Highly Photocatalytically Active Iron(III) Titanium Oxide Thin films *via* Aerosol Assisted Chemical Vapour Deposition

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Abstract

This paper presents, for the first time, the synthesis via aerosol assisted chemical vapour deposition (AACVD) followed by annealing at 620 °C for 5 hours of pure Fe_2TiO_5 thin films on glass. The thin film was deposited from a one pot solution containing titanium isopropoxide and tris(acetylacetonato)iron in ethyl acetate solvent. The film was characterised using a range of techniques including powder X-ray diffraction, wavelength dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy (SEM) and UV-visible spectroscopy. The photocatalytic activity of the film under UVA and visible light irradiation was also tested. The results showed that Fe_2TiO_5 was able to degrade resazurin redox dye under UVA illumination at a rate much higher than Pilkington NSG Activ^{TM} with a formal quantum efficiency an order of magnitude superior.

Keywords: Photocatalysis, TiO_2, Fe_2TiO_5, CVD

Introduction

TiO_2 in the anatase phase is an important semiconductor for photocatalysis applications.[1],[2],[3],[4] This is primarily due to its high photoelectrochemical stability, ability to break water for the production of H_2 as a clean energy source and capability to photo-mineralise organic dirt.[2],[3],[5] Thus, TiO_2 based devices are highly applicable in energy production and decontamination of air and water. Current research is concerned with improving the efficiency of TiO_2 and narrowing of its wide indirect bandgap (3.2 eV), which can only be activated by radiation with wavelengths below 385 nm that account for only 5% of the solar spectrum.[6],[7],[8] In an effort to harness energy from the visible portion of the solar spectrum TiO_2 has been manipulated *via* many different methods. Principally through extrinsic doping with metals (such as Fe, Cu and V) and non-metals (such as N, S and C) and also *via* self-doping through the introduction of oxygen vacancies and Ti^{3+} species.[9],[7],[10] Composite formation with metal oxides, including SnO_2 and Fe_2O_3 have also been widely investigated in an effort to improve efficiency by the increase in photogenerated electron hole recombination time and the capture of visible light.[11],[12],[13], [14]

Fe_2O_3 is semiconductor with a bandgap of 2.2 eV that lies in the visible region.[15],[16] It has many applications such as an electrode in solar cells, but due to the short diffusion length of the photogenerated charge carriers, the use of Fe_2O_3 as a photocatalyst is not effective.[17], [18] The combination of both TiO_2 with Fe_2O_3 to produce Fe_2TiO_5, a single-phase (pseudobrookite) material that has a bandgap of 2.18 eV, although not widely investigated shows potential as a useful photocatalyst.[19],[20],[21]

To the best of our knowledge the formation of thin films of pure Fe_2TiO_5 *via* CVD have not been produced before. Previously reported methods of Fe_2TiO_5 preparation usually involve sol gel or hydrothermal techniques that either require a high temperature (>500 ^{o}C) firing step or calcining step.[20],[21],[22] Here we present the formation of Fe_2TiO_5 *via* aerosol assisted chemical vapour deposition (AACVD) - a specialised form of CVD that involves the transport of the precursors into the deposition chamber using aerosol droplets – is reported.[23] AACVD is a low cost and tunable technique that is easily scalable. The as-deposited X-ray amorphous film was subsequently annealed at 620 ^{o}C for 5 hours to produce the translucent orange polycrystalline Fe_2TiO_5.

The photocatalytic activities of the film were tested under both UVA irradiation and visible light using resazurin redox dye and stearic acid respectively. The rate of dye/acid degradation was calculated as well as the formal quantum yields and efficiencies.

Results and Discussion

A Fe_2TiO_5 thin film was produced on SiO_2 coated float glass *via* aerosol assisted chemical vapour deposition (AACVD) at 450 ^{o}C. A one pot solution containing molar equivalents of titanium isopropoxide and tris(acetylacetonato)iron was used as the titanium and iron sources respectively in ethyl acetate as the solvent and oxygen source. The as deposited film was amorphous and brown in colour, upon annealing in air at 620 ^{o}C for 5 hours a polycrystalline pseudobrookite Fe_2TiO_5 phase was obtained. The annealed film was orange and optically translucent with interference fringes indicating variation in film thickness along the substrate. The film was well adhered to the substrate and passed the Scotch^{TM} tape test.

Characterisation

The material and functional characteristics of the Fe_2TiO_5 thin film was determined using a range of techniques.

X-ray diffraction

The XRD pattern for the Fe_2TiO_5 film is shown in Figure 1 with reflections corresponding to (200), (101), (230), (301), (420), (331), (002) and (232) observed at 18.1^{o}, 25.5^{o}, 32.5^{o}, 36.5^{o}, 41.0^{o}, 45.9^{o}, 48.8^{o} and 59.9^{o} 2θ respectively matching the standard pattern for the psedobrookite phase of Fe_2TiO_5. The lack of any other peaks in the XRD indicates the film was phase pure.

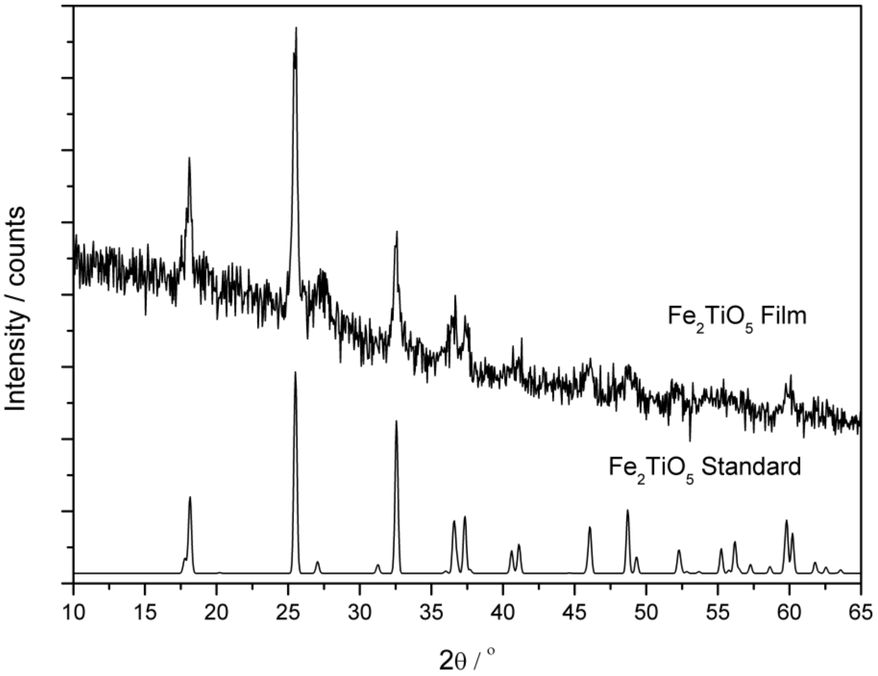

Figure 1: XRD pattern of the Fe_2TiO_5 thin film and Fe_2TiO_5 standard, formed by annealing at 620 °C for 5 hours a AACVD deposited film on glass.

X-ray photoelectron spectroscopy (XPS)

XPS was used to infer the oxidation state of the Fe and Ti on the surface of the film. The XPS of Fe_2O_3 was also run as a standard. Due to sufficient separation between the Fe $2p_{3/2}$ and $2p_{1/2}$ spin orbit split components only the more intense Fe $2p_{3/2}$ peak was deconvoluted. The Fe $2p_{3/2}$ peak was fitted taking into account multiplet structure (as calculated by Gupta and Sen).[24], [25] The XPS results show the principle peak at 709.3 eV and this compares well with the Fe_2O_3 standard where the principle peak appears at 708.9 eV indicating the Fe is in the 3+ oxidation state that is expected for Fe_2TiO_5. The results are also comparable with literature examples for Fe^{3+} where the main peak appears at 709.8 eV.[26],[27] The Ti $2p_{3/2}$ transition appears at 457.5 eV and matches well with literature findings for Ti in the 4+ oxidation state.[28]

Energy dispersive X-ray analysis (EDX)

EDX was used to confirm that the Fe_2TiO_5 film was contaminant free, containing only Fe, Ti and O and also to calculate the overall Fe to Ti ratio in the film. The EDX results showed the film to be homogeneous across all areas analysed. The ratio of Fe to Ti in the as deposited and the post annealed film was 2:1, this supports the evidence from XRD (Figure 1) for the formation of only Fe_2TiO_5.

Scanning electron microscopy (SEM)

The morphology of the film was studied using scanning electron microscopy (SEM). The surface of the Fe_2TiO_5 film consists of domes that are roughly 100 nm in diameter that cover the regions analysed uniformly (Figure 2). The morphology is similar to what is typically seen in literature for TiO_2 and Fe_2O_3 films grown *via* similar CVD techniques.[29]

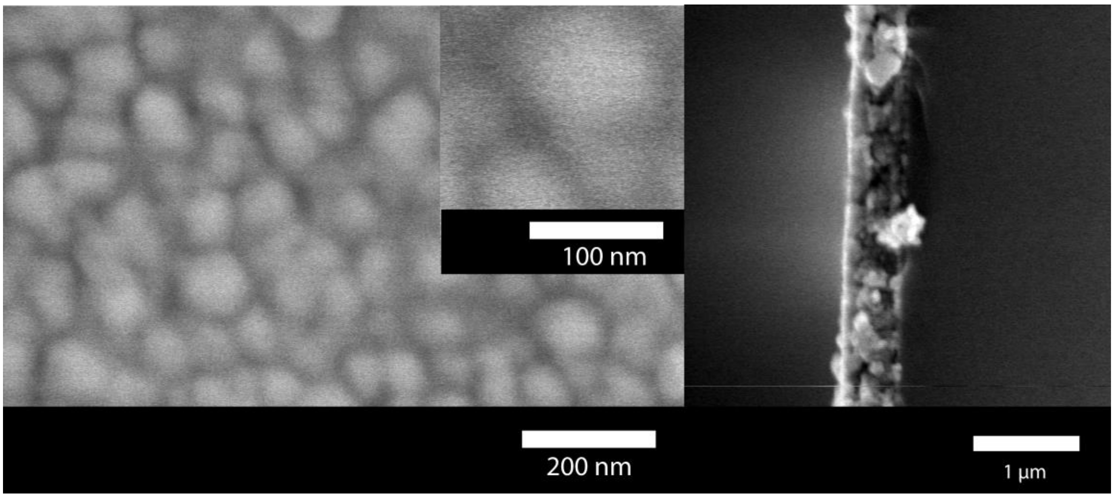

Figure 2: SEM micrograph of the Fe_2TiO_5 film grown via AACVD and annealed at 620 °C in air showing the dome like features uniformly covering the substrate. The side on SEM shows the film to be *ca.* 600 nm thick.

UV-visible spectroscopy (UV-vis)

UV-visible measurements taken from 320 nm to 2500 nm showed that the optical transparency of the Fe_2TiO_5 film was between 60 and 80% (Figure 3A). A sharp decrease around 560 nm is observed corresponding to the band edge. The reflectance spectrum shows the film to have between 15 and 20% reflectance between 750 and 2500 nm and below 750 nm it increases gradually with a peak of 50% at 550 nm. The optical bandgap of the film was calculated using the Tauc plot (Figure 3B) for an indirect system and was determined to be at 2.0 eV, below the expected value of 2.18 eV for Fe_2TiO_5, this could be due to the small grain sizes observed in SEM images (Figure 2).[19] The bandgap is ideal as it is in the visible region, even narrower than the bandgap observed for Fe_2O_3 films (2.20 eV).[30] The bandgap of Fe_2TiO_5 in the visible region of the solar spectrum allows for the potential for visible light photocatalysis.

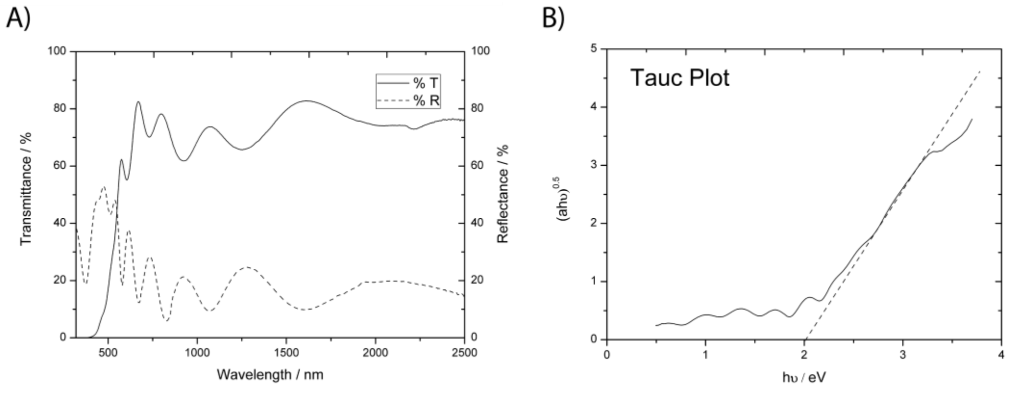

Figure 3: A) Uv-vis spectrum for Fe_2TiO_5 film grown via AACVD and annealed at 620 ^{o}C. B) Tauc plot for the Fe_2TiO_5 film shows the indirect optical bandgap to be 2.0 eV.

Photoinduced wettability

The photoinduced wettability is a phenomenon seen with some semiconductors such as TiO_2 and ZnO.[31] It was determined by placing a 3 μm droplet of water on the surface of the film pre and post irradiation with UVA (254 nm) light for 10 hours. Prior to irradiation the water contact angle was 50^{o}, this was reduced to 30^{o} upon post irradiation suggesting that Fe_2TiO_5 does indeed show photoinduced wettability.

Photocatalysis study

The photocatalytic activity of the Fe_2TiO_5 under UVA illumination was studied using resazurin dye ‘intelligent ink’. The test involves spraying an even layer of the ‘intelligent ink’ that contains resazurin redox dye, hydroxy ethyl cellulose, glycerol and distilled water. The UVA induced photoreduction on the surface of the film results in a colour change from royal blue (resazurin) to pink (resorufin intermediate) then to the colourless product only in the presence of a photacatalytically active material.[32] The resasurin based photocatalytic study has been well documented previously and a more detailed discussion can be found in literature.[28] This change was monitored quantitatively using UV-visible absorption spectroscopy to determine the rate of dye degradation. An estimate of the formal quantum efficiency (FQE), the measure of the number of dye molecules destroyed per incident photon, and the formal quantum yield (FQY), the measure of the number of dye molecules destroyed per absorbed photon.

The results show that the Fe_2TiO_5 film is indeed photocatalytically very active when illuminated by UVA radiation (Figure 4). The film was able to degrade the resazurin to resorufin with a rate of 7.1 x 10^{11} molecules s^{-1} cm^{-2}. This was almost three times better than the rate observed for Pilkington Activ^{TM} (a commercially available self cleaning, 15 nm TiO_2 anatase film that is widely used as a photocatalytic benchmark)[29], which showed a rate of 2.7 x 10^{11} molecules s^{-1} cm^{-2}.

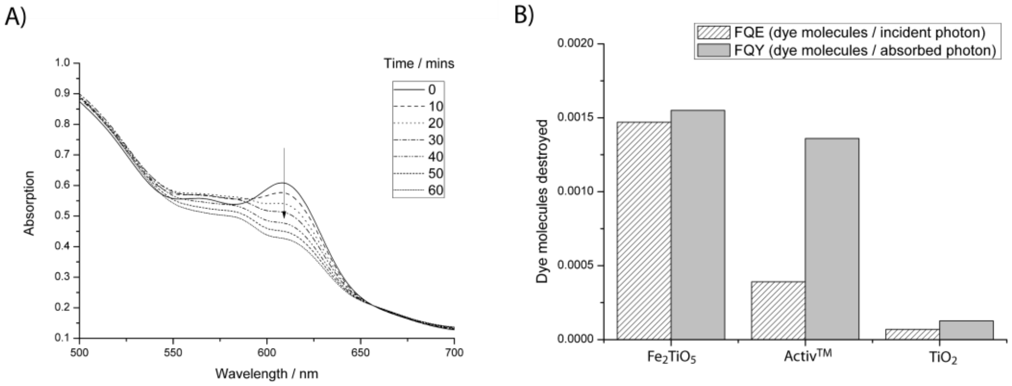

Figure 4: A) The UV-vis absorption spectrum of rezasurin on the Fe_2TiO_5, the spectrum shows the decrease in intensity of the peak at 608 nm with irradiation time. B) The formal quantum efficiency (FQE) and formal quantum yield (FQY) for the degradation of rezasurin on Fe_2TiO_5, Pilkington NSG Activ^{TM} and TiO_2.

The FQE for the Fe_2TiO_5 film (1.48 x 10^{-3} molecules / incident photon) was an order of magnitude better than that determined for Activ^{TM} (3.91 x 10^{-4} molecules / incident photon) showing the film to be an excellent UV light photocatalyst. The FQY of the iron titanium oxide film (1.55 x 10^{-3} molecules / absorbed photon respectively) was also better than Activ^{TM} (1.36 x 10^{-3} molecules / absorbed photon respectively). This displays the film was able to produce useful work from the absorbed photons with good efficiency and there is indication that the charge carrier mobility and lifetimes in the Fe_2TiO_5 film were comparable to that of TiO_2 than Fe_2O_3. Also, the Fe_2TiO_5 film is far superior to a TiO_2 film grown under the same condition, at 450 °C from titanium isopropoxide that displayed a FQE of 6.98 x 10^{-5} molecules / incident photon and a FQY of 1.27 x 10^{-4} molecules / absorbed photon.[11]

Although the Fe_2TiO_5 thin film possessed a band gap in the visible region (2.0 eV) of the solar spectrum, it displayed weak visible light photo activity. Tests carried out on the sample using stearic acid showed there was minimal change in the concentration of stearic acid over a seven day period. This was determined by monitoring the Infar red stretches for C-H between 2700 and 3000 cm^{-1}.

Conclusion

The first CVD synthesised thin film of pure Fe_2TiO_5 shown in this paper was grown *via* aerosol assisted chemical vapour deposition followed by annealing in air for 5 hours has been shown. XRD analysis showed the film to be in the pseudobrookite phase and matching well with the standard pattern for Fe_2TiO_5. The film was adhered well to the glass substrate and had an optical band gap of 2.0 eV therefore allowing absorption of visible light. The UVA (365 nm) photocatalytic properties of the Fe_2TiO_5 film were determined using the resazurin based ‘intelligent ink’, the dye degradation rate was found to be 7.1×10^{11} molecules s^{-1} cm^{-2}, which was three times better than the results seen for Pilkington Activ^{TM} self-cleaning glass. The formal quantum efficiency of the Fe_2TiO_5 film was 1.48×10^{-3} molecules / incident photon, again much better than what was observed for Acitv^{TM}. This shows the potential for iron titanium oxide as an excellent UV light photocatalyst.

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Experimental

General Procedure

Depositions were carried out under nitrogen (99.99% from BOC). Precursors were placed in a glass bubbler and an aerosol mist was created using a piezoelectric device (Vicks ultrasonic humidifier, model number: 4022167500175). All chemicals were procured from Sigma Aldrich and used as bought.

Titanium isopropoxide (0.5 g, 1.8 mmol) and tris(acetylacetonato)iron (0.6 g, 1.8 mmol) were dissolved in ethyl acetate (20 ml). The resulting solution was stirred for 20 minutes and then atomised. The precursor flow was kept at 1 $l.min^{-1}$. The glass substrate was SiO_2, precoated (*ca*. 50 nm thick SiO_2 barrier layer) standard float glass (Pilkington) 15 cm × 4 cm × 0.3 cm. A top plate was suspended 0.5 cm above the glass substrate to ensure a laminar flow.

The substrate temperature was kept at 450 °C. Deposition time was 20 minutes. At the end of the deposition the nitrogen flow through the aerosol was diverted and only nitrogen passed over the substrate. The glass substrate was allowed to cool with the graphite block to less than 100 °C before it was removed. Coated substrate was then annealed in air at 620 ^{o}C for 5 hours. The sample was stored and handled in air.

Physical Properties

X-ray diffraction (XRD) was used to analyse the samples in a modified Bruker-Axs D8 diffractometer with parallel beam optics equipped with a PSD LinxEye silicon strip detector to collect diffracted X-ray photons. This instrument uses a Cu source for X-ray generation with $CuK\alpha_1$ and $CuK\alpha_2$ radiation of wavelengths 1.54056 Å and 1.54439 Å respectively, emitted with an intensity ratio of 2:1, a voltage of 40 kV and current of 30 mA. The incident beam angle was kept at 1° and the angular range of the patterns collected was $10° < 2\theta < 65°$ with a step size of 0.05° counted at 1 s/step. Energy dispersive (EDX) analysis was carried out on a JOEL JSM-6301F Field Emission instrument with acceleration voltage of 20 kV. The Ti atom% was derived from the Ti-K_α line (4508 eV) and the Fe atom% derived from the Fe-K_α (6395 eV). X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Scientific *K*-Alpha instrument with monochromatic Al-K_α source to identify the oxidation state and chemical constituents. High resolution scans were done for the Ti (3d), Fe (2p), O (1s) and C (1s) at a pass energy of 40 eV. The peaks were modelled using CasaXPS software with binding energies adjusted to adventitious carbon (284.5 eV). SEM images were taken on a JOEL JSM-6301F Field Emission instrument with acceleration voltage of 5 kV. Images were captured using SEMAfore software. Samples were cut to 10 mm x 10 mm coupons and coated with a fine layer of gold to avoid charging. The optical transmission was measured over 320 – 2000 nm range using a Lamda 950 instrument.

Functional Properties

Water droplet contact angles were measured using a First Ten angstroms 1000 device with a side mounted rapid fire camera fire casting 3 μL droplet from a fixed height onto the surface. Photoinduced wettability was tested by placing the samples under a UVC (254 nm) lamp for 4 hours then measuring the water contact angle by placing a 3 μL droplet onto the surface of the films.

Before assessing the photocatalysis, the film was washed with distilled water, rinsed in isopropanol, allowed to air dry and irradiated for 30 minutes with UVC (254 nm) light to thoroughly clean and activate the surface from any residual grease. The photocatalysis test first involved spraying a Resazurin-based "intelligent ink" (*i.e.* provide "intelligent" information concerning the photocatalytic activity on the surfaces by which they are applied), formulated as originally prepared by Mills *et al*. evenly over a select area of film.[32] The photocatalytic reduction of the resazurin redox dye was induced by UVA (365 nm) light and monitored using UV-visible absorption spectroscopy (using Lamda 25 instrument between 400 nm and 700 nm) of the film and the degrading ink layer at time intervals. The formal quantum efficiency (FQE) was calculated by rate of dye molecules destroyed by the number of incident photons. The formal quantum yield (FQY) was calculated by dividing the rate of dye molecules destroyed/sec/cm^2 by the number of photons absorbed by the films.

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