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The application of Raman and anti-stokes Raman spectroscopy for in situ monitoring of structural changes in laser irradiated titanium dioxide materials

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Abstract

The use of Raman and anti-stokes Raman spectroscopy to investigate the effect of exposure to high power laser radiation on the crystalline phases of TiO_2 has been investigated. Measurement of the changes, over several time integrals, in the Raman and anti-stokes Raman of TiO_2 spectra with exposure to laser radiation is reported. Raman and anti-stokes Raman provide detail on both the structure and the kinetic process of changes in crystalline phases in the titania material. The effect of laser exposure resulted in the generation of increasing amounts of the rutile crystalline phase from the anatase crystalline phase during exposure. The Raman spectra displayed bands at 144 cm^{-1} (A1g), 197 cm^{-1} (Eg), 398 cm^{-1} (B1g), 515 cm^{-1} (A1g), and 640 cm^{-1} (Eg) assigned to anatase which were replaced by bands at 143 cm^{-1} (B1g), 235 cm^{-1} (2 phonon process), 448 cm^{-1} (Eg) and 612 cm^{-1} (A1g) which were assigned to rutile. This indicated that laser irradiation of TiO_2 changes the crystalline phase from anatase to rutile. Raman and anti-stokes Raman are highly sensitive to the crystalline forms of TiO_2 and allow characterisation of the effect of laser irradiation upon TiO_2. This technique would also be applicable as an in situ method for monitoring changes during the laser irradiation process.

Keywords: TiO_2; Photocatalyst; Raman spectroscopy; Laser irradiation

1. Introduction

The use of titanium dioxide (TiO_2) as a photocatalyst for the degradation of chemical and biological species in the environment has generated a significant level of scientific interest over the past 20 years [1–4]. This material has also been used in novel solar cells where TiO_2 acts as a dye-sensitised photo-anode [5,6]. The photo-catalytic activity of TiO_2 is dependent upon a number of factors including, surface area, annealing temperature, crystalline structure light intensity and substrate adsorption and concentration [1–6]. Consequently, unless all these factors are similar for different materials it may be difficult to compare the photocatalytic activity of different TiO_2 photocatalyst materials. Thus, the results of work performed in one laboratory may not always be compared with that of another. Frequently, however, the effectiveness of photocatalysts is compared in terms of the rates of pollutant destruction over a particular time period together with the photonic efficiencies for these processes. The two most important photo-active forms of TiO_2 are anatase and rutile, though in many photocatalytic reactions anatase has been reported to show a higher activity than rutile [7]. This increased performance in photo-activity has been explained by the fact that the Fermi level of anatase is higher than that of rutile by 0.1 eV [2]. Interestingly, however, one of the most photocatalytically active TiO_2 materials, Degussa P25, contains a small amount of rutile in the predominantly anatase structure (approximately 25% rutile to 75% anatase) [4]. This enhancement in photo-activity cannot be explained by individual activity of each crystalline phase but is probably related to the

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creation of complex structures (for example capped or coupled type heterostructures) of rutile and anatase [2]. One problem with the argument that rutile is less photocatalytically active than anatase is the fact that when anatase material is converted to rutile by sintering above 600 °C, not only is the crystal structure changed, but the particle size and surface area are changed. It is, therefore, possible that the reduction in photocatalytic activity may be due to the reduction in surface area rather than the change in crystal structure.

TiO_2 is known to exist in three crystalline phases rutile, anatase (both tetragonal) and brookite (orthorhombic) [1–3]. The anatase and rutile phases have the same fundamental structural unit but different modes of arrangement and links. Each crystalline form belongs to a different space group [1–3]. The rutile structure has a space group D_{4h}^{14} and lattice constants $a = 0.4954$ and $c = 0.2958$ nm, while anatase belongs to the space group D_{4h}^{19} and has lattice constants $a = 0.3783$ and $c = 0.951$ nm. Brookite has a rather different space group—D_{2h}^{15} and lattice constants $a = 0.9184$, $b = 0.5447$ and $c = 0.5145$ nm.

Raman spectroscopy is a very effective means of detecting these different crystalline phases in TiO_2 powders and the assignment of observed bands to rutile, anatase and brookite has been reported [8–14]. These crystalline phases are not thermodynamically stable as both anatase and brookite transform irreversibly and exothermically to rutile when heated to high temperatures [10,15,16]. We have previously reported that, when irradiated with laser light the crystal phase of anatase TiO_2 transforms to rutile with the simultaneous generation of Ti(III) sites in the material [17–19]. The particle size and surface area or the laser treated materials, however, were unchanged. Interestingly, the photocatalytic activity of this material was unaltered following treatment. To date, there have been no reports of the use of Raman spectroscopy to monitor the effect of intense laser irradiation upon the crystalline phases of TiO_2. This technique would be particularly useful as a method where the changes could be monitored in situ while the materials were be subjected to the laser treatment. In this paper, we report some of the application of Raman and anti-stokes Raman spectroscopy to monitor laser induced effects on Degussa P25 TiO_2 powders.

2. Experimental

TiO_2 (Degussa P25) was used as supplied. The laser source for irradiation of the TiO_2 was a Continuum Surlite tripled Nd:YAG laser operating at 355 nm. This produced 4.5 ns pulses of 10 MW peak pulse power. Irradiation of the samples was carried out by placing 20 mg of TiO_2 directly in the laser beam for varying times. The TiO_2 powder was shaken every 2 min during laser radiation. Heating of the samples, where applicable, was performed in an oven set at 450 °C.

Raman spectroscopy measurements were recorded using an Argon ion laser operating at 514 nm. The laser power directed at the sample was measured to be 100 mW. The laser line was filtered to remove any traces of plasma lines using a 1 nm interference filter centred at 514 nm. A silver spot mirror with 3 mm diameter was used to direct the laser beam onto the sample. The laser spot size at the sample is about 25 μm in diameter, which was imaged at the slit (slit width 10 μm) of the spectrograph (Oriel 260i spectrograph) using a 180°-back scattering geometry as shown in Fig. 1. The Raman signal was filtered before passing through the spectrograph using a notch filter. The Raman signal was detected using a water-cooled front illuminated CCD detector (Oriel model DU401) cooled to −80 °C and analysed using a PC. A schematic representation of the experimental set-up is given in Fig. 1.

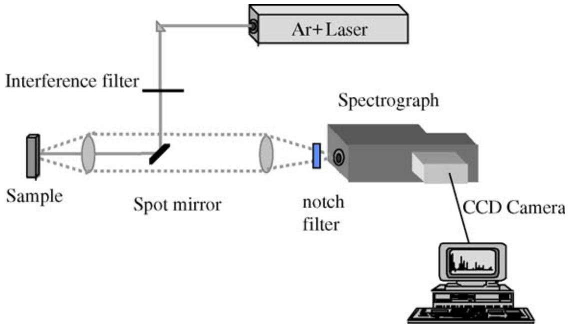

Fig. 1. Schematic diagram of the Raman system.

3. Results and discussion

Raman spectra of the three crystalline phases of TiO_2 have been well reported [8–14]. Rutile has four Raman active modes A1g + B1g + B2g + Eg [15], anatase has six Raman active modes A1g + 2B1g + 3Eg [15] and Brookite has 36 Raman active modes [20]. The Raman stokes spectrum of TiO_2 before and after laser irradiation treatment for 10 min is shown in Fig. 2. Fig. 2(a) shows the Raman spectra of the untreated TiO_2.

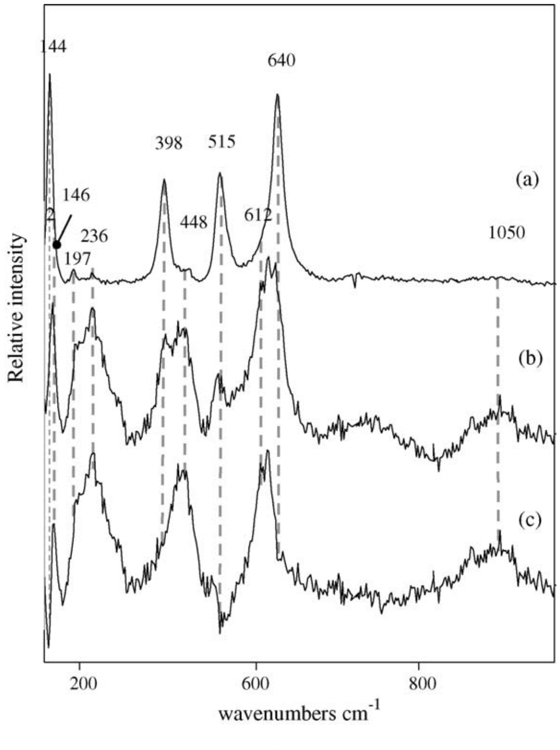

Fig. 2. Raman spectra of TiO_2, λ_{ex} 514 nm, energy at sample 100 mW: (a) initial sample, (b) irradiation for 10 min, and (c) a–b.