of the laser treated Degussa P25 for the destruction of methylene blue[4]. The laser treatment was also found to alter the colour and particle size and shape of the photocatalyst. The particle size, shape and polarity of the surface are known to influence the effectiveness of a catalyst. These parameter, are also known to influence the surface second harmonic(SSH) generation properties of a material.

In this paper we report the use of SSH to monitor in real time laser induced changes in the photocatalyst Degussa P25. An experiment was setup to study the photolysis effect of a sample of TiO_2 after irradiation with laser pulses at 355 nm. The laser irradiation can effect both the physical and chemical characteristics of the TiO_2 sample. Finding a sensor to detect both of these changes can be a hard task. Here we have developed such sensor, detecting both the chemical and physical changes using surface second harmonic sensor.

2. Experimental

2.1 Laser treatment of titanium dioxide

A tripled Nd:YAG laser (Continium Surlite), producing 4.5 nsec pulses of up to 140mJ pulse power was used for the laser treatment. TiO_2 (Degusa P25) compromising roughly 80:20 anatase:rutile, with the shape of non-porous polyhedral particles of ca. 30nm mean size and a surface area $50m^2/g$, was used. The TiO_2 powder was irradiated with laser light at 355 nm at a repetition rate of 10 Hz and energy of 45 mJ at varying lengths of time over 10 minute period. After laser exposure, surface second harmonic characteristics were examined.

2.2 Surface second harmonic measurement system

The SSH system used to characterise the laser reacted TiO_2 is shown schematically in figure 1. The laser used in the system was a low repetition rate (typically 10 Hz) flash lamp pumped Q-switched Nd:YAG laser (Spectron LS400). This provide 5 nsec pulses (FWHM) of between 0.1–1 MW at 1064 nm and had a beam diameter of 4 mm. A colour glass filter is used to block all the visible light produced by the flash lamp of the laser. A polarising cube and $\lambda_{½}$ plate are used to clean and control the polarisation of the laser beam. A 5 mm Iris is used to control the beam size and to ensure that the laser beam will not strike the edges the sample holder. A beam splitter (typically 20%) is used to select a portion of the beam for the reference arm. The reference arm consisted of a set of filters and a thin layer of $LiNbO_3$ powder to produce the reference SSH signal. The sample of TiO_2 to be examined was placed on a X-Y scanner (Hook & Tucker Instruments Ltd) which has a scanning resolution of 100μm. The laser beam direction and angle was controlled using dichroic mirrors. The SSH signal was collected in a back geometry set-up using a bundle of 60 optical fibers. A photomultiplier tube with high gain in the green was used to detect the SSH signal generated from the sample. Two filters were used in front of the photomultiplier tube. The first is to block the signal associated with the fundamental laser wavelength and the second is a 10nm band pass filter at 532nm that will allow only the signal produced by the SSH to reach the photomultiplier tube.

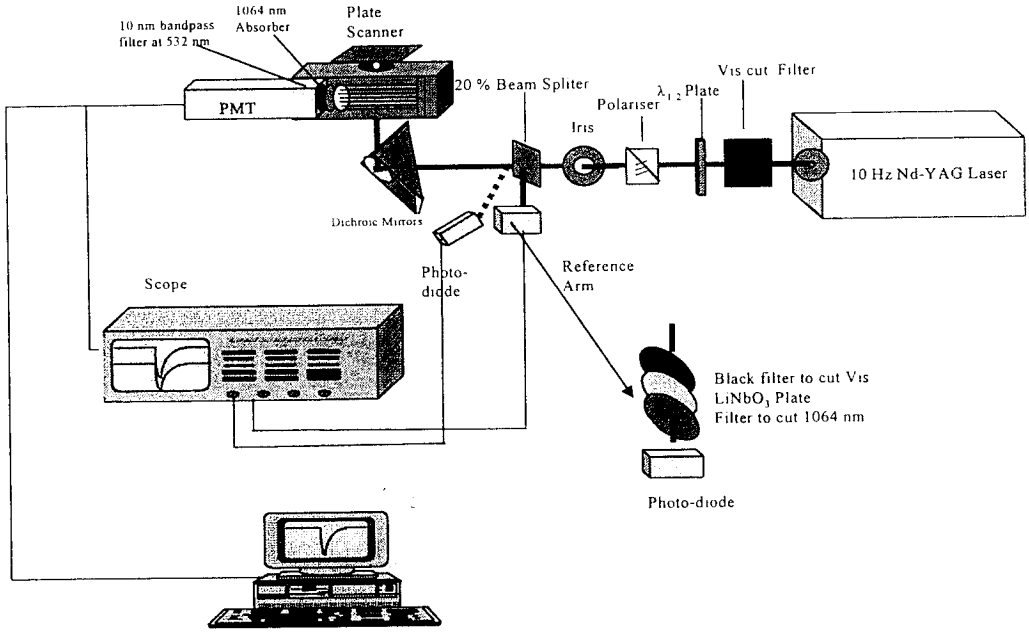

Figure 1. Schematic diagram of the SSH sensor.

The output from the photomultiplier tube was subsequently digitised by a digital storage oscilloscope for direct reading of the SSH signal.

2.3 Measurement

All the SSH measurements were performed using 2 mJ laser pulses with the photomultiplier tube was set at a voltage of 1.2 kV. An area of 5x5 mm was scanned with several steps to generate an average SSH value. Prior to the SSH measurements the TiO_2 powder sample with particle size of ~30 nm was placed in the quartz sample holder.

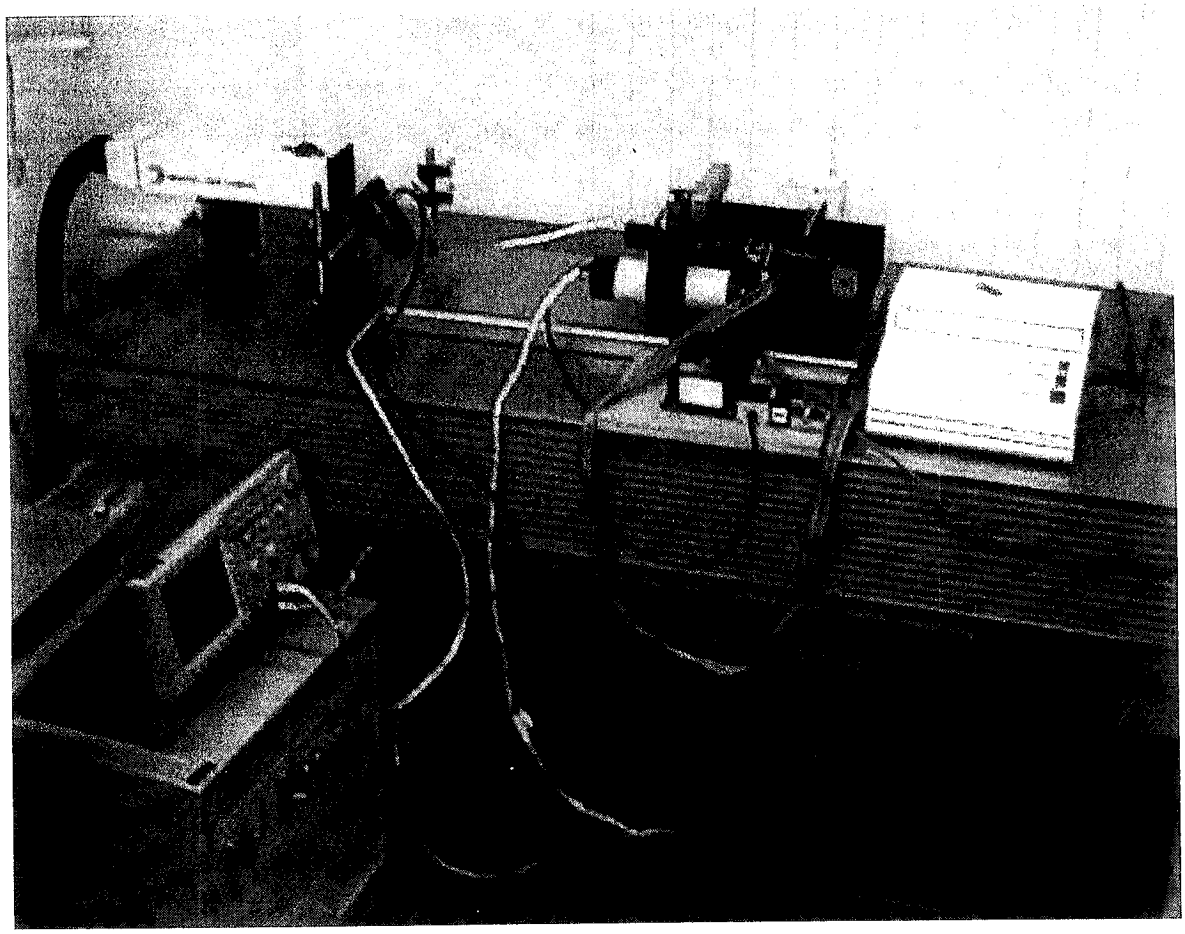

Figure 2. Photograph of the SSH sensor.

3. Results and Discussions

The SSH signal was recorded for each TiO_2 sample before and after being exposed to the laser irradiation. Figure 3 shows the SSH signal intensity with the respect to the laser treatment time of the TiO_2 samples. From the figure it can be seen that the SSH intensity falls into three regions, corresponding to different exposure times to the 355 nm laser light. The first, corresponding to a relative intensity of 2, is assigned to the initial form of the TiO_2. The second, corresponding to a peak of 15, is associated with an observable colour change of the TiO_2 and therefore, could be assigned to a change in the chemical characteristics of the TiO_2. This assumption has support from ESR studies of the laser irradiated TiO_2 which indicated that a reduction of the Ti^{4+} to Ti^{3+} had taken place. This could be due to the transformation of the TiO_2 to Ti_2O_3 which could account for the colour change. Further irradiation with the

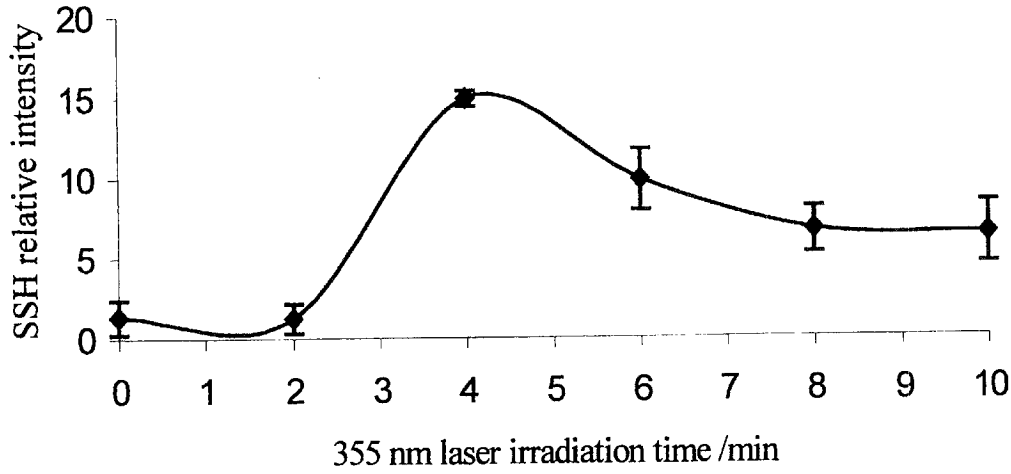

Figure 3. SSH signal intensity with the respect to the laser treatment time.

Figure 4 shows the TEM images of the TiO_2 before and after laser treatment. The particle size and shape is observed to be much the same as that for the untreated TiO_2 and that subjected to 4 minutes of 355 nm laser light. A significant change in the particle size and shape is, however observed in figure 4 (c) for 10 minutes exposure. As can be seen in figure 3, this corresponds to the exposure times where the SSH signal decreases.

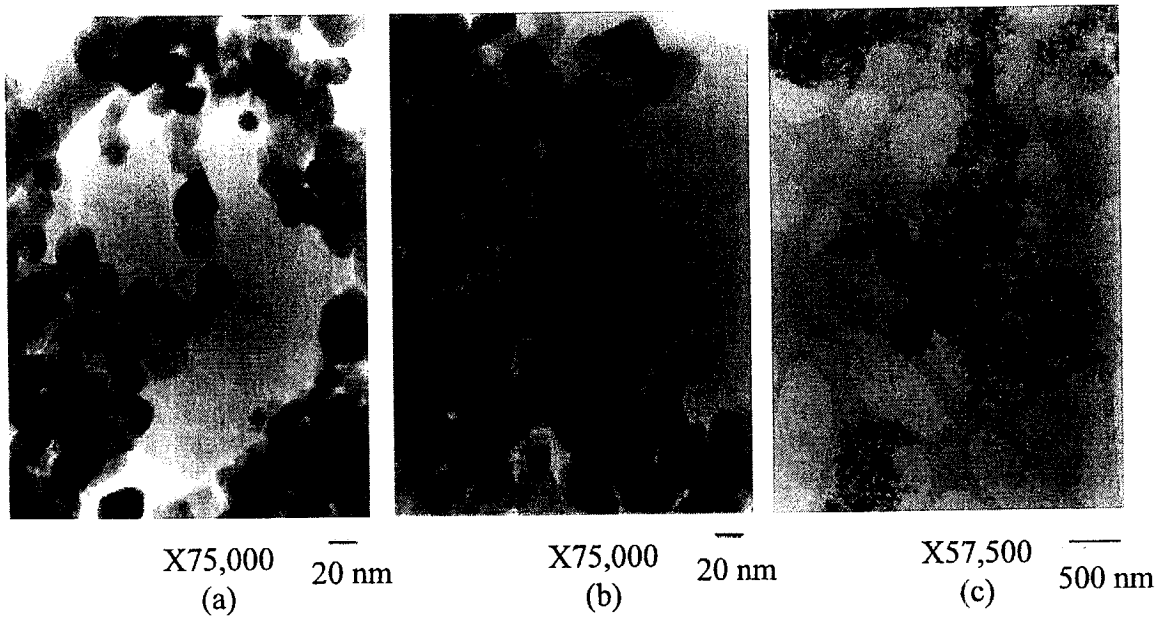

Figure 4. TEM photographs of TiO_2 samples (a) no laser treatment (b) 4 minutes laser treatment (c) 10 minutes laser treatment.

4. Conclusions

Surface second harmonic measurements have been shown to be an effective and relatively simple method of probing changes of crystal phase structure and reduction of TiO_2. 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.

Acknowledgement

We thank the Johnson Matthey Research Centre for assistance with the TEM analysis. We are also grateful to Rowett Research Institute for the assistance of ESR analysis.

References

[1] Mills A, Davis R H and Worsey D 1993 Chem. Soc. Rev. 417

[2] Augustynski A, 1993 J. Electrochim. Acta **38** 43.

[3] Ferch H, Habersang S 1982 Technical Bulletin Pigments no. 64, The Biological Effects of SiO_2, Al_2O_3, and TiO_2, Degussa AG, Frankfurt

[4] Lee S, Robertson P K J, Mills A and McStay D 1999 J. Photochem. Photobiol. A: Chemistry, **122**, 69