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# On titanium dioxide thin films growth from the direct current electric field assisted chemical vapour deposition of titanium (IV) chloride in toluene

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ABSTRACT

Titanium dioxide thin films were deposited from the aerosol assisted chemical vapour deposition reaction of titanium tetrachloride in toluene (1 M) at 600 °C and 5 L min$^{-1}$. Direct current electric fields were applied and increased in a range of 0 to 30 V during the reaction. Changes in particle size, agglomeration and particle shape were observed. Raman spectroscopy analysis revealed different composition of anatase and rutile and crystal phase depending on the field strength applied. The photocatalytic activity was calculated from the half-life or time needed by the films to degrade 50% Resazurin dye-ink initial concentration. High photocatalytic performance with high anatase content (98.3%) was observed with half-life values of 3.9 min. Deposited films with pure content in rutile showed better photocatalytic performance than films with mix of crystal phases with anatase content below 40%.

## 1. Introduction

Titanium dioxide is well known for its exceptional photocatalytic properties leading to innovative applications such as self-cleaning for different types of surfaces [1–3]. Titanium dioxide naturally occurs in three crystal phases; anatase, rutile and brookite. Among them, anatase is believed to give the highest photocatalytic performance which has been attributed to a more efficient bulk transport of excitons to the surface comparing to rutile crystal phase [4]. The photocatalytic performance of rutile has also been investigated [5,6] and has been reported to be more photoactive than anatase in nitrogen and osmium co-doped $TiO_2$ due to a synergy effect of rutile with the dopants [7]. Photocatalytic synergy between anatase and rutile has also been reported in a 1:1 ratio [8]. However, it was found that increasing the rutile content had a detrimental effect on the photoactivity for dense deposited films [8].

$TiO_2$ has been extensively produced using different technologies such as sol–gel [9–11], magnetron sputtering [12,13], and chemical vapour deposition (CVD) [14–16], among others. Primarily, investigations on $TiO_2$ have aimed to increase the photo-response in the visible light range which have included methods such as the incorporation of nanoparticles into $TiO_2$ coating [17,18], coupling with visible light absorber semiconductors [19,20] and doping with different metals [21,22]. Novel methods such as electric field assisted CVD has been proven to improve material's properties by inducing changes in the microstructure [23–26]. In particular, the electric field aerosol assisted CVD (EACVD) from titanium isopropoxide (TTIP) in toluene has been reported to improve titania photocatalytic properties by inducing changes in the size and morphology of nanoparticles and crystal orientation [27,28]. These studies showed that the application of AC electric fields induced more photoactive films than DC electric fields, which was attributed to a significant increase of film thickness for the last ones and thus, there was poor transfer of excitons to the surface of the material [27]. We have previously shown that the application of AC electric fields during the CVD deposition of $TiO_2$ thin films from 1 M solution of $TiCl_4$ in toluene induced changes in crystal phases that lead to a photocatalytic synergy for anatase to rutile ratio close to 1:1 [22,29].

This paper presents the results on the DC electric field assisted CVD growth of $TiO_2$ thin films from the reaction of titanium (IV) tetrachloride ($TiCl_4$) in toluene.

## 2. Experimental section

### 2.1. Film synthesis

The deposition of titanium dioxide thin films was carried from the direct current (DC) electric field assisted aerosol chemical vapour deposition (EACVD) reaction of 5 ml titanium (IV) chloride (1 M solution in toluene, Aldrich) until the depletion of the precursor (7 ± 2 min). The substrate and top plate were glass sheets (90 mm × 45 mm × 4 mm) coated by a fluorine doped tin oxide layer (Tec 15 Pilkington®) with a gap of 1 cm between them. The experimental set has been previously

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schematised [27]. The aerosol was produced using a Mini-fog & Multi-LED Mystery Wonder (Maplin Electronics) humidifier (240 V, 50 Hz), introducing the carrier gas flow once the mist had formed. The carrier gas used was $N_2$ (99.9% British Oxygen Company), which transported the precursors to cylindrical quartz cold wall reactor with dimensions of 6 cm diameter and 17 cm length at a gas flow rate of 5 L $min^{-1}$. The temperature of the reactor was set at 600 °C by heating a graphite block containing a Whatman heating cartridge, which was controlled by a Pt–Rh thermocouple. A small quantity of oxygen was able to enter the reactor through an imperfect seal in the baffle block of the reactor system. An electric field was generated by applying a potential difference across the electrodes and regulated from a variable voltage supply unit between 0 and 30 V (Table 1). Depositions were repeated at least twice in order to check and ensure the reproducibility of the system.

### 2.2. Materials' characterisation

Scanning electron microscopy (SEM) was completed using a FEI Inspect F Scanning Electron Microscope. X ray diffraction (XRD) analysis was conducted using Siemens D5000 (Karlsruhe, Germany) with $Cu_{k\alpha1}$ X-ray source in grazing incidence mode. However, no information about the material's phase could have been obtained from XRD as most of peaks corresponded to the substrate. Raman spectroscopy was carried out using a Renishaw (UK) Raman system 1000 with a helium neon laser of wavelength 514.5 nm. UV/VIS spectroscopy was conducted using a Perkin Elmer Lambda 950 UV/VIS Spectrometer. Film thickness was calculated from SEM cross-sectional images selecting at least 8 different points along of a sample extracting from the centre of the substrate. Band gaps were calculated using the Tauc method [30].

### 2.3. Properties' characterisation

Photocatalytic behaviour was monitored using an intelligent ink based on the dye Resazurin (Rz) [31–33]. The ink was made up of 40 mL of deionized water, 3 g of a 1.5 wt.% aqueous solution of 2-hydroxyl ethyl cellulose (HEC) polymer (Aldrich), 0.3 g of glycerol (Aldrich) and 4 mg of Rz (Aldrich). Titania thin films were sprayed with the ink solution using an aerosol spray gun and subsequently irradiated with a 365 nm lamp. The dye coated films changed colour from blue (photoreduction of Rz) to pink (rezofurin). Further photodegradation of the dye produces a colourless state indicating the total reduction of rezofurin. More accurate measurements were subsequently made using UV/Vis spectroscopy and monitoring the reduction of a dye absorption peak at 630 nm using a Perkin Elmer Lambda 35 instrument. In order to study the wetting characteristics of the deposited films, water contact angle measurements before and after 30 min of irradiation with 254 nm light were carried out using a Goniometer Kruss DSA100 drop shape analyser.

**Table 1**
Experimental conditions and material phase of deposited films from the EACVD reaction of 5 ml titanium (IV) chloride 1 M solution in toluene. Deposited films were produced at 600 °C and gas flow rate of 5 L $min^{-1}$ with an applied DC electric field and deposition time of 7 min.

| Sample | Applied voltage (V) | Field strength ($Vm^{-1}$) | Substrate bias | Material phase |
|---|---|---|---|---|
| A | 0 | 0 | | Rutile |
| B | 1 | $1 \times 10^2$ | Positive | Anatase–rutile |
| C | 5 | $5 \times 10^2$ | Positive | Anatase–rutile |
| D | 10 | $10 \times 10^2$ | Positive | Rutile–anatase |
| E | 15 | $15 \times 10^2$ | Positive | Anatase–rutile |
| F | 20 | $20 \times 10^2$ | Positive | Anatase–rutile |
| G | 30 | $30 \times 10^2$ | Positive | Anatase–rutile |
| H | 1 | $1 \times 10^2$ | Negative | Anatase–rutile |
| I | 5 | $5 \times 10^2$ | Negative | Rutile |
| J | 10 | $10 \times 10^2$ | Negative | Anatase–rutile |
| K | 15 | $15 \times 10^2$ | Negative | Rutile–anatase |
| L | 20 | $20 \times 10^2$ | Negative | Anatase–rutile |
| M | 30 | $30 \times 10^2$ | Negative | Anatase–rutile |

## 3. Results

### 3.1. Film synthesis and characterisation

The as deposited films were white and opaque white suggesting that pre-nucleation occurred in the gas phase. At positive biased low field strength values ($1 \times 10^2$–$10 \times 10^2$ V $m^{-1}$) no birefringence was observed which indicates minimal deposition. The deposition was not uniform across the substrate. However, at negative biases uniform deposition was obtained for field strength $10 \times 10^2$–$20 \times 10^2$ V $m^{-1}$.

Scanning electron microscopy images of the deposited titanium dioxide films are shown in Fig. 1. Films deposited with no electric field showed angular agglomerations 150 nm in length (Fig. 1A) and 60 nm wide. The introduction of a positively biased field ($1 \times 10^2$ V $m^{-1}$, Fig. 1B) induced changes in the morphology to a porous orthogonal microstructure 100 nm in length. Increasing the field strength produced rod-like nanoparticles 170 nm in length ($5 \times 10^2$ V $m^{-1}$; Fig. 1C) and elongated nanoparticles of 120 nm length and angular agglomerations of 320 nm ($10 \times 10^2$ V $m^{-1}$; Fig. 1D). The increase of field strength to $15 \times 10^2$ V $m^{-1}$ caused further changes to the morphology to spherical nanoparticles of 110 nm diameter (Fig. 1E). The increase of field strength to $20 \times 10^2$ V $m^{-1}$ produced rod-like nanoparticles 175 nm in length with angular agglomerations (Fig. 1F). At $30 \times 10^2$ V $m^{-1}$ (Fig. 1G) the morphology changed to spheres 135 nm in diameter. When applying a negatively biased electric field ($1 \times 10^2$ V $m^{-1}$, Fig. 2H) the microstructure showed angular agglomerations 75 nm in length. Increasing the field strength ($5 \times 10^2$–$15 \times 10^2$ V $m^{-1}$) produced an agglomeration of angular (Fig. 1I) and spherical (Fig. 1J & 1K) nanoparticles forming clusters in the range of 410–540 nm. The increase of field strength up to $30 \times 10^2$ V $m^{-1}$ produced angular nanoparticles of 110 nm length (Fig. 1L) and spherical nanoparticles 100 nm in diameter (Fig. 1M).

X-ray diffraction analysis was carried out and compared with previous investigations (JCPDS database file 021-1272) to investigate the material's phase. As indicated in Section 2, XRD pattern did not show clear evidence of the material's phase. As Fig. 2 shows only cassiterite $SnO_2$ peaks from the substrate appear for most of the deposited films indicating poor crystallinity of $TiO_2$ thin films. However, all negative bias deposited films showed peaks at 2 theta = 54.3° corresponding to rutile (211). Deposited films B & F showed a peak of anatase (101) but the last one showed particularly poor crystallinity. Negative biased deposited films were more amorphous than positive biased films as shown in XRD pattern. Samples H–L showed a peak at 2 Theta = 29.6° which corresponds to $SiO_2$ from the substrate [34].

Raman analysis was conducted to investigate materials' phase as not reliable information was obtained from XRD. Anatase crystal phase was identified at Raman shifts 144 $cm^{-1}$, 197 $cm^{-1}$, 399 $cm^{-1}$, 513 $cm^{-1}$, 519 $cm^{-1}$ and 639 $cm^{-1}$ [35] (Fig. 3). Likewise, rutile crystal phase was identified at Raman shifts 446 $cm^{-1}$ and 610 $cm^{-1}$ [15]. Quantifiable values of the content of anatase and rutile in deposited films were obtained by deconvoluting the overlapping rutile $A_{1g}$ (612 $cm^{-1}$) and anatase $E_g$ (639 $cm^{-1}$) contributions and inserting the percent area of contribution of rutile component (x) into a predetermined equation derived from powder standards as previously reported [8]. The percentage of anatase and rutile for all deposited film before and after annealing is shown in Table 2. It was found that for the same experimental conditions the material phase was different depending on the field strength applied. Pure rutile was found for the film produced with no field strength (Sample A). When applying electric fields the percentage of anatase dramatically increased to 98.3% in all cases except for Samples C, D, I & K. In particular, Samples D & K showed mostly rutile crystal phase with a percentage greater than 60% and Sample I showed purely rutile.