

Fabrication of single- and mixed-phase titanium dioxide photocatalysts

Author:

Hanaor, Dorian Amir Henry

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Fabrication of Single- and Mixed-Phase Titanium Dioxide Photocatalysts

A Thesis by Dorian Amir Henry Hanaor

Submitted in Partial Fulfilment of the Requirements for the Degree of

Doctor of Philosophy

in

Materials Science and Engineering

School of Materials Science and Engineering

**THE UNIVERSITY OF
NEW SOUTH WALES**



October 2011

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Abstract

Multifaceted research was conducted into the fabrication of single- and mixed-phase titanium dioxide photocatalysts using organometallic precursors and commercially available powders. Three photocatalyst immobilisation techniques involving the use of electrophoretic deposition, spin coating of sol-gels and the deposition of coatings on sand grains were explored. Associated enabling work involved the development of novel methods for the enhancement of dispersion and aqueous electrophoretic deposition of oxides on large-scale surfaces. Similar work was done on the coating of small-scale surfaces in the form of TiO_2 coatings on sand grains, which are a potential low-cost support for water purification photocatalysts.

The preceding studies were interpreted in terms of the anatase to rutile and brookite to rutile phase transformation behaviour was investigated through the thermal treatment of supported and powdered TiO_2 materials. Various compositional and morphological factors were found to have significant effects on the anatase to rutile phase transformation and the temperatures at which mixed-phase TiO_2 materials were obtained. These effects were discussed in light of an interpretive and predictive review of the phase transformations.

The performance of these single- and mixed-phase supported titanium dioxide materials were investigated in pilot-scale water purification studies through the inactivation of bacteria and through the photo-oxidation of methylene blue. The similarity in the results was such that it was not possible to determine if these data resulted from the impact of insufficient sensitivity of the testing and analytical procedures on the ability to differentiate between the competing effects of compositional and morphological aspects of the phase assemblage.

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Preface

The present work is a publication-based thesis describing work carried out for a Ph.D. in Materials Science and Engineering at the University of New South Wales. Therefore, the thesis consists of a series of manuscripts both in print (four papers), in press (two papers), and under revision (two papers).

A short introduction to the thesis is presented in Chapter 1. The initial literature review, presented in Chapter 2, is of a generic and wide-ranging nature as each manuscript includes its own literature survey applicable to the work undertaken. The works that form Chapters 3–10 are the manuscripts resulting from the individual research efforts. These manuscripts focus on a range of processing, characterisation, analysis, and performance aspects of the single- and mixed-phase titanium dioxide photocatalysts for environmental applications.

1. Introduction:

1.1 Background

As semiconductor oxide photocatalysts, titanium dioxide materials in various forms are being widely researched around the world owing to the potential of these materials in high value environmental applications of which solar driven water purification and generation of hydrogen are most prominent. Various crystalline phases are exhibited by TiO_2 , with anatase, rutile and brookite being the only phases studied as photocatalysts. It is widely considered that compositions of mixtures of these phases exhibit properties that impart superior performance in photocatalytic applications relative to single-phase material of comparable morphologies. Frequently, such mixed-phase TiO_2 is studied in the form of powders. However, for real-world applications, finely dispersed powders are problematic owing to associated difficulties in materials recovery. For this reason, the immobilisation of TiO_2 on recoverable support materials is desirable.

In the course of the doctoral research program to which this thesis is a conclusion, various research efforts aimed at developing and understanding methods for fabricating and applying titanium dioxide photocatalysts in different forms were undertaken. This research program led to the in-depth investigation of synthesis methods and phase transformation behaviour of titanium dioxide in the form of immobilised materials on different support materials and in the form of loose unsupported powders. To understand better the effects of various fabrication methods and phase compositions brought about through thermal treatments, the assessment of titanium dioxide materials in simulated water purification applications was carried out. The

characterisation of photocatalytic performance is relevant, particularly in environmental applications, water treatment and environmental remediation through the destruction of pollutants and micro-organisms in water. Such environmental applications are of growing importance as human activity is placing a growing strain on water resources through pollution and increased consumption.

1.2. Thesis overview

The present work incorporates eight manuscripts, six of which have been peer reviewed and published or are in press in academic journals as indicated below:

- Review of the anatase to rutile transformation – Journal of Materials Science, 2011, volume 46(4) 855–874
- Morphology and photocatalytic activity of highly oriented mixed phase titanium dioxide thin films – Surface and Coatings Technology, 2011, volume 205(12) 3658–3664
- Anodic aqueous electrophoretic deposition of TiO_2 using carboxylic acids as dispersing agents – Journal of the European Ceramic Society, 2011, volume 31(6) 1041–1047
- The effects of firing conditions on the properties of electrophoretically deposited titanium dioxide films on graphite substrates - Journal of the European Ceramic Society, 2011, volume 31(15) 2877–2885
- The effects of carboxylic acids on the aqueous dispersion and electrophoretic deposition of ZrO_2 - Journal of the European Ceramic Society, 2011, in press, DOI 10.1016/j.jeurceramsoc.- 2011.08.015
- Single- and Mixed-Phase TiO_2 Powders Prepared by Excess-Hydrolysis of a Titanium Alkoxide - Advances in Applied Ceramics: Structural, Functional and Bioceramics, 2012, in press

The different peer-reviewed publications listed above, with the addition of two manuscripts under revision, comprise the individual chapters of this thesis. The text that appears in these chapters is unchanged from that of the original manuscripts. Formatting and numbering of headings, subheadings, figures, tables and equations have been altered for the purposes of amalgamation to form the present thesis. The underlying theme that has guided the research shown in this thesis has been the development of mixed-phase titanium dioxide photocatalysts in conjunction with appropriate novel fabrication techniques for water purification applications.

The first manuscript presented, which forms Chapter 3 of this thesis, is an interpretive review of the anatase to rutile phase transformation in TiO_2 . The knowledge gained in the course of preparing this paper has been highly relevant to the work performed and reported in other manuscripts. In addition to a comprehensive review of the literature concerning the phase transformation from anatase to rutile in TiO_2 , this paper involves the predictive analysis of the consequences of dopants, impurities and firing conditions on the kinetics of this transformation. This analysis allowed for the discussion of the effects of support materials, synthesis parameters and firing conditions used in the bodies of work presented in subsequent chapters on the phase transformation behaviour observed in these studies.

In Chapter 4 the fabrication of thin films on quartz substrates is reported. This work draws on the information in Chapter 3 and demonstrates the inhibition and promotion of the anatase to rutile transformation through dopant and substrate effects. The formation of rutile in a unique banded morphology was further observed in the work presented in Chapter 4 and discussed in light of mechanistic aspects of the phase transformation also presented in Chapter 3. The use of expensive flat single crystal quartz substrates as carried out in the work presented in Chapter 4 was a precursor to the use of cheaper quartz sand as catalyst support material as carried out in the work presented in Chapter 9.

The fabrication of thick titanium dioxide films through electrophoretic deposition (EPD) is an alternative immobilisation approach which, in similarity to thin film fabrication, is chiefly relevant for the deposition onto two dimensional support materials. In contrast to the work presented in Chapter 4, EPD methods allow the utilisation of prefabricated powders exhibiting a given phase composition and morphology. Chapters 5–7 report the development of a novel fabrication technique for the synthesis of thick TiO_2 films using electrophoretic deposition. Chapters 5 and 7 focus chiefly on dispersion and particle charging phenomena achieved through the use of carboxylic acids while Chapter 6 involves the study of thermal treatment processes applied to these materials.

Although not directly involving the use of titanium dioxide, the work presented in Chapter 7, which involves the mechanistic study of carboxylic dispersion of zirconia particles, is relevant to understanding the dispersion phenomena which facilitated the preparation of materials used in Chapters 5 and 6.

The work presented in Chapter 8 focuses on the fabrication of TiO_2 in powder form through the hydrolysis of titanium alkoxides and thus is the only component of this thesis which does not involve the immobilisation of TiO_2 . Notwithstanding, the materials fabricated in Chapter 8 are candidates for immobilisation using the techniques reported in the preceding chapters and are thus part of a nexus with this component of the thesis. As with other components of this work, the phase formation and transformation behaviour observed in the synthesis of powders by hydrolysis and subsequent thermal treatments are discussed in the light shed by the review presented in Chapter 3.

The fabrication and study of sand supported TiO_2 , a body of work presented in Chapter 9, is the result of efforts to produce immobilised TiO_2 on support materials of enhanced surface area. The phase transformation behaviour was found to be resemblant of that observed in the case of TiO_2 immobilisation on flat quartz substrates as reported in Chapter 4.

The final episode of this thesis is the presentation of unusual findings of abnormal grain growth of rutile in the presence of solid state ZrSiO_4 dopants. The observations of this phenomenon came about during studies reported in the preceding chapters of the thesis, including thin films on quartz substrates and coatings on grains of sand. The observations reported and explored in this component of the present thesis require further examination, and thus the work as presented here is in essence a phenomenological overture drawing on findings gathered along the way.

The essence of the linkages and nexuses formed by this thesis is distilled into the conceptual flowchart shown below in Fig 1.1.

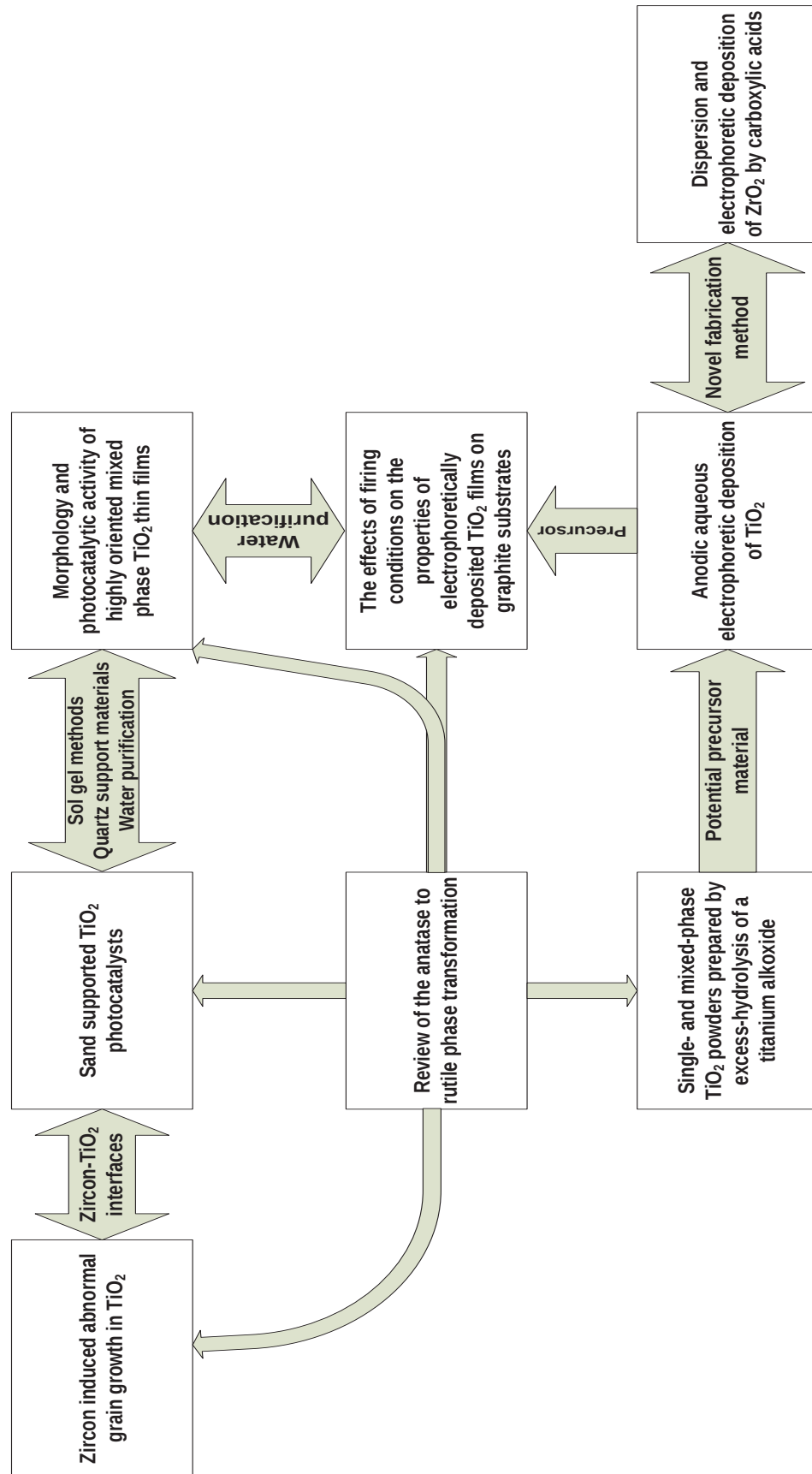


Fig. 1.1. Schematic conceptual diagram of the components of the research program presented in the present thesis

2. Literature survey

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2.1. Photocatalysis – a background

In photocatalysis chemical reactions are facilitated through the presence of a non-consumable catalyst material subjected to irradiation. As will be discussed in greater detail in the present chapter, semiconductor photocatalysis takes place through the irradiation induced generation of electron-hole pairs, excitons, and the subsequent formation of reactive radicals on the photocatalyst surfaces. Various oxide materials have shown promise as semiconductor photocatalysts, including WO_3 [1], CeO_2 [2] and TaON [3]. However it has been titanium dioxide TiO_2 which has been the subject of greatest interest for its ability to function as a photocatalyst. This is a result of the electronic properties of this particular semiconductor material and specifically the distinct energy levels of the valence band and conduction band which allow for the photogeneration of charge carriers with sufficient energy to facilitate desired reduction/oxidation reactions. The typically high surface areas exhibited by TiO_2 , a property which contributes to this materials usefulness as a high refractive index white pigment (the main application of TiO_2), contributes further to its merit as a photocatalyst, as too do the low cost and ready availability of this material.

It was the publication of Fujishima and Honda in 1972 [4] which brought to light the potential of TiO_2 to function as a photocatalyst. This study, which investigated the generation of hydrogen through TiO_2 photocatalyzed water splitting, precipitated great interest in TiO_2 photocatalysis and led to the investigation of this material in various applications including:

- Water Purification [5]
- Splitting of water molecules to generate hydrogen [6]
- Evaporative cooling coatings [7]
- Self cleaning coatings [8]

- Self sterilising materials [9]
- Air purification [10]

These applications are of great importance particularly as water and energy resources become increasingly scarce [11]. While many studies into TiO_2 photocatalysts have utilised artificial irradiation sources for the study of TiO_2 photocatalysis owing to the reproducibility of such methods in laboratory conditions, environmental applications of TiO_2 photocatalysts can be facilitated using solar irradiation, without the consumption of non-renewable energy resources.

2.2. Titanium dioxide

In the Ti-O system TiO_2 is by far the most commonly occurring oxide, it also the only oxide readily formed in air through common synthesis routes [12]. The various compounds in the Ti-O system are shown in the phase equilibrium diagram shown in Fig. 2.1, from Murray and Wriedt's publication of 1987 [13]. This diagram shows the presence of various lower oxides of titanium.

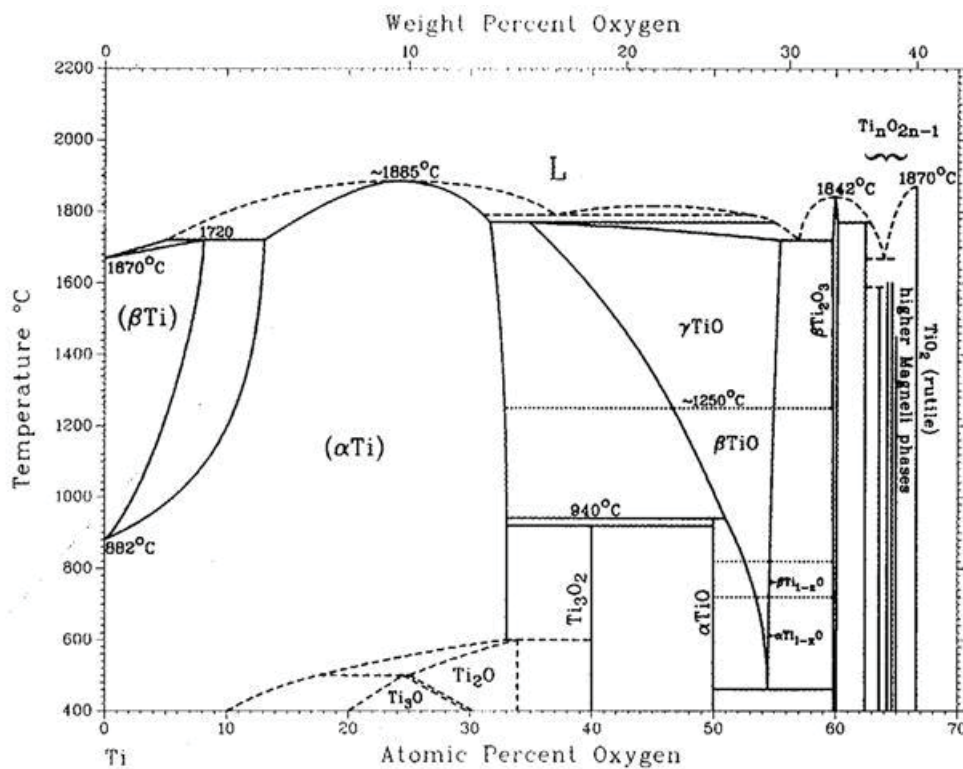


Fig. 2.1. Ti – O phase diagram [13]

These oxides include 5 titanium monoxide phases (TiO), Ti_3O_2 , Ti_2O_3 , Ti_3O_5 and Magneli shear phases of the composition $\text{Ti}_n\text{O}_{2n-1}$ where $n < 20$. Further studies of phase equilibria in the Ti-O system and lower titanium oxides have been reported elsewhere [12, 14–21]. The fabrication of lower oxides of titanium generally involves the controlled oxidation of titanium metal in oxygen deficient atmosphere as TiO_2 is the most stable oxide of titanium, exhibiting the lowest bulk Gibbs free energy [12, 16].

Titanium dioxide occurs naturally in three crystalline modifications: rutile, anatase and brookite, with the former being the equilibrium phase at all temperatures at atmospheric pressure and the latter two being metastable phases [22]. Anatase and rutile are the only commercially produced phases of TiO_2 and whilst the use of TiO_2 as a photocatalyst is of increasing importance, these phases find contemporary use chiefly as white pigments. The use of TiO_2 in pigmentary applications is a result of its very high refractive index, which is the highest of all oxides [23], as well as its biological inertness and ease of synthesis [24]. TiO_2 is used extensively as a white pigment in paints, plastics, textiles, paper, and food. Overall, pigments account for more than 95 wt% of TiO_2 usage and so the production of pigmentary titania is the main driver for the mining of titanium-bearing minerals [25, 26]. For these applications, TiO_2 is present generally in the form of rutile or anatase. The metastable anatase phase is considered advantageous for use in the paper and textile industries owing to its lower costs, greater uniformity in particle size distribution, and lower abrasiveness in comparison with rutile pigments [23, 27]. However, for use in paints, rutile is preferred owing to its higher refractive index and the tendency of anatase pigment based paints to undergo *chalking*, which is caused by photo-oxidation of the paint binder. Overall, rutile accounts for the majority of industrially produced titania pigments [25, 28, 29]. Brookite is not produced on an industrial scale and so does not find use as a pigment.

In addition to pigmentary uses, titanium dioxide is utilised also in electroceramics, fluxing agents for use on welding electrodes, vitreous enamels, refractory coatings and catalysts for the removal of nitrogen oxides from industrial waste gases[23, 26, 29, 30].

2.2.1. Crystallography of titanium dioxide

Anatase and rutile crystallise in tetragonal structures whilst brookite possesses an orthorhombic structure [23, 31]. In all three modifications of TiO_2 , each Ti atom is surrounded octahedrally by six oxygen atoms. These octahedra share four edges in anatase and two edges in rutile, as shown in Fig. 2.

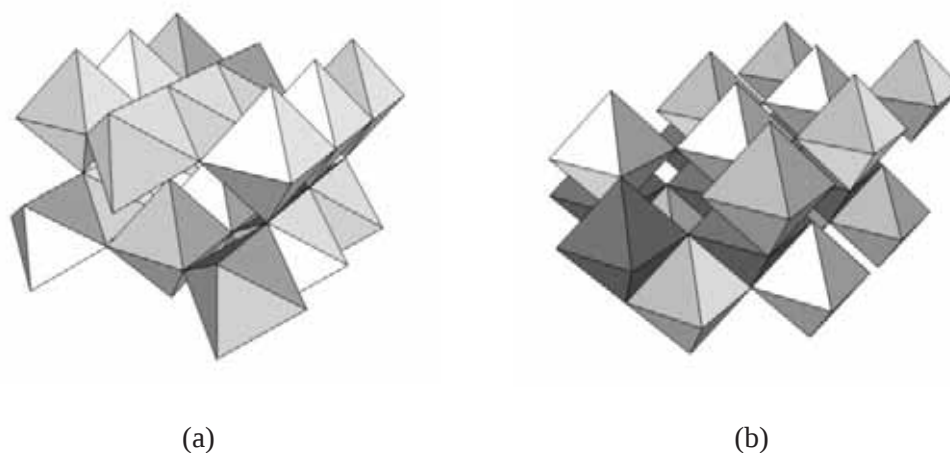


Fig. 2.2. Arrangement of TiO_6 Octahedra in (a) Rutile and (b) Anatase

Brookite has a more complex structure comprised of distorted TiO_6 octahedra sharing three edges, with varying Ti-Ti distances [32–35]. In anatase, the edge sharing connectivity occurs in chains along the tetragonal c axis and thus the Ti atoms are closer to each other along this axis. The tetragonal structure of Anatase and rutile causes anisotropy in the electrical and optical

properties of these materials, however due to the fact that these materials are typically used in polycrystalline form with a random orientation of crystallites, it is the mean value of these properties which is significant [29]. The crystallographies and some fundamental properties of TiO_2 phases are outlined in Table 2.1. The difference in crystal structure gives rise to divergent physical properties of the different phases. The contraction along the c-axis gives rise to the higher density of rutile relative to anatase. It has been reported that the wider band gap in anatase TiO_2 is a consequence of this phase exhibiting a higher charge carrier mobility and Fermi level [36–38].

Table 2.1. Properties of Anatase, Brookite, and Rutile Polymorphs of TiO_2 [31, 33, 39–41].

Parameter	Rutile	Anatase	Brookite	
Crystal structure	Tetragonal, Z = 2	Tetragonal, Z = 4	Orthorhombic, Z = 8	
Lattice parameters (nm)	$a = 0.459$	$a = 0.378$	$a = 0.918$	
	$c = 0.296$	$c = 0.951$	$b = 0.545$	
			$c = 0.524$	
Space group	$D_{4h}^{14} - P4_2/mnm$	$D_{4h}^{19} - I4_1/amd$	$D_{2h}^{15} - Pbca$	
Hardness (Mohs)	~7	~6	~6	
True density (kg·m ⁻³)	4200	3800	4100	
Refractive index (500 nm)	3	2.5	2.6	
Band gap	(eV)	~3.05	~3.2	3.1–3.4
	nm	~407	~387	365–400

2.2.2. Phase stability and transformations in TiO_2

As will be discussed in greater detail in Chapter 3 of this thesis, the metastable anatase and brookite phases of TiO_2 transform to the equilibrium rutile phase at elevated temperatures. The bulk free energy of rutile is lower than that of anatase or brookite at all temperatures and pressures [42]. The temperatures at which metastable phases transform to rutile depend on a range of parameters. In essence, the transformation takes place when thermal energy present is sufficient to facilitate the rearrangement of bonds in the metastable phase to form the rutile phase. This atomic rearrangement requires higher temperatures if the structure is constrained, through grain boundary pinning or other mechanisms, and it may take place at lower temperatures if greater freedom is present due to higher levels of oxygen vacancies.

2.2.2. High pressure phases of titanium dioxide

In addition to the main phases obtainable at atmospheric pressure, five high-pressure phases of TiO_2 have been reported [43–45]. These phases exhibit orthorhombic, monoclinic, and cubic structures and form from anatase or rutile at high pressures [45]. The most notable of these is the $\alpha\text{-PbO}_2$ structured TiO_2 (II) phase [46], which has been observed in pressure-shocked TiO_2 found in geological formations and meteor craters [47]. This phase is of particular importance since it has been suggested to exhibit an equilibrium phase boundary with rutile at high pressures [43, 48]. The pressure at which the TiO_2 (II) is likely to be in the region of several GPa.

2.2.3. Production of titanium dioxide

Commercially, titania is synthesised from naturally occurring iron-containing rutile ($\text{Ti}_{1-x}\text{Fe}_x\text{O}_2$), ilmenite (FeTiO_3), leucoxene (a weathering product of ilmenite), and from ilmenite rich slags formed as by-products of iron production. These materials are processed by acid leaching

(chloride process or sulphate process) in order to produce salts as precursors to calcining to form TiO_2 . These industrial processes can be designed to yield a particular phase of titania by using TiO_2 seed grains, the addition of dopants, and variation of the pH [25, 39, 49].

In the chloride process, TiO_2 present in the dried raw material is converted to titanium tetrachloride in an exothermic reaction according to the formula:



The TiCl_4 is separated from other chlorides present in the reaction gases and purified to remove impurities such as vanadium tetrachloride [24, 29].

TiO_2 is manufactured from the tetrachloride by the reaction



The production of TiO_2 from the tetrachloride can be carried out by hydrolysis in aqueous solution or by flame pyrolysis and frequently results in a powder of titanium dioxide in the anatase phase although the use of rutile seeds can result in the fabrication of this phase. Degussa P-25, a commercially produced titanium dioxide powder of high purity and non-uniform crystalline structure is produced by flame hydrolysis of the tetrachloride, and typically consists of 80% anatase and 20% rutile. This product has been utilised extensively as a reference materials in research into photocatalysis as its mixed phase composition contributes to its good photocatalytic performance [50–53].

Titanium dioxide in the rutile phase can be produced in the chloride process using the addition of AlCl_3 to the tetrachloride [29]. This dopant also brings about a smaller particle size of the product. The chloride process is the most widely employed and is more favourable for the production of high quality anatase pigments. An alternative method for pigment production is the sulphate

method which involves the digestion of the raw materials in sulphuric acid, removal of FeSO_4 and subsequent hydrolysis. The hydrate produced in the sulphate method can be doped prior to calcining to give the desired phase of TiO_2 . For the production of rutile using this method, rutile nuclei are added, whilst for the production of anatase pigments phosphoric acid is added [29].

As will be discussed in greater detail in Chapter 6, fabrication of titanium dioxide for photocatalytic studies is often carried out through the hydrolysis of titanium alkoxides or through the use of hydrothermal synthesis methods.

2.3. TiO_2 in photocatalysis

2.3.1. Photoexcitation

The excitation of semiconducting anatase or rutile by photons exceeding the $\sim 3.0\text{--}3.2$ eV band gap creates electron-hole pairs, known as excitons. These electrons and holes typically have very short lifetimes in the order of femtoseconds [52, 54–57]. The recombination of electron hole pairs and their reaction with adsorbed species at the photocatalyst surface are competing phenomena. It has been reported that excitons require a lifetime of at least 0.1 nano-seconds for any chemical reactions to be facilitated [58, 59]. This means that for the achievement of effective photocatalysis, enhanced charge carrier separation or trapping is required.

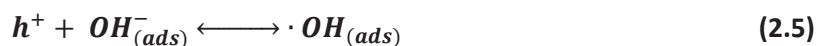
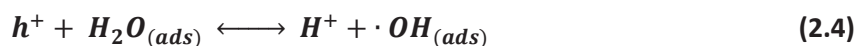
The photogeneration of electron hole pairs, by a photon of energy $h\nu$ exceeding the materials band gap, is described by **equation 2.3**.



In this equation h^+ and e^- represent valence band holes and conduction band electrons respectively.

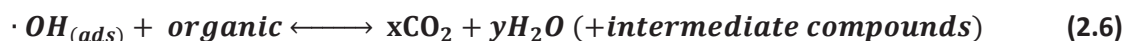
2.3.2. Decomposition of organic compounds

The photogenerated holes in the TiO_2 valence band have a strong oxidizing potential and can bring about the direct oxidation of organic compounds, or alternatively these can react with adsorbed H_2O or OH^- to create adsorbed hydroxyl radicals which in turn facilitate the indirect oxidation the organic matter [60–65]. The formation of adsorbed radicals on TiO_2 surfaces is described by **Equations 2.4 & 2.5**.



The photo-oxidation of organic matter enables the use of titanium dioxide photocatalysts in water and air purification as well as anti-microbial and self-cleaning coatings.

Adsorbed radical species facilitate the oxidation of organic compound through various processes generally represented by the reaction shown in **equation 2.6**.



The oxidation of organic compounds may proceed to completion or may occur partially with the formation of intermediate products which are difficult to destroy [66]. This may cause the deactivation of the photocatalyst through the build up of a non-reactive layer on the surface.

In addition to the formation of radicals from adsorbed water or hydroxyl species, the formation of highly reactive oxygen radicals can occur through the following processes [62]



These reactions are particularly relevant in the use of titanium dioxide coatings for the oxidation of airborne pollutants [66–68]. The formation of such oxygen radicals has been reported to facilitate the photo-oxidation of deposited soot on self cleaning TiO₂ coatings. This is of great interest in applications of TiO₂ in architectural applications such as Pilkington Activ self cleaning windows [69]. The overall reaction describing the photocatalytic oxidation of soot is shown in **equation (2.9)** [63, 70].

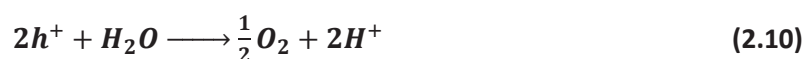


The oxidation of pollutants on self cleaning surfaces can take place remotely as well as directly on the photocatalyst surfaces. The maximal distance at which this remote oxidation can take place has been reported as 20µm [64] from the photocatalyst surface, however other studies have shown remote oxidation at distances of 0.7mm [63, 66, 68, 70].

2.3.3. Water splitting

One of the most promising photocatalytic applications of TiO_2 is the splitting of water molecules to form hydrogen and oxygen. This phenomenon was first achieved with an anatase photocatalyst by Fujishima and Honda in 1972[4]. The concept of water splitting through TiO_2 photocatalysis has given rise to the prospect of the solar generation of hydrogen fuel, a highly attractive form of renewable energy [71, 72].

In TiO_2 photocatalysed water splitting electrons and holes react with adsorbed water to yield hydrogen gas as described by **equations 2.10 and 2.11** [4, 60, 62, 73, 74].



The overall photocatalysed generation of solar hydrogen is described by **equation 2.13**.



Although electron hole pairs can be generated on clean TiO_2 surfaces, the application of TiO_2 for water splitting applications requires the use of a noble metal cathode, typically platinum often in conjunction with a weak electrical bias applied. This is a consequence of the electrochemical potentials of the $\text{H}_2/\text{H}_2\text{O}$ and $\text{O}_2/\text{H}_2\text{O}$ reduction/oxidation couples [4, 71, 73, 75].

2.3.4. Importance of phase composition in TiO_2 photocatalysts

In spite of a larger band gap in comparison with rutile, anatase is reported as having better photocatalytic performance than rutile in self cleaning coatings and other photocatalytic

applications [76–78]. The advantage of anatase is likely to be mainly due to its higher surface area [50, 79, 80] and more prominent hydrophilicity [81].

The lower surface area observed in rutile is a natural consequence of the significant grain growth which accompanies the anatase to rutile phase transformation [82–84]. As higher levels of surface area translates to higher levels of adsorbed species and improved exciton lifetime [74], the grain growth which occurs when rutile forms from anatase results in lower photocatalytic activity.

As shown in Table 2.1, the atomic arrangement in anatase is less dense than that of rutile. The looser atomic packing in anatase translates to a higher density of surface terminated bonds and thus more exciton-trapping surface states [85, 86]. The higher density of surface terminated bonds also gives rise to a higher surface free energy in anatase and consequently enhanced hydrophilicity [87–91]. Both of these factors contribute to higher levels of adsorbed reactive species on anatase photocatalysts relative to rutile [86].

The reported increased photocatalytic performance in anatase could also be the result of this phase's higher Fermi level [36, 92]. However, it should be noted that Rutile has been reported to have superior properties for water splitting applications [50, 75].

The brookite form of TiO_2 has been studied for use as a photocatalyst and is reported to exhibit good photocatalytic activity [93, 94]. However, this phase is unlikely to provide any significant advantages over anatase or mixed anatase-rutile photocatalysts as a result of its larger band gap and difficulties in its production.

An increasing numbers of publications report that a *mixed* anatase and rutile phase composition exhibits superior photocatalytic performance owing to improved charge carrier separation relative to single-phase anatase or rutile [51, 78, 95–97]. The improved charge carrier separation in mixed phase titanium dioxide is, at least in part, a consequence of valence and conduction band bending which occur at anatase-rutile interfaces [98].

Enhanced charge carrier separation has been reported to occur through the accumulation or trapping of conduction band electrons in the anatase phase while the holes flow into the valence band of rutile [98–100]. The mechanism of enhanced charge carrier separation in mixed phase Degussa P-25 catalysts has also been explained by the transfer of photogenerated conduction band electrons from rutile to anatase lattice trapping sites of lower energy, and migration of valence band holes to surface sites [51, 101]. Conversely it has also been suggested that owing to the lower energy of the rutile conduction band, electrons are transferred from the anatase phase to the rutile phase [102, 103].

Regardless of the electron-hole transfer mechanisms, the synergism between anatase and rutile in photocatalytic applications can be understood as a combination of the slower charge carrier recombination in the high surface area anatase phase alongside the increased exciton generation and broader optical response in the lower band gap rutile [100, 104]. This synergistic effect is highly dependent on the morphology of phase interfaces and consequently the synthesis route through which biphasic TiO_2 photocatalysts are obtained is of great significance on the performance [95, 105]. The fabrication of mixed phase anatase-rutile TiO_2 through partial transformation of the anatase phase to rutile by thermal treatment is likely to result in good inter-phase contact and high levels of synergism [92].

In addition to biphasic anatase-rutile photocatalytic materials, it also has been reported that titania photocatalysts consisting of equal portions of anatase, rutile, and brookite exhibit enhanced photocatalytic activity in comparison to biphasic material [106].

2.3.5. Importance of morphology in TiO_2 photocatalysts

TiO_2 photocatalysts have been fabricated with a large variety of crystallite morphologies these include flower-like clusters [37, 107], nanofibres [108], nanobelts [109], nanotubes [110] and

needles [111] of rutile and/or anatase as well as more commonly produced spherical nanoparticles of these phases [112, 113]. These different morphologies are achieved through control of acidity levels, peptization, the use of various dopant compounds and thermal processing methods and have important consequences on the phase, morphology, surface area and resultant photocatalytic performance of the material [114–119].

In general it is clear that a smaller grain size is advantageous in photocatalysis owing to the higher resultant surface area. For this reason various studies have endeavoured to inhibit grain growth during the anatase to rutile phase transformation in TiO_2 and lower the temperature at which this transformation takes place, through the addition of dopants [120–124], enabling the formation of mixed phase TiO_2 photocatalysts with intimate inter-phase contact and high surface area values.

Certain planes in anatase and rutile exhibit enhanced levels of photo-excitation, adsorbed species and improved charge carrier separation. For this reason various researchers have sought to increase the exposure of the more reactive facets of anatase and rutile [107, 125, 126]. The type of surface terminating groups alters the different energy of exposed planes, thus it is possible to control the expression of exposed planes through imparting different surface adsorbates using acidic and basic synthesis conditions or using halogen doping [87, 126, 127].

2.4. Applying TiO_2 photocatalysts

2.4.1. Self cleaning and self sterilising applications

The deposition of TiO_2 films to impart coatings with solar-induced self cleaning ability has been attracting increasing attention in the last two decades and has been the subject of numerous patents [128]. The ability of TiO_2 to function as a self cleaning material is a result of the material's

aforementioned ability to bring about the photo-oxidation of pollutants on the surface, such as soot particles resulting from air pollution, as well as the hydrophilicity of the material which enables an even film of water to form and clean the surface during rainfall [81, 129, 130]. Architectural applications of self-cleaning films are of great value in urban high-rise structures where the cost and difficulty of aesthetic maintenance through conventional methods can be high and consequently TiO_2 is finding new applications in this purpose [61, 68, 69, 128].

In addition to self cleaning coatings, titanium dioxide is attracting research attention for use in self sterilising coatings in the biomedical industry as well as food packaging [131, 132]. The bactericidal activity of TiO_2 occurs in a similar manner to the photo-oxidation of organics, as the cell membrane undergoes photocatalyzed degradation resulting in the inactivation of the microorganism [133–135]. Anti viral activity has also been demonstrated [136] and future use of TiO_2 coatings in self-sterilising applications may facilitate the reduction of infection without the necessitation of anti-microbial reagents.

2.4.2. Wastewater treatment

Waste water treatment, alongside generation of hydrogen is one of the most promising applications of TiO_2 in photocatalysis. Photocatalysis is a highly attractive approach to water purification owing to several factors:

- Ability to harness solar energy
- No requirement for chemical reagents
- Ability to treat hydrocarbons, pesticides viruses and bacteria
- Low cost and simplicity, enabling application in remote regions in developing countries

As a result of these factors, increased research efforts are being directed towards the application of TiO_2 photocatalysts in simulated water treatment situations [5, 137–140].

Generally water treatment is achieved by using titanium dioxide on a catalyst support designed to maximise surface area and thus enhance water- TiO_2 contact. For waste water treatment applications, titanium dioxide can be immobilised on various support materials including silica gel [141], sand [142], glass beads [143], tubes [144], activated carbon [145] or porous molecular sieves such as Zeolites [146, 147]. The alternative to catalyst immobilisation is the use of titania powder in suspension, or as a slurry. This approach has the key advantage of giving a high level of available surface area however such application of titanium dioxide photocatalysts creates a significant problem of catalyst recovery, involving the separation of the catalyst powder from the treated water, a step which is complex and inappropriate for large scale water treatment applications. Effective photocatalyzed reactions can be carried out using supported TiO_2 in a fluidized bed photo-reactor [148] in which the contaminated water flows through a bed of coated particles or beads. This fluidized bed is exposed to UV radiation to facilitate the photocatalytic decomposition of toxins or other pollutants

2.4.3. Solar hydrogen generation

Since Fujishima and Honda's seminal discovery reported in 1972 [4], the production of hydrogen through water splitting has been the subject of much research. Levels of efficiency obtained using TiO_2 photoanodes for solar hydrogen generation have been very low and this is currently an obstacle to the implementation of such energy generation systems [6, 71]. Titanium dioxide for water splitting applications can be utilised as a thin films connected through a slight applied bias to a noble metal cathodes, or through the use of suspensions of platinum loaded particles [73]. As with other applications, phase composition, morphology, and dopants play an important role in the development of practical materials for this application.

2.5. Fabrication of TiO₂ photocatalysts

2.5.1. TiO₂ powders

Aside from the previously described industrial fabrication of pigmentary TiO₂, fabrication of TiO₂ powders for studies into photocatalysis typically utilise either organometallic compounds such as titanium alkoxides [149–152], or titanium tetrachloride TiCl₄ [153–155].

Scientific studies frequently use titanium alkoxides for photocatalyst fabrication owing to the fine crystallite sizes that can be obtained through the use of such precursors and the lack of harmful HCl gas which is generated when TiCl₄ is used. These alkoxide reagents typically have the formula Ti(OR)₄ where R represents an alkane chain. The formation of TiO₂ through hydrolysis of alkoxides proceeds according to the overall reactions shown in **equation 2.14**:



As will be discussed later in this thesis, such reactions often do not proceed stoichiometrically and partially hydrolysed titanium dioxide exhibiting residual alkoxide, or chloride groups in the case of TiCl₄ hydrolysis, may be formed as product materials.

Peptization, thermal treatment and acidity are important factors in determining the dispersion, crystallite morphology, phase composition and photoactivity of titanium dioxide powders resulting from the hydrolysis of alkoxide compounds. The addition of hydrolysis catalysts or peptizing agents and the control of reaction temperatures further determine whether the hydrolysis of titanium alkoxides will give rise to precipitated powders or a sol-gel suitable for the fabrication of thin films through spin coating methods [149, 150, 152, 156–158].

Fabricated TiO_2 powders can be used directly in aqueous dispersions or alternatively immobilised through various methods to produce durable supported material suitable, as mentioned previously, for use in water purification applications.

2.5.2. Thin films

For self cleaning coatings, self sterilising coatings as well as for photoanodes for the production of hydrogen, the application of thin films of TiO_2 is carried out.

Methods for thin film fabrication include

- Spin coating – using a sol-gel precursor onto a flat substrate [159, 160].
- Dip coating – using a sol-gel precursor onto substrates of various shapes [8, 161].
- Chemical Vapour Deposition - spraying or otherwise depositing Ti-bearing precursor chemicals onto substrates at room temperature and subsequently firing to achieve crystallization of TiO_2 phases, or alternatively spraying precursor compounds onto hot substrates [67, 162].
- Physical Vapour Deposition – sputtering methods used in conjunction with a Ti or TiO_2 target in controlled atmospheres [61, 163].

Thin film fabrication is often carried out in situations where good optical transparency and/or flat 2 dimensional surfaces are desired and typically results in films of 50–500nm in thickness [8, 164]. The disadvantage associated with TiO_2 thin films is the high density typically exhibited by these materials and the consequent low exposed surface area. In water purification applications this can be addressed by applying thin films to high surface area support materials, giving high surface area immobilised TiO_2 .

2.5.3. High surface area immobilised TiO₂

Methods used to fabricate thin films on various flat surfaces as described above can be used to fabricate high surface area immobilised TiO₂ on high surface area support materials suitable for water purification applications. In addition to immobilised thin films, TiO₂ powders can also be supported on high surface area substrates [141, 147]. One method of anchoring TiO₂ powders to substrates, flat or otherwise, is the use of electrophoretic deposition.

2.5.4. Electrophoretically deposited thick films

Electrophoretic deposition, known as EPD is a method through which charged particles in suspension are deposited onto an electrode under an applied electric field. In essence, the EPD process consists of the migration of charged particles (electrophoresis) and their compaction on electrode surfaces (deposition) as described in greater detail in various reviews of this process [165–167].

The attractiveness of EPD for TiO₂ photocatalyst fabrication is a result of the rapidity and low cost at which supported photocatalytic TiO₂ can be fabricated from suspensions of low solids loading [168, 169]. Moreover, EPD processes utilise prefabricated TiO₂ powders in contrast to CVD, PVD or sol-gel spin/dip coating methods which involve the deposition of precursor materials to form dense films. The ability of EPD to utilise prefabricated TiO₂ powders is attractive as this allows the conservation of pre-existing optimised high surface area morphologies and phase assemblages in the powders.

As will be explained in greater detail later in this thesis, EPD processes are controlled by electrokinetic phenomena. As shown in Fig. 2.4, surface charge carrying particles in suspension

become surrounded by a layer of ions of opposite charge, known as an electrochemical double layer. As the particle migrates through the suspending medium under an applied electric field the potential at the slipping plane is known as zeta potential [165, 166, 170, 171]. The zeta potential is a key parameter in evaluating EPD behaviour and the sign and magnitude of this parameter are governed by the species present in the suspending medium.

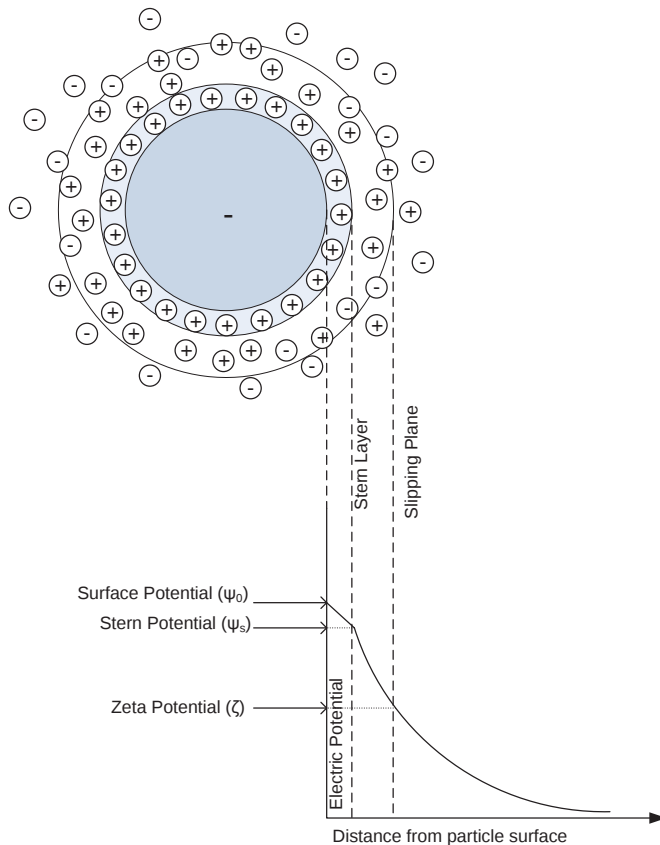


Fig. 2.4. Diagram of electrochemical double layer surrounding a suspended particle.

As will be discussed later in this thesis, EPD can be carried out in organic or aqueous suspensions. EPD in aqueous suspension is associated with a problem of water electrolysis which causes bubble damage in deposited material. EPD in organic medium is however more costly and less appropriate for large scale fabrication.

2.6. Doping TiO₂

The expansion of the applicability of TiO₂ as a photocatalyst is contingent on improving its efficiency. Currently the use of titanium dioxide as a photocatalyst is fairly limited, with its use confined to specialised applications, self cleaning windows in particular, where the low levels of photonic efficiency are outweighed by the unique capabilities of the material. For titania photocatalyst to gain a wide acceptance we seek a reduction of charge carrier recombination, higher levels of photonic excitation, higher levels of exposed active surfaces and lower-cost synthesis methods.

Dopants are frequently used in attempts to accomplish the heretofore mentioned enhancements to titanium dioxide photocatalysts. The term *dopants* generally refers to intentionally introduced elements or compounds added in different forms during various processing stages. However, dopants may also be present in titanium dioxide photocatalysts through unintentionally impurities in raw materials and through the diffusion of elements from substrates in supported TiO₂ photocatalysts. These phenomena are relevant to much of the work included in the present thesis.

Various transition metal dopants have been reported to enhance photocatalytic activity through reaction with photo-generated electrons or holes and consequent valence change [74, 172]. Such effects are reported to essentially act to extend the lifetime of photo-induced reactive species by acting as intermediary compounds. In contrast, it has been reported that higher levels of transition metal doping causes the inactivation of photocatalyst as a result of enhanced charge carrier recombination [61]. It is likely that the size and dispersion of transition metal dopant particles has significant consequences on whether these elements are beneficial or detrimental for photocatalytic activity.

Noble metal compounds have been used to achieve similar enhancement in reactivity of excitons [98, 173]. Similarly to transition metal dopants, noble metals are reported to enhance photoactivity through improved charge carrier separation by trapping of electrons in noble metal ions which act as electron sinks [174]. The disadvantage of such doping methods is the high associated costs involved in producing such materials.

The use of dopant compounds has been used to promote the formation of microstructures exhibiting higher levels of surface area. Dopants have been used to achieve this through the inhibition of grain growth [122, 175], through the formation of porous microstructures [79, 176], through phase assemblage optimisation and by enhancing levels of exposure of more reactive facets [74, 126].

Anionic dopants have been reported to enhance levels of charge carrier generation through reduction of the band gap and the formation of new inter band gap electronic states [177–179]. Nitrogen doping in particular has been the subject of a significant research attention and is reported to extend the photo response of TiO_2 into the visible range of the spectrum [180–182]. Carbon too has been reported to enhance photocatalytic performance through interband states and through phase composition optimisation [181, 183]. The effects of such doping on the anatase to rutile phase transformation are discussed further in this thesis.

2.7. Evaluation of TiO_2 photocatalysts

The evaluation of photocatalytic performance of TiO_2 photocatalysts in powder form and as supported films is an essential step in materials research and development. Comprehensive characterisation of TiO_2 photocatalysts typically involves the evaluation of photocatalytic performance directly or indirectly.

The direct assessment of photocatalytic activity involves the use of TiO_2 as a photocatalyst in a representative reaction, simulating the application of interest.

For water purification applications TiO_2 photocatalysts are often evaluated through the decomposition of dyes in aqueous solutions subjected to UV irradiation [144, 184–186]. Methylene blue [185] and rhodamine [184, 187] are commonly used dyes for this purpose. This method of photocatalyst evaluation enables easy determination of photodegradation kinetics as the concentration of dyes can be rapidly determined using UV-visible spectroscopic methods. Furthermore such dyes are often considered to represent organic pollutant molecules in effluent streams.

In addition to dyes, studies of water purification have frequently examined the photo-oxidation of phenol in water [98, 145, 188–190]. This compound is of interest as it representative of pesticide contaminants which can be present in water resources. Concentration of phenol during photocatalytic degradation can be determined from samples directly using Total Organic Carbon analysis methods [98], or indirectly, by using gas chromatography to analyse reaction products [191].

In addition to the photo-oxidation of various organic compounds which may represent pollutant chemicals in water resources, examining anti bacterial and anti viral activity of TiO_2 is also of great importance with respect to water purification by photocatalysis as inactivation of these contaminants is an essential requirement in water purification. The inactivation of bacteria and virus in the presence of irradiated TiO_2 is reported to occur through the photocatalyzed degradation of organism membranes [9, 133, 135, 136, 192]. The assessment of photocatalytic performance in the inactivation of micro-organisms involves using water inoculated with a particular concentration of micro-organisms and determining the rate at which microbial inactivation takes place and/or the length of time required for complete sterilisation of a predetermined volume of inoculated water. Determining the microbial concentration of micro-

organisms in water generally involves spread-plating serially diluted aliquots of treated water and enumerating bacterial colonies subsequent to plate incubation as described in greater detail in this thesis.

Decomposition of soot [70, 193] and/or stearic acid [186] are commonly used methods to evaluate the performance of TiO_2 photocatalysts applied for use as self-cleaning coatings. In these situations the performance of the material may be assessed through visual assessment or by using Fourier Transform Infrared Spectroscopy (FTIR) to study the presence of the chosen organic material present of the coated surface and/or the generation of CO_2 by photocatalytic reactions.

Aside from directly examining photocatalyzed reactions, other parameters, which are relevant to the photocatalytic performance, can be analysed and the results projected to have relevance on the photocatalytic performance. Such parameters include radiative charge carrier recombination, surface area, band gap and UV-vis absorption.

A useful technique to establish charge carrier recombination is photoluminescence, this is an indirect approach which examines the photonic emissions resulting from radiative recombination of photo-generated charge carriers [56, 194–196]. As will be discussed later in this thesis, photoluminescence is a problematic evaluation technique as lower photoluminescent emission may be the consequence of lower charge carrier generation or reduced recombination. For this reason, this technique is appropriate only when used in conjunction with other analytical methods.

2.8. Enhanced performance of TiO_2 photocatalysts- a summary

In this literature survey the various potential uses of titanium dioxide photocatalysts have been reviewed as have the various methods of fabricating and applying this material. The merit of TiO_2

has been shown as have the drawbacks and obstacles to wide scale implementation of this material as a photocatalyst. The development of novel methods for applying mixed phase photocatalysts and enhancing the performance of these materials is of great importance. The literature surveyed in this chapter serve to highlight the motivation for the various individual bodies of work presented in this thesis.

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3. Review of the anatase to rutile phase transformation

This chapter presents a review paper published in February 2011 in the Journal of Materials Science, volume 46, issue 4, pg 855–874. This paper has been selected by the Journal of Materials Science as the best paper of February 2011 and has been nominated for the Journal's Sapphire Prize to be announced in November 2011.

The occurrence of the anatase to rutile phase transformation is widely reported and discussed in scientific studies involving thermal treatment of titanium dioxide in various forms both doped and undoped. This phase transformation has significant consequences on the properties of TiO_2 materials and thus gaining an understanding of the mechanism of this phase transformation and the factors which affect it is highly pertinent to such studies.

A comprehensive review dedicated to the phenomenon of the anatase to rutile phase transformation was absent from the literature until the publication of the paper presented in the current chapter of this thesis. The manuscript which comprises in this chapter reviews a large number of publications which have reported observations concerning the anatase to rutile phase transformation and interprets these to present a discussion and build an understanding of the mechanism of the anatase to rutile along with the various factors affecting the kinetics of this transformation. The information reviewed and presented has been used to perform a predictive analysis of the effects of untested dopants on the phase transformation in TiO_2 .

This chapter is highly relevant to much of the work included in this thesis, as an understanding of the anatase to rutile phase transformation is essential in the fabrication of mixed phase TiO_2 photocatalysts through the heat treatment of anatase (and/or brookite). The current chapter sheds light on the effects which dopants, impurities and catalyst support materials may have on

the phase transformation in the materials fabricated in the course of the multi-faceted doctoral research program of which this thesis is the culmination.

A breakdown of the contributions of the authors to the preparation of the manuscript presented in this chapter is shown below:

	Primary Author	Manuscript Preparation	Literature Research	Data Analysis	Editing and Revision	Supervisory Role	Formatting and Layout	Data Interpretation
Dorian A. H. Hanaor	✓	✓	✓	✓	✓		✓	✓
Charles C. Sorrell				✓	✓	✓	✓	✓

Key Findings

- The various phases of TiO_2 are reviewed and discussed
- Phase stability and transformation kinetics are reviewed
- Mechanisms of the inhibition/promotion of the phase transformation are analysed
- Dopant effects are comprehensively summarised and interpreted in terms of valence and ionic radii
- The effects of dopant valence change on the enhancement or inhibition of the anatase to rutile phase transformation are discussed
- Effects of untested dopants are predicted
- Advantages and disadvantages of different methods of mineralogical analyses are discussed
- The effects of morphology on phase stability and transformations are discussed

Review of the Anatase to Rutile Phase Transformation

Dorian A.H. Hanaor* and Charles C. Sorrell

School of Materials Science and Engineering, University of New South Wales / Kensington,
NSW 2052, Australia

dorian@student.unsw.edu.au, c.sorrell@unsw.edu.au

* D.A.H Hanaor; Tel.: +61-2-9398-4095; Fax: +61-2-9385-5956 (School of Materials Sci. & Eng., UNSW, Sydney, NSW 2052, Australia)

Abstract: Titanium dioxide, TiO_2 , is an important photocatalytic material that exists as two main polymorphs, anatase and rutile. The presence of either or both of these phases impacts on the photocatalytic performance of the material. The present work reviews the anatase to rutile phase transformation. The synthesis and properties of anatase and rutile are examined, followed by a discussion of the thermodynamics of the phase transformation and the factors affecting its observation. A comprehensive analysis of the reported effects of dopants on the anatase to rutile phase transformation and the mechanisms by which these effects are brought about is presented in this review, yielding a plot of the cationic radius *versus* the valence characterised by a distinct boundary between inhibitors and promoters of the phase transformation. Further, the likely effects of dopant elements, including those for which experimental data are unavailable, on the phase transformation are deduced and presented on the basis of this analysis.

Keywords: Titanium dioxide; anatase; rutile; phase transformation; photocatalysis; mixed-phase

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3.1. Background

Titanium dioxide, also known as titania, is of growing interest due to its proven ability to function as a photocatalyst and facilitate important environmentally beneficial reactions, such as water splitting to generate hydrogen and treatment of polluted air and water.

Titanium dioxide occurs as two important polymorphs, the stable rutile and metastable anatase. These polymorphs exhibit different properties and consequently different photocatalytic performances. Anatase transforms irreversibly to rutile at elevated temperatures. This transformation does not have a unique temperature and the processes that are involved in the transformation as well as the methods to inhibit or promote this transformation have not been reviewed comprehensively to date.

The present work aims to clarify the differences between the two main polymorphs of titanium dioxide, the nature of the anatase to rutile transformation, and the principles of controlling phase composition through the inhibition or promotion of the transformation of anatase to rutile.

3.1.1. Titania polymorphs

Titanium dioxide, the only naturally occurring oxide of titanium at atmospheric pressure, exhibits three polymorphs: rutile, anatase, and brookite [1–7]. While rutile is the stable phase, both anatase and brookite are metastable; the latter is difficult to synthesise and so is seldom studied [8]. Another five high-pressure phases of TiO_2 have been reported:

- TiO_2 II or srilankite, an orthorhombic polymorph of the lead oxide structure
- Cubic fluorite-type polymorph
- Pyrite-type polymorph
- Monoclinic baddeleyite-type polymorph
- Cotunnite-type polymorph

The stability of these phases has been discussed in several publications [4, 7, 9–12]. However, these are of minor significance for research and development applications.

3.1.2. Titania properties

Table 3.1 outlines the basic properties of rutile and anatase.

Table 3.1. Properties of anatase and rutile.

Property	Anatase	Rutile	Reference
Crystal structure	Tetragonal	Tetragonal	[13]
Atoms per unit cell (Z)	4	2	[14, 15]
Space group	$I \frac{4}{a} md$	$P \frac{4_2}{m} nm$	[14, 16]
Lattice parameters (nm)	$a = 0.3785$ $c = 0.9514$	$a = 0.4594$ $c = 0.29589$	[14, 15]
Unit cell volume (nm ³)*	0.1363	0.0624	
Density (kg.m ⁻³)	3894	4250	[14, 15]
Calculated indirect band gap (eV) (nm)	3.23–3.59 345.4 – 383.9	3.02–3.24 382.7 – 410.1	[8, 17–20]
Experimental band gap (eV) (nm)	~3.2 ~387	~3.0 ~413	[8, 19, 21]
Refractive index	2.54, 2.49	2.79, 2.903	[13, 22]
Solubility in HF	Soluble	Insoluble	[23]
Solubility in H ₂ O	Insoluble	Insoluble	[13]
Hardness (Mohs)	5.5 – 6	6 – 6.5	[24]
Bulk modulus (GPa)	183	206	[20]

*Since the numbers of atoms per unit cell is halved upon going from rutile to anatase, the lattice parameters and unit cell volumes must be viewed accordingly.

3.1.3. Titania applications

The primary application of titanium dioxide is as a white pigment in paints, food colouring, cosmetics, toothpastes, polymers, and other instances in which white colouration is desired [13]. The reason for this is the high refractive indices of rutile and anatase, which result in high reflectivity from the surfaces. Consequently, titanias of small particle size and correspondingly high surface areas are used owing to the resultant opacifying power and brightness. However, paints utilise polymeric binders to fix the pigment and, when in contact with titania, the polymer may oxidise when exposed to sunlight. This effect is known as *chalking* and, in addition to the direct degrading effect of ultraviolet (UV) radiation, is accelerated by the photocatalytic activity of TiO₂, which also is enhanced by the high surface area of this material [25].

The potential for the application of the photocatalytic effect in TiO_2 has attracted considerable interest over the last three decades. Titania photocatalysts are known to be applicable in a range of important technological areas:

- **Energy**
 - Electrolysis of water to generate hydrogen [26–30]
 - Dye-sensitised solar cells (DSSCs) [31–33]
- **Environment**
 - Air purification [34, 35]
 - Water treatment [36–40]
- **Built Environment**
 - Self-cleaning coatings [34, 38, 39, 41–51]
 - Non-spotting glass [47, 52]
- **Biomedicine**
 - Self-sterilising coatings [53, 54]

3.1.4. Photocatalytic effect

Photocatalysed reactions for applications such as those mentioned above are facilitated through the presence of adsorbed radicals (from air or water) on the TiO_2 surface [28, 44, 45, 47, 49, 51, 55–57]. These radicals, which are atomic species with a free unpaired electron, are formed upon reaction of an adsorbed molecule (such as O_2 or H_2O) with a photo-generated charge carrier (from an electron-hole pair or *exciton*) when TiO_2 is exposed to radiation exceeding its band gap; this radiation normally is in the UV wavelength region (290–380 nm). These electron-hole pairs are formed when an electron is elevated from the valence to the conducting band, leaving behind an electron hole, as shown in Figure 3.1.

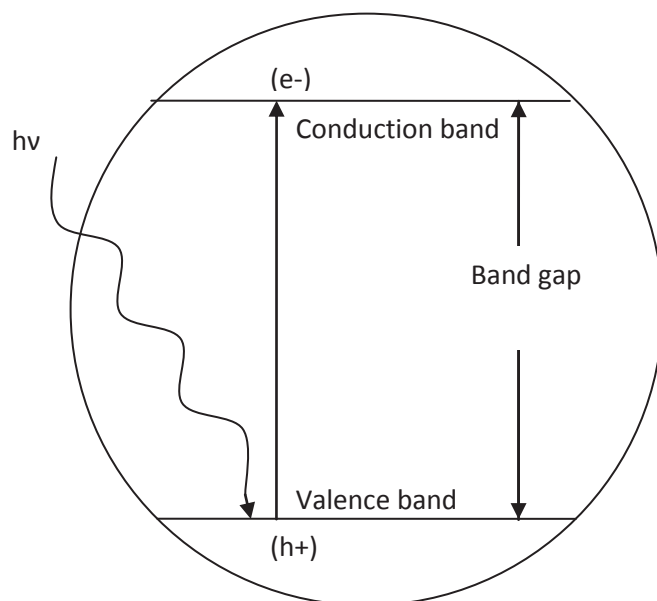


Fig. 3.1. Schematic illustration of photo-generation of charge carriers in a photocatalyst.

The electrons in the conduction band facilitate reduction of electron acceptors and the holes facilitate oxidation of electron donors [58]. Examples of the photo-generation of radicals in atmospheric and aqueous environments are given in the following reactions [28, 58–60]:



In this notation, an unpaired electron is represented by a point, a valence band electron hole is represented by h^+ , and a conduction band electron is represented by e^- .

These mechanisms have been described elsewhere in greater detail for the decomposition of organic pollutants, as shown in Fig 3.2, [38, 51, 57, 58, 61] and the splitting of water [26, 27, 29].

The generation of positive and negative charge carriers by UV radiation and their tendency to recombine are competing phenomena, the rates of which govern whether or not a semiconductor can function as a photocatalyst [62]. A key factor in titania's photocatalytic ability is its high surface area, the same property that contributes to its optical properties. A high surface area leads to a higher density of localised states, which involve electrons with energies between the conduction band and valence band [63]. These electrons are present owing to terminated and unsaturated bonds on the surfaces, and these localised states provide beneficial charge separation in the form of trapping sites for photo-generated charge carriers [64]. Titania has a relatively slow rate of charge carrier recombination in comparison with other semiconductors [65], which is an advantage since it has been suggested that a photo-generated electron-hole pair needs a lifetime of at least 0.1 nanosecond for chemical reactions to be facilitated [65, 66].

In the presence of reactive species adsorbed on the catalyst surface, photogenerated charge carriers may transfer to these adsorbates to form radicals rather than recombine [28]. Thus, an effective photocatalyst also is likely to have a high density of reactive adsorbed species for good performance to be achieved.

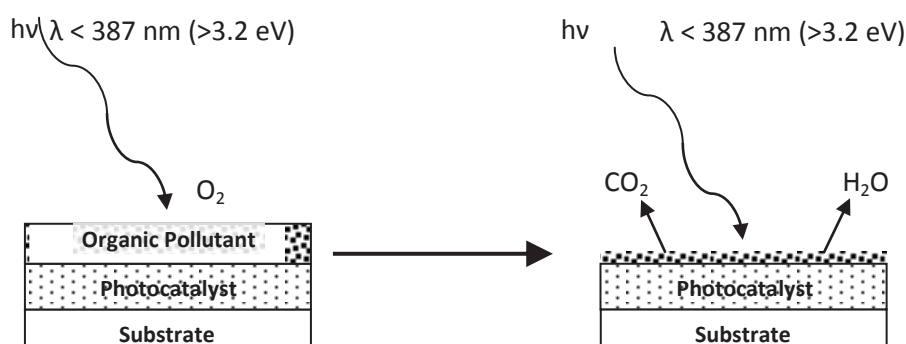


Fig. 3.2 schematic illustration of the photo-oxidation of an organic pollutant on a photocatalyst surface.

Despite the larger experimental band gap of anatase of ~ 3.2 eV, compared with ~ 3.0 eV for rutile [8, 67–69], the photocatalytic performance of anatase generally is considered superior to that of the more stable rutile. This is attributed to a higher density of localised states and consequent

surface-adsorbed hydroxyl radicals and slower charge carrier recombination in anatase relative to rutile [59, 61, 70–73], parameters that contribute to improved performance. The higher rate of electron-hole recombination in rutile is considered to result from this material's typically larger grain size [56, 74] and its resultant lower capacity to adsorb species [61, 75, 76].

It may be noted that, owing to the different crystal structures and associated exposed planes of the two polymorphs, anatase has been reported to have a lower surface enthalpy and lower surface free energy than rutile [77]. Hence, it would be expected that the wetting of anatase by water would be less than that of rutile since higher surface free energies generally contribute to hydrophilicity [78]. Since a high density of adsorbed species would be expected from a hydrophilic material, rutile could be anticipated to exhibit superior photocatalytic performance. It may be noted that there are no reports of rutile's exhibiting higher levels of adsorbed species.

The photoactivity of anatase and rutile have been examined and interpreted by Scalfani and Herrmann [59] with reference to the densities of surface-adsorbed species. This study showed that higher levels of radicals adsorbed on the anatase surface gives rise to significantly higher photoactivity than rutile. This result was reported to be due to a higher surface area as well as a higher photoactivity per unit of surface area. A similar result was found by Augustynski [72], who reported that surface-bonded peroxy species on anatase were absent from rutile surfaces.

In contrast to the widely reported photocatalytic superiority of anatase, several publications have suggested that, in some cases, rutile may be advantageous for certain applications [23, 25, 79–81]. These studies involved high-surface-area rutile of acicular morphology [25], rutile containing residual anatase [79], and iron-doped rutile [82]. It is possible that electron transfer between rutile and a residual quantity of anatase [79] may facilitate improved photo-oxidative reactions, as in mixed-phase titania catalysts. Therefore, in light of importance of surface area, morphology, and doping, an understanding of the titania polymorphs, their transformation, and the methods

by which they can be controlled are likely to be critical to achieving phase-optimised photocatalytic performance.

3.2. Titania

3.2.1. Phase formation during synthesis of TiO_2

In the synthesis of TiO_2 films by various methods, the initial crystalline TiO_2 phase formed is generally anatase [83, 84]. From a structural perspective, this could be due to the greater ease of the short-range ordered TiO_6 octahedra in arranging into long-range ordered anatase structure owing to the less-constrained molecular construction of anatase relative to rutile [85]. Alternatively, from a thermodynamic perspective, the more rapid recrystallisation of anatase could be due to the lower surface free energy of this polymorph, despite the lower Gibbs free energy of rutile [6, 77]. That is, the higher surface free energy of rutile crystallites may favour the crystallisation of anatase.

Table 3.2. Common Synthesis Methods of Titanium Dioxide and Resultant Phases.

Synthesis Method	Mechanism	Phases Formed				References
		Amorphous	Anatase	Rutile	Anatase + Rutile	
Room temperature hydrolysis of TiCl_4	Precipitation from room temperature solutions of TiCl_4					[86, 87]
Room temperature sol-gel synthesis	Hydrolysis of TiCl_4 or an organo-metallic compound					[88–91]
Flame pyrolysis of TiCl_4	Combustion of TiCl_4 with oxygen; used in industrial					[92–94]

	processes					
Solvothermal/hydrothermal	Precipitation of TiO ₂ from aqueous or organic solution at elevated temperatures					[67, 85, 95–100]
Chemical vapour deposition	Spraying of Ti-bearing solution					[101, 102]
Physical vapour deposition	Deposition of evaporated Ti and its subsequent oxidation					[21, 103]

It should be noted that it is possible to form rutile under near room temperature conditions [55, 84, 104, 105]. Hydrothermal methods of synthesis, which can facilitate the precipitation of crystalline TiO₂ directly from a liquid phase, can be controlled to precipitate rutile. Aside from this method, rutile is obtained only through high-temperature treatment.

3.2.2. Anatase to rutile transformation

Control of the conditions that affect the kinetics to control the anatase to rutile phase transformation is of considerable interest. This is particularly the case for high-temperature processes and applications, such as gas sensors and porous gas separation membranes [106–108], where the phase transformation may occur, thereby altering the properties and performance of these devices. Therefore, an understanding of the stabilities of the TiO₂ polymorphs, the kinetics of their phase transformation, and the processes involved in controlling them is essential to the ability to obtain single-phase or multiphase microstructures. These issues are critical to the long-term consistency of devices, where retention of anatase or a multiphase microstructure may not be possible, thereby potentially requiring processing designed to produce single-phase rutile. Similarly, limitations in temperature while desiring a specific polymorph, such as rutile, may require manipulation of the materials and processing conditions so as to enhance the direction formation of rutile.

As shown in Table 3.2, the generation of the phases of TiO_2 depends significantly on the synthesis parameters, which in turn affect the product. The kinetics of these processes typically are considered in terms of temperature and time. In terms of the former, pure bulk anatase is considered widely to begin to transform irreversibly to rutile in air at $\sim 600^\circ\text{C}$ [6, 67, 100] however, the reported transition temperatures vary in the range $400^\circ\text{--}1200^\circ\text{C}$ [42, 67, 109–113] owing to the use of different methods of determining the transition temperatures, raw materials, and processing methods. The anatase to rutile transformation is not instantaneous; it is time-dependent because it is reconstructive [2, 110, 114]. Consequently, the kinetics of the phase transformation must be interpreted in terms of all of the factors that influence the requisite temperature-time conditions. These parameters for undoped anatase are:

- Particle size
- Particle shape (aspect ratio)
- Surface area
- Atmosphere
- Volume of sample
- Nature of sample container
- Heating rate
- Soaking time
- Impurities (from raw materials and container)
- Measurement technique

The anatase to rutile transition, sometimes referred to as the *ART*, is a nucleation and growth process [107, 110]. As mentioned, the kinetics of this transition are dependent on variables such as impurities, morphology, sample preparation method, heat flow conditions, *etc.* In the absence of impurities, dopants, secondary phases, or other types of contamination, rutile forms as fine laths with the product phase's (100) planes parallel to the (112) planes of the parent anatase [107, 112, 115]. In pure anatase, rutile may nucleate at (112) twin interfaces in anatase [107, 115] as these sites are structurally similar to rutile.

Both anatase, space group $I4_1/amd$, and rutile, space group $P4_2/mnm$, are tetragonal in structure. Both crystal structures consist of TiO_6 octahedra, sharing four edges in anatase and two in rutile [8, 9, 70, 116, 117]. These structures are illustrated in Figs 3.3 and 3.4.

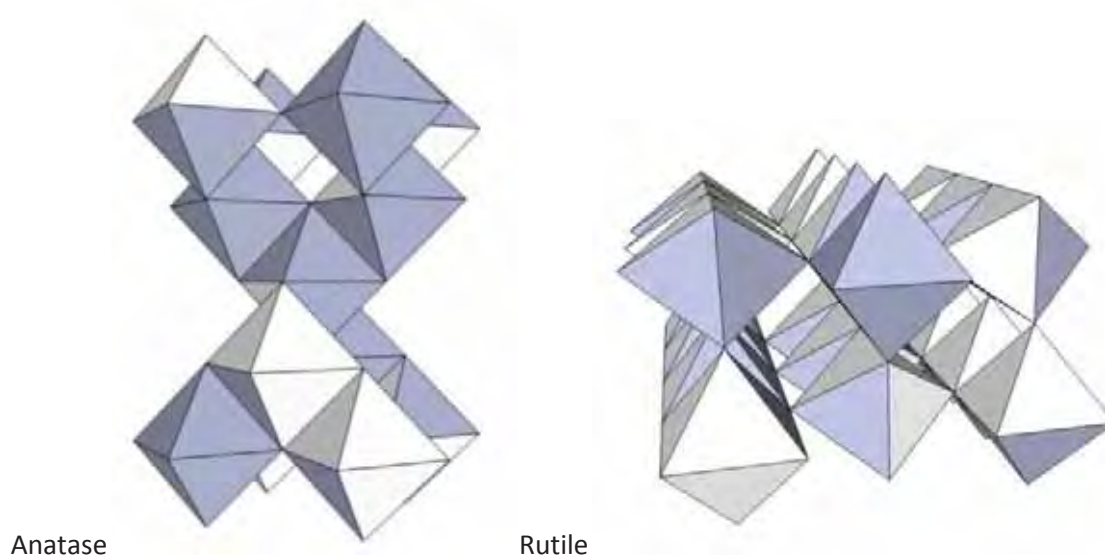
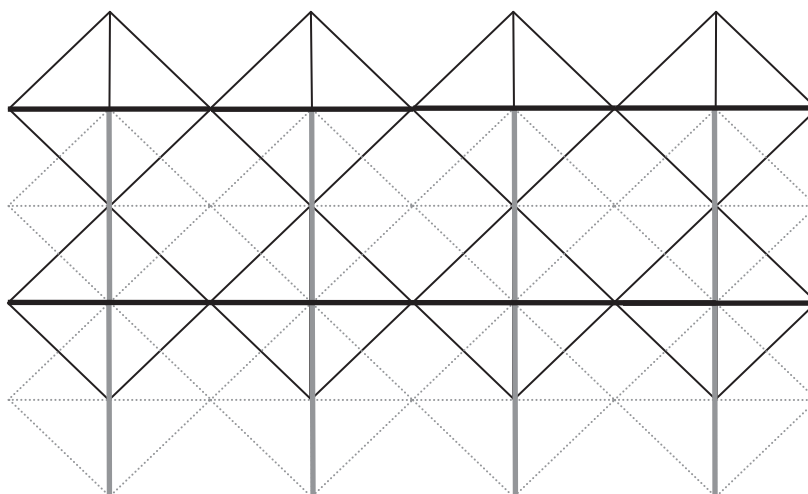


Fig. 3.3 Three-dimensional representation of the arrangement of TiO_6 octahedra in anatase and rutile showing 4 edge sharing connectivity in anatase and 2 edge sharing connectivity in rutile.

Anatase



Rutile

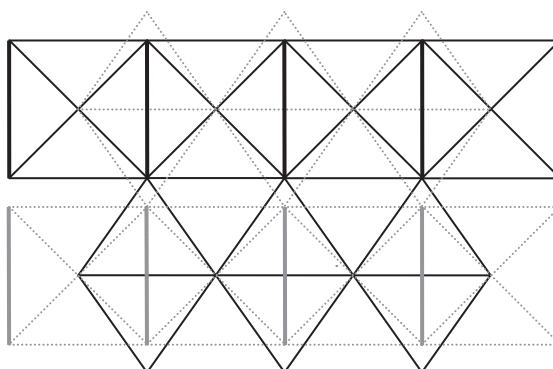


Fig. 3.4 Two-dimensional projection, down the c -axis, of the TiO_6 octahedra in anatase and rutile; shared edges in bold lines.

The anatase to rutile transformation is reconstructive, which means that the transformation involves the breaking and reforming of bonds [118]. This is in contrast to a displacive transformation, in which the original bonds are distorted but retained. The reconstructive anatase to rutile transformation involves a contraction of the *c*-axis and an overall volume contraction of ~8% [110, 119, 120]. This volume contraction explains the higher density of rutile relative to anatase. In the course of the transition to rutile, the (112) planes in anatase are retained as the (100) planes in the rutile product [68, 116]. The *c*-axis of anatase appears to be significantly longer than that of rutile only because anatase has more atoms per unit cell than rutile.

3.2.3. Phase differentiation and quantification of anatase/ rutile ratio

3.2.3.1. X-Ray Diffraction

Examination of the kinetics of the anatase to rutile phase transformation may involve assessment of the relative quantities of anatase and rutile following heating in specific conditions of heating rate, soak temperature, and soak time in order to examine the effects of parameters such as dopants, particle size, and atmosphere on the resultant phase assemblage.

Quantification of phase proportions usually is carried out by X-ray diffraction (XRD) [1, 79, 82, 106, 121–126]. Such analyses often are done using the method of Spurr and Myers [127], which utilises the ratio of the rutile (110) peak at 27.355° 2θ to the anatase (101) peak at 25.176° 2θ. The ratio of the intensities of these peaks, I_R/I_A , is used in the empirically determined formula in **equation 3.5** to give the weight fractions of anatase and rutile:

$$\frac{W_R}{W_A} = 1.22 \frac{I_R}{I_A} - 0.028 \quad (3.5)$$

Despite the number of the above researchers who have utilised this formula in their investigations into the ART, consideration of the relevant issues reveals a number of factors that may affect the accuracy of the results:

- **Preferred orientation:** Rutile and/or anatase crystallites may be present in preferred orientation owing to morphological and/or sample preparation effects, which may lead to altered XRD relative peak intensities.
- **Encapsulation:** Rutile crystallites may grow as an overlayer of rutile on anatase particles [81] or, alternatively, rutile may form in the bulk of the anatase grains, leaving a surface layer of anatase on rutile particles [113], thereby compromising the basis for the intensities of the XRD peaks.
- **Lattice distortion:** The presence of dissolved dopants and/or impurities, especially if differential solubility occurs, may alter the peak heights and areas, thereby altering the relative intensities of the XRD peaks.
- **Degree of crystallinity:** The presence of dopants may increase (nucleation) or decrease (lattice distortion/stress) the degree of crystallinity, which would alter the consequent peak intensities, particularly if these dopants are preferentially present in one of the phases.
- **Grain size:** The transition to rutile is accompanied by significant grain growth [128, 129], resulting in large rutile grains and small anatase grains, which would alter the ratios of XRD peak intensities.
- **Morphology:** Rutile may form in an acicular morphology, which would alter the XRD peak intensities of these grains relative to typically equiaxed rutile [130].
- **Surface nucleation of rutile:** Enhanced surface nucleation of rutile owing to heat (thermal gradients) and segregation (chemical gradients) effects would increase the XRD peak intensities of this phase; this would be similar to encapsulation.

Thus, it is important to consider that the validity of the data resulting from equation 3.5. depends on adequate assessment of the preceding parameters and the application of materials and processes designed to achieve samples of representative chemistry, mineralogy, and microstructure. If these cannot be attained, alternative materials, fabrication methods, and analytical techniques may be required.

3.2.3.2. *Laser Raman microspectroscopy*

Laser Raman microspectroscopy also has been employed effectively to differentiate the anatase and rutile [25, 81, 125, 131–134]. The titania polymorphs exhibit distinct Raman spectra that can be used for qualitative and quantitative mineralogical analysis. Laser Raman microspectroscopy has been applied quantitatively for on-line process control in the manufacture of titania powder by Huntsman Tioxide, Inc. [135].

Laser Raman microspectroscopy has several advantages:

- Minimal or no sample preparation
- Nondestructive
- Local and general phase analyses ($\leq 1 \mu\text{m}$ beam diameter)
- Mapping capability
- Rapid analyses (~ 1 min scan)
- No preferred orientation effect
- Greater sensitivity than XRD
- Sensitive to nanoscale phases

Figure 3.5 contrasts experimental scans of identical samples of rutile and anatase TiO_2 by XRD and laser Raman microspectroscopy carried out by the authors and confirmed by comparison with reference patterns and spectra [136–138].

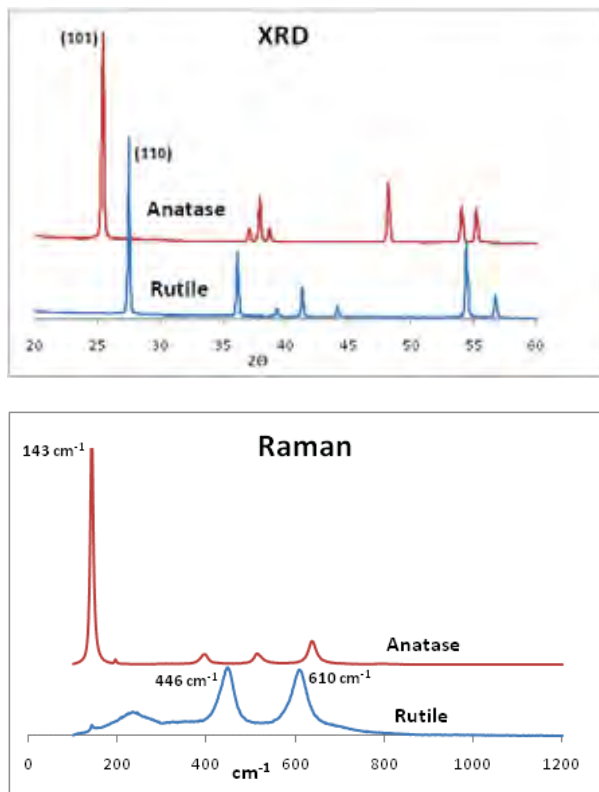


Fig. 3.5 XRD patterns and laser Raman spectra of rutile and anatase powders [130].

The main strength with laser Raman microspectroscopy is its applicability to nanoscale thin films. When glancing-angle XRD is used, the instrument requires considerable calibration, the peaks are very diffuse, and the background is such that any amorphous phase, if present, cannot be ascertained. With laser Raman microspectroscopy, none of these problems are experienced, so the analyses are more efficient and more sensitive.

3.2.3.3. *Differential solubility*

A more direct method of measuring the rutile/anatase proportions was employed by Ohno *et al.* [23, 79, 139]. This method involved using hydrofluoric acid (HF) to dissolve the anatase phase, leaving the rutile phase intact. This method has the disadvantages of health risk, potential loss of material during washing, loss of anatase, and potential for slight solubility of rutile. However, this

method could be useful for the removal of trace levels of anatase in order to enhance the purity of rutile powders.

3.2.3.4. *Impedance spectroscopy*

Another method of measurement was employed by Suresh *et al.* [140], who applied impedance spectroscopy to examine the anatase to rutile transformation. Since this method relies on the difference in resistivity between the two phases, it suffers two innate uncertainties associated with electrical resistivity measurement. First, the resistivity is a function of the grain connectivity, which is a microstructural factor rather than a mineralogical one. Second, dopants and impurities have a profound influence on the electrical properties, so their presence inevitably would affect the resistivities in a differential manner. Despite these reservations, this method has been used in conjunction with XRD and differential thermal analysis (DTA) to ascertain the effect of doping with silica [141].

In general, the XRD method of phase analysis is the most generally used for bulk qualitative and quantitative analyses (using equation 3.5). Experimental calibration has demonstrated that, despite a number of potential flaws in the quantitative method of XRD phase analysis of titania, this method gives reasonably accurate and consistent results [130].

3.2.4. Rutile-anatase mixtures

Mixed-phase photocatalysts with rutile-anatase compositions have been reported to exhibit enhanced photoactivity relative to single-phase titania [23, 34, 55, 56, 69, 74, 81, 111, 113, 126,

131, 132, 142–147]. It is considered widely that this is a result of improved charge carrier separation, possibly through the trapping of electrons in rutile and the consequent reduction in electron-hole recombination [79, 118, 148]. Surface trapping of holes together with lattice trapping of electrons also has been reported [79, 126]. In consequence, Degussa P-25 is marketed as a mixed-phase titania photocatalyst and it is utilised as a reference material in many studies. It should be noted that the high performance observed for Degussa P-25 is reported to stem primarily from this material's high specific surface area [59]. This nanocrystalline material, formed by flame pyrolysis, consists of 80 wt% anatase and 20 wt% rutile. However, Bacsá and Kiwi [55] reported that a photocatalyst containing 70 wt% anatase and 30 wt% rutile, with a surface area of 72.0 m²/g exhibited greater photocatalytic performance than the Degussa P-25 reference, which has a specific surface area of 49.2 m²/g.

Since the particle size and surface area depend strongly on the preparation method, it would be misleading to interpret the photocatalytic performance solely in terms of the phase composition. As an example of the importance of the effect of the processing conditions on these parameters, variations in grain size, crystallite size, surface area, morphology, and phase distribution obtained during sol-gel synthesis have been observed to be highly dependent on the precursor solutes and solvents used [36, 46, 55], calcining temperatures [56, 111, 149, 150], and pH [55, 74, 84, 115, 140, 151].

Within a certain set of processing protocols, it is possible to obtain mixed-phase photocatalysts of nominally pure titania through variation of the kinetics (heating rate, soak time, and soak temperature). In such cases, a comprehensive understanding of the following effects must be in place:

- Time
- Temperature
- Atmosphere
- Intrinsic chemical composition (purity of raw materials)

- Extrinsic contamination (from processing)
- Chemical homogeneity (*e.g.*, segregation)
- Microstructural homogeneity (*e.g.*, grain boundary precipitates)
- Thermal homogeneity during heating (*e.g.*, resulting from sample size and shape)
- Mineralogical phase assemblage
- Particle size distribution
- Agglomerate size distribution
- Grain morphology
- Agglomerate morphology

In contrast to the processing of nominally pure samples, mixed-phase titania of controlled rutile/anatase ratios also can be obtained by doping. However, doping inevitably affects the semiconducting properties of materials, which may be disadvantageous to the photocatalytic performance. Alternatively, as discussed subsequently, doping also may act advantageously through reduction in the band gap and improvement in the charge carrier separation and associated extended exciton lifetime [18, 69, 74, 152].

3.3. Thermodynamics and kinetics

3.3.1. Stability of the TiO₂ phases

At all temperatures (**Figure 3.6**) and pressures (**Figure 3.7**), rutile is more stable than anatase. This has been confirmed by thermodynamic studies [5, 9, 77, 149, 153], which show that negative pressures would be required for anatase to be more stable than rutile [2]. The transformation to rutile thus is irreversible.

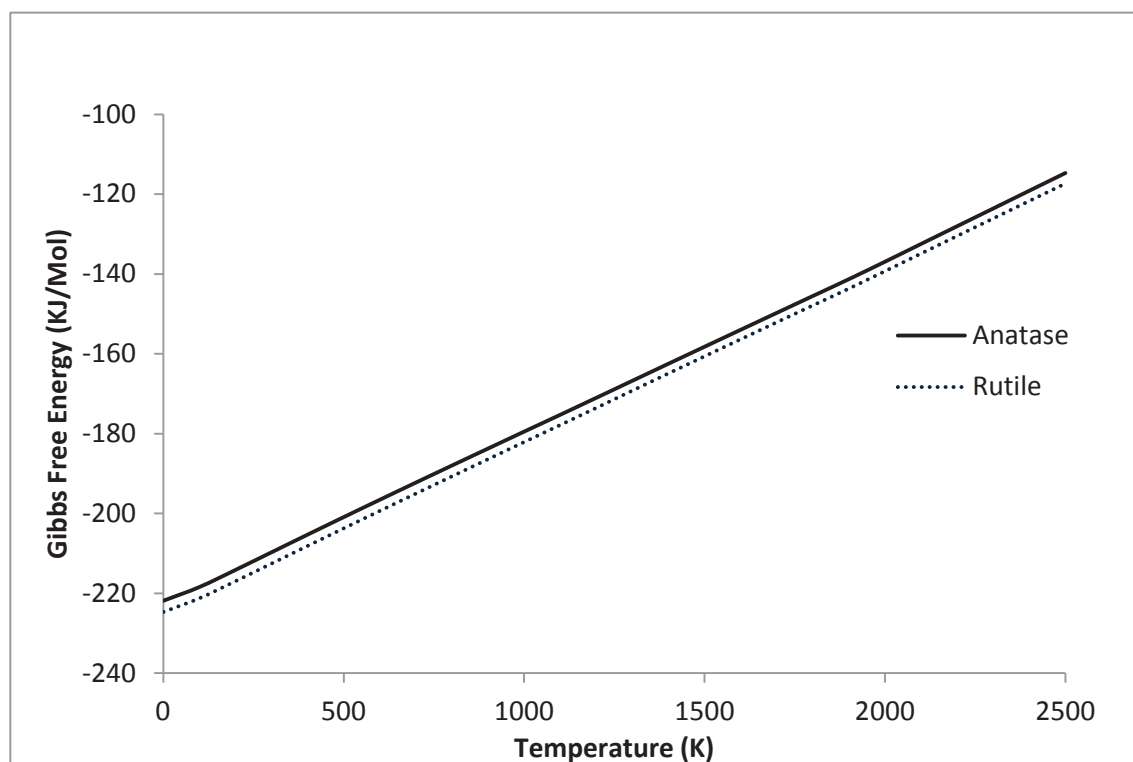


Fig. 3.6 Plot of Gibbs free energy of anatase and rutile versus temperature [154].

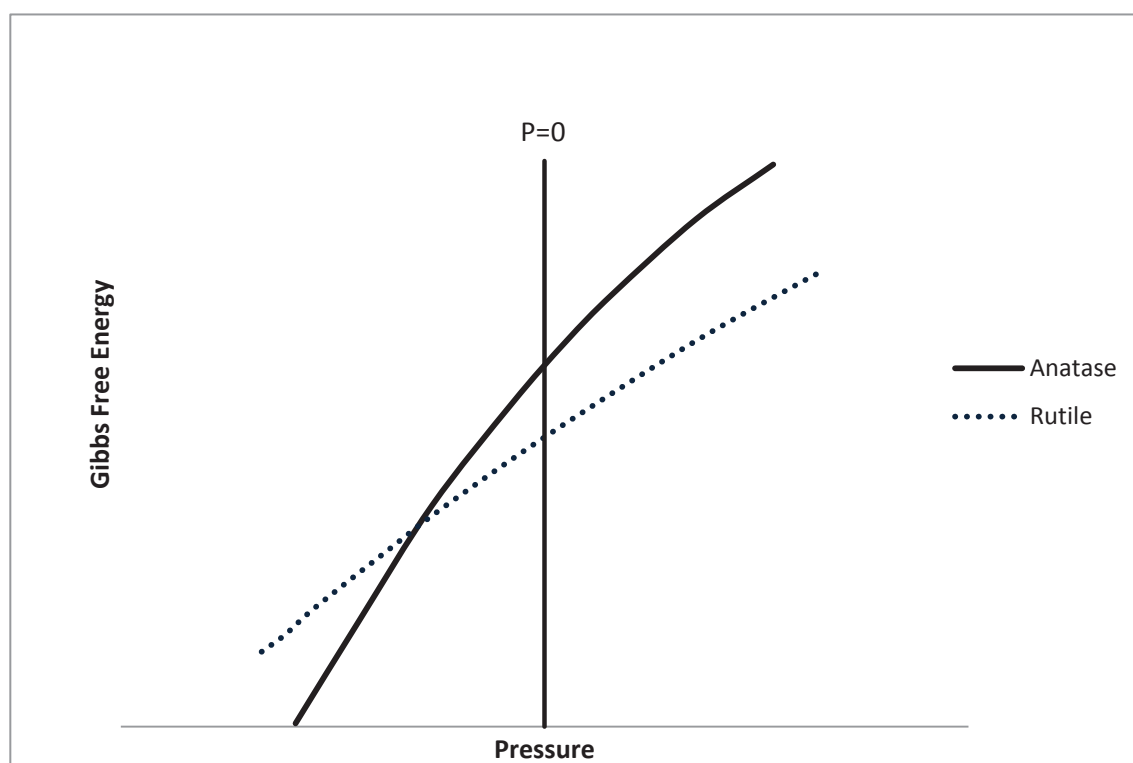


Fig. 3.7 Schematic plot of Gibbs free energy versus pressure (assumed to be at room temperature) [2].

Table 3.3 gives the reported standard-state thermodynamic data for the anatase to rutile phase transformation.

Table 3.3. Summary of thermodynamic data from literature.

Publication Year	ΔH_{298} (kJ/mol)	ΔS_{298} (J/mol.K)	ΔG_{298} (kJ/mol)	Reference
1967	-5.19	0.42	-5.32	[149]
1971	-11.7	0.42	-11.84	[154]
2009	-1.70	0.556	-1.87	[5]

These data indicate that there remains some uncertainty about the energetics of the phase transformation.

Over the last 50 years various studies involving the kinetics of the transition to rutile have reported various transition temperatures. A comprehensive survey of these reported temperatures is shown in Table 3.4.

Table 3.4. Summary of reported temperatures for the ART.

Year	Temp. (°C)*	Fabrication Details	Definition	Ref
1961	610	Highly pure powder	Onset temperature observed by XRD after firing for 24 hours	[114]
1965	(1190)	Powders from three different suppliers	Apices of DTA peaks (data not shown)	[110]
	(1138)			
	(1115)			
1968	610	Commercially available reagent grade powder	Onset temperature observed by XRD after extended firing (1–5 days)	[155]
1995	390	Sol-gel synthesised powder	Appearance of detectable rutile peak by XRD after 1 week	[124]
1996	675	Sol-gel synthesised powder	Appearance of detectable rutile peak by XRD after 4 minutes	[1]
1997	(787)	Sol-gel synthesised powder	Reported Value: Apex of DTA peak	[156]
	720		Corrected Value: Onset of DTA peak	
1997	465	4–6 nm particles prepared through a sol-gel method	Appearance of detectable rutile peak by XRD	[157]
1999	(616)	Sol-gel synthesised powder	Reported Value: 50% transformation observed by XRD	[158]
2001	(680)	Sol-gel synthesised powder	Reported Value: 50% transformation observed by XRD	[83]
	600		Onset temperature from graph	
2001	600	Sol-gel synthesised powder	Appearance of detectable rutile peak by	[109]

			XRD	
2002	(700)	Sol-gel synthesised powder	50% transformation observed by XRD	[125]
	600		Appearance of detectable rutile peak by XRD	
2005	600–700	Highly pure nanocrystals synthesised from TiCl_4 Sol-gel	Appearance of detectable rutile peak by XRD	[100]
2007	(900)	Sol-gel synthesised powder	Reported Value: Apex of broad DTA peak (data not shown)	[159]

*Data in parenthesis do not correspond to the onset of the transformation

Table 3.4 shows that there are different methods that be used to define the phase transformation temperature. As discussed previously, the temperature at which the transition is observed depends on a number of parameters and so it is not surprising that a range of values has been reported. However, assessment and consideration of these data lead to the general conclusion that fine powders of high purity show phase transformation temperatures at $\sim 600^\circ\text{--}700^\circ\text{C}$.

Excluding studies which used titania of unusually small particle size or long soak times, and studies which did not use onset temperatures as the defined transition temperatures, it can be seen that the reported transition onset temperatures, as determined by XRD, appear to converge around 600°C . Although it is difficult to ascertain the intrinsic behaviour of titania, this is accepted to be the region of the onset temperature of the anatase to rutile transformation in bulk pure anatase in air [2, 7, 124, 155]. This can be seen in **Fig 3.8**.

The one early study from 1965 [110] that reported anomalously high temperatures may have obtained these results owing to the use of powders contaminated with impurities that inhibit the phase transformation, as discussed subsequently, the use of the differential thermal analysis (DTA) peak apices rather than the onsets, and/or the use of very high heating rates.

The data in Table 3.4 suggest that DTA analysis yields higher transformation temperatures than XRD analysis. This probably is a result of the sigmoidal form of the kinetics curve, as shown subsequently. That is, the phase transformation commences slowly at an onset temperature of $\sim 600^\circ\text{C}$ and so it is more likely that the exotherm maximum (*viz.*, the apex) is observed later in the

phase transformation process, when the transformation rate is greatest; the rate of transformation subsequently decreases along with the corresponding latent heat as anatase converts to rutile. Despite the potential uncertainties, DTA peak apices can be considered to be applicable for *comparative* analysis of the phase transformation.

The assessment of DTA data must be done with care since the curves and their interpretation can be influenced significantly by experimental conditions that can cause shifts to lower temperatures: (1) a slow heating rate results in peak broadening, which lowers the onset temperature; (2) a slow heating rate also causes the entire peak to shift; (3) fine particle size shifts and narrows the entire peak; and (4) the static enclosed atmosphere induces a slightly reducing atmosphere, which enhances oxygen vacancy formation in oxides.

Rao [114] carefully examined the kinetics of the phase transformation, based on a soak of 24 h and XRD analysis, using very pure powders and fit the data to an Arrhenius relation. The rate of transformation decreased with temperature to a practical limit $610^{\circ} \pm 10^{\circ}\text{C}$, at which point the transformation became immeasurably slow. Despite the age of this study, it is consistent with later studies [155, 158, 160, 161].

Since rutile is the equilibrium phase [2, 7, 9, 20, 77, 114, 149, 153], the presence of anatase demonstrates that these studies cannot represent equilibrium conditions, which normally employ phase diagrams for illustration. Dachille *et al.* [155] reported what was considered to be an pressure-temperature diagram approximating equilibrium for TiO_2 , which is shown in **Fig. 3.8**. The key observation of these data is the apparent anatase to rutile phase transformation conditions of 605°C at 1 atm (101 kPa) pressure, which is quite similar to the values indicated in Table 3.4.

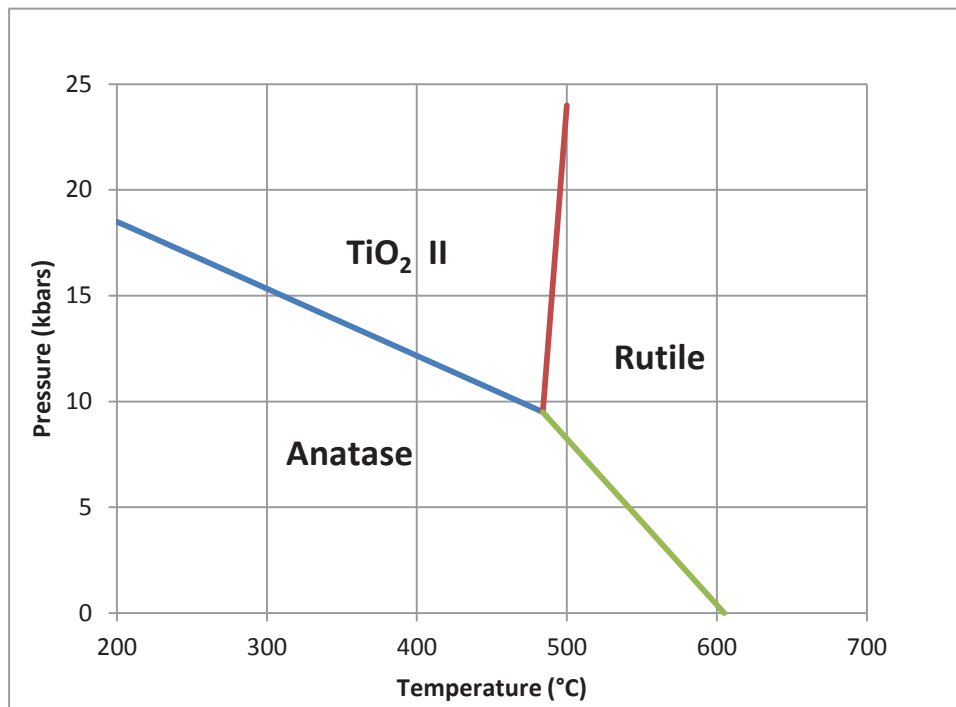


Fig. 3.8 Reaction boundaries of phase transitions in TiO₂ [2].

Jamieson and Olinger [2] subsequently qualified the description of this diagram by describing the phase boundaries as *reaction boundaries*. Current practice is to refer to functional diagrams such as these as *behavioural diagrams*.

Although it is widely accepted that rutile cannot be transformed to anatase. It has been suggested that at high pressures rutile can transform to the α -PbO₂ structured TiO₂ II polymorph [12, 162]. This behaviour is outlined by the inferred behavioural diagram shown in **Fig. 3.9**, which is derived from mineralogical samples exposed to high pressures in the earth's crust.

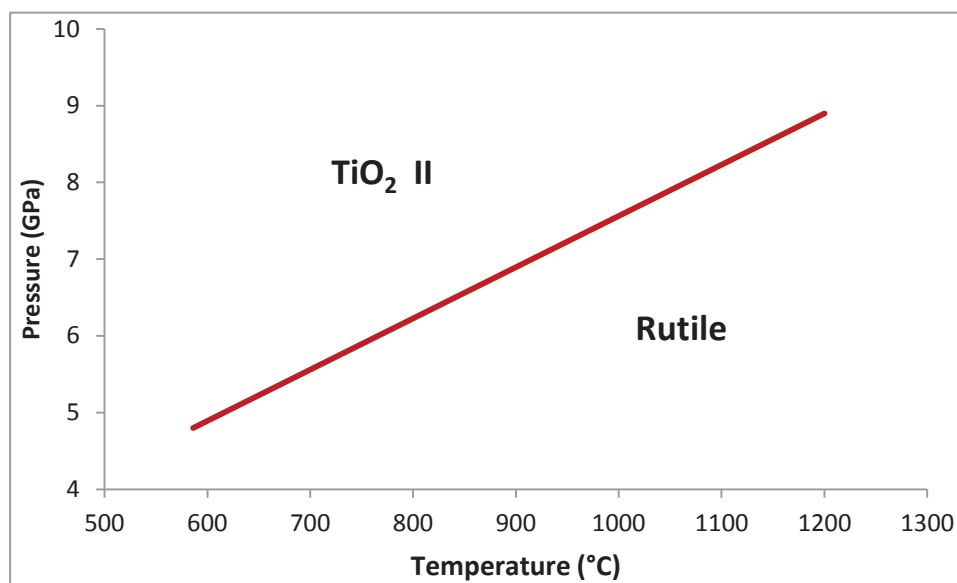


Fig. 3.9 Proposed behavioural diagram of the transformation of rutile to TiO_2 II [12, 162].

3.3.2. Kinetics of the Anatase to Rutile Phase Transformation

For the transformation of Anatase to Rutile to proceed at a measureable rate, sufficient thermal energy is required to facilitate the rearrangement of atoms. As described above, it is likely that, for typical bulk titania powders (*i.e.*, not nanoparticles), this energy requirement is reached at $\sim 600^\circ\text{--}700^\circ\text{C}$ in air in the absence of dopants or impurities, although this is subjective since impurities are always present at a finite level. As will be discussed in detail subsequently, the transformation can be enhanced or impeded by influencing the rearrangement of the atoms in the anatase and rutile lattices. It is perceived widely that the most important factor affecting the phase transformation is the presence and amount of defects on the oxygen sublattice, *viz.*, TiO_{2-x} [68, 158, 163, 164]. Ease of rearrangement and transformation are enhanced by relaxation (lessening of structural rigidity) of the large oxygen sublattice through the increased presence of oxygen vacancies [110, 165, 166].

This effect has been shown through firing in different atmospheres, as shown in Fig. 3.10, where neutral or reducing conditions of low oxygen partial pressure generally greatly enhance the anatase to rutile transformation [3, 68, 167], although contrary effects have been reported as vacuum conditions have been observed to slow the phase transformation[110]. This could be a result of reduced heat transfer because vacuum conditions give lower convective heat transfer than air. The promotion of the phase transformation through the use of a reducing atmosphere is considered to be due largely to the increased levels of oxygen vacancies during heating in such atmospheres.

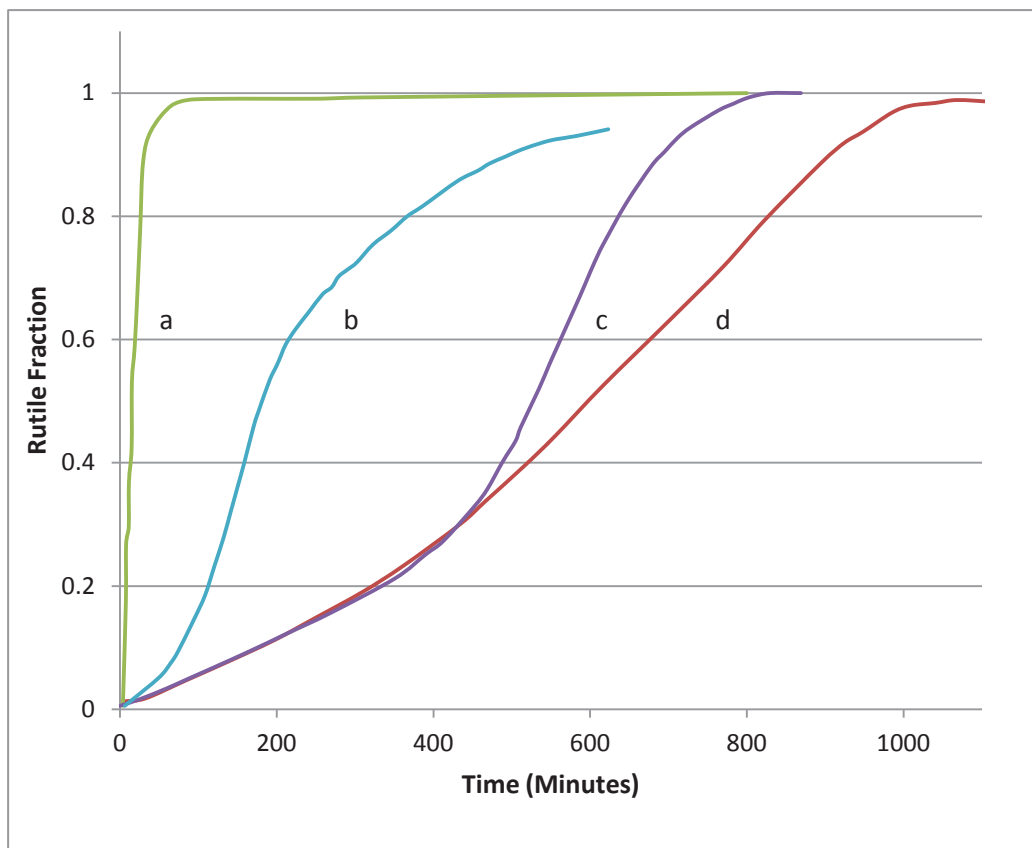


Fig. 3.10 Known time-transformation curves of various titania samples.

- a. Fe_2O_3 -doped titania fired in a reducing atmosphere at 1000°C [168]
- b. Undoped titania powder fired in air at 1050°C [110]
- c. MnO_2 -doped titania fired in air at 945°C [165]
- d. Undoped titania fired in air at 945°C [165]

Although these data are limited, the interpretations of the trends are straightforward:

- Sample a:** Doping with Fe_2O_3 (assuming substitution of Ti^{4+} by Fe^{3+}) in a reducing atmosphere can increase the levels of oxygen vacancies by three potential mechanisms: (1) the maintenance of charge balance; (2) spontaneous reduction Fe_2O_3 to Fe_3O_4 or FeO , which are thermodynamically stable at temperatures as low as 400°C and low oxygen partial pressures [169]; and (3) reduction of TiO_2 to TiO_{2-x} .
- Samples b & d:** Assuming that powders used in these two studies are similar, the only difference is the temperature. If this comparison is valid, then it is clear that the phase transformation is accelerated with the use of the higher temperature, which is as expected.
- Samples c & d:** Doping with MnO_2 , while suggesting that no effect on oxygen vacancy formation should be observed, actually is similar to Fe_2O_3 because Mn^{4+} reduces spontaneously in air to Mn^{3+} and then Mn^{2+} , with the transformation's near-completion by $\sim 450^\circ\text{C}$ [170]. Again, the assumption of substitution of Ti^{4+} by Mn^{3+} and Mn^{2+} requires the generation of oxygen vacancies.

3.4. Impurities and dopants

3.4.1. Dopant effects

Many studies of photocatalysis by TiO_2 have attempted to utilise dopants in order to improve the photocatalytic activity. In general, the role of dopants is considered to be:

- Reduction of the band gap in titania [18, 152]
- Introduction of mid-gap states [57, 171]
- Improvement in charge carrier separation [69, 74]
- Increase in the levels of surface-adsorbed species (*e.g.*, hydroxyl radicals) [43]

It often is not appreciated that all titania is contaminated with some levels of impurities. The presence of unintentional impurities or intentional dopants has a strong effect on the kinetics of the anatase to rutile transition [172]. Variable results have been reported in the sense that dopants can have the effect of *hindering* or *enhancing* the transition to rutile. In the case of substitutional solid solution formation, dopant ions can enter the anatase lattice and influence the level of oxygen vacancies, thereby promoting or inhibiting the transformation to rutile. In the case of interstitial solid solution formation, lattice constraint may result in destabilisation or

stabilisation, depending on size, valence, and content effects, again promoting or inhibiting the transformation. If the solubility limit for impurities or dopants is exceeded, then their precipitation can facilitate the phase transformation through heterogeneous nucleation [68, 173].

3.4.1.1. Cationic dopants

Numerous cationic dopants have been investigated in terms of their effect on the kinetics of the anatase to rutile transition. It has been suggested that cations of small radii and low valence accelerate the transition to rutile owing to the increase in oxygen vacancies that result from the assumed substitution of Ti^{4+} ions with cations of lower valences [43, 110, 158, 165, 166]. Charge neutrality thus requires an increase in the level of oxygen vacancies and/or the formation of Ti interstitials of lower valence [83, 174]. Conversely, when cations of valence higher than 4 are assumed to substitute for Ti ions on the anatase lattice, this gives rise to the annihilation of existing oxygen vacancies and the formation of Ti interstitials of the same or lower valence. These processes can be viewed in light of the inertia to alteration (through ionic transport) of the relatively large and rigid oxygen sublattice, which largely determines the structural stability and the capacity to reorganise the chemical bonds to form rutile. From these considerations, the assumption of substitutional solid solubility leads to the conclusion that small cations of low valence (<4) should promote the anatase to rutile transformation and large cations of high valence (>4) should inhibit it.

However, the assumption of substitutional solid solubility may be incorrect and interstitial solid solubility occurs. In this case, the insertion of a cation results in constraint of the required lattice contraction largely in the c direction upon the transformation from anatase to rutile [175], without apparent effect on the charge neutrality. Although there are reports of interstitial stabilisation of the titania lattice and consequent inhibition of the transformation [156, 176, 177],

there do not appear to be any reports of destabilisation (from structural instability) and consequent promotion of the transformation.

A comprehensive summary of the cationic dopant effects from the literature sources is given in

Table 3.5:

Table 3.5. List of dopants in titania.

Phase Transformation Inhibitors	
<i>Cation</i>	<i>Dopant Phases Used</i>
Al	AlOOH [178], Al(OC ₄ H ₉) ₃ [109], AlCl ₃ [120, 179], Al(NO ₃) ₃ [177]
Au	HAuCl ₄ [180]
B	BCl ₃ [121]
Ba	Ba(NO ₃) ₂ [158]
Ca	Ca(NO ₃) [158]
Ce	CeO ₂ [181]
Dy	Dy ₂ O ₃ [182]
Eu	EuCl ₃ [71] Eu ₂ O ₃ [57]
Er	Er(NO ₃) ₃ [158], Er ₂ O ₃ [183]
Fe	FeCl ₂ [173]
Ho	Ho ₂ O ₃ [183]
La	La(NO ₃) ₃ [158, 184], La ₂ O ₃ [183]
Mn	Mn(NO ₃) ₂ [185], <1 mol% Mn(CH ₃ COO) ₂ [186]
Nb	NbCl ₅ [187]
Nd	Nd ₂ O ₃ [183]
P	PO ₄ H ₂ K [119], POCl ₃ [121]
Si	Si(OC ₂ H ₅) ₄ [83, 109, 129, 177], SiCl ₄ (g) [121]
Sm	SmCl ₃ [71], Sm ₂ O ₃ [183]
Sr	Sr(NO ₃) ₂ [158]
Tb	Tb ₄ O ₇ [183]
Tm	Tm ₂ O ₃ [183]
Y	Y(NO ₃) ₃ [158], Y ₂ O ₃ [183]
Zr	Zr(OC ₃ H ₇) ₄ [109, 188], Zr(SO ₄) ₂ [67], ZrOCl ₂ [88]

Phase Transformation Promoters	
<i>Cation</i>	<i>Dopant Phases Used</i>
Al	AlCl ₃ (g) [189]
Cd	CdO [166]
Co	CoO [166]

Cr	CrCl ₃ [187]
Cu	CuO [110, 128, 165]
Fe	Fe [41], Fe ₂ O ₃ [128, 165, 168]
Li	LiF [119]
Mn	MnO ₂ [165, 166], Mn(NO ₃) ₂ [185, 190], MnSO ₄ [68]
Na	NaF [166]
Ni	Ni(NO ₃) ₂ [129] Ni(CH ₃ COO) ₂ [191]
Sb	Sb ₂ O ₃ [192]
Sn	SnO ₂ [159], SnCl ₂ [150]
V	VO ₂ [129], V ₂ O ₅ [193]
Zn	ZnO [166]

The effects of the dopant cations in terms of the valences and ionic radii are illustrated in **Fig. 3.11**. These data have been compiled on the basis of the following conditions:

- Shannon-Prewitt ionic radii in sixfold coordination [175], which is the case for both anatase and rutile [14], were used.
- The most common valence for each cation has been used, without regard to oxidation-reduction effects (except as noted below).
- The valences for Mn, Fe, and Co are assumed to be 2 as these species would be likely to reduce spontaneously to show this valence state upon heating at temperatures approaching the ART temperature [168, 170, 194].
- Inhibition or promotion of the phase transformation is reported on the basis of the effects described in the literature sources given in Table 3.5.
- In the case of cations for which contradictory effects are reported (Mn and Fe), the most common finding was used.

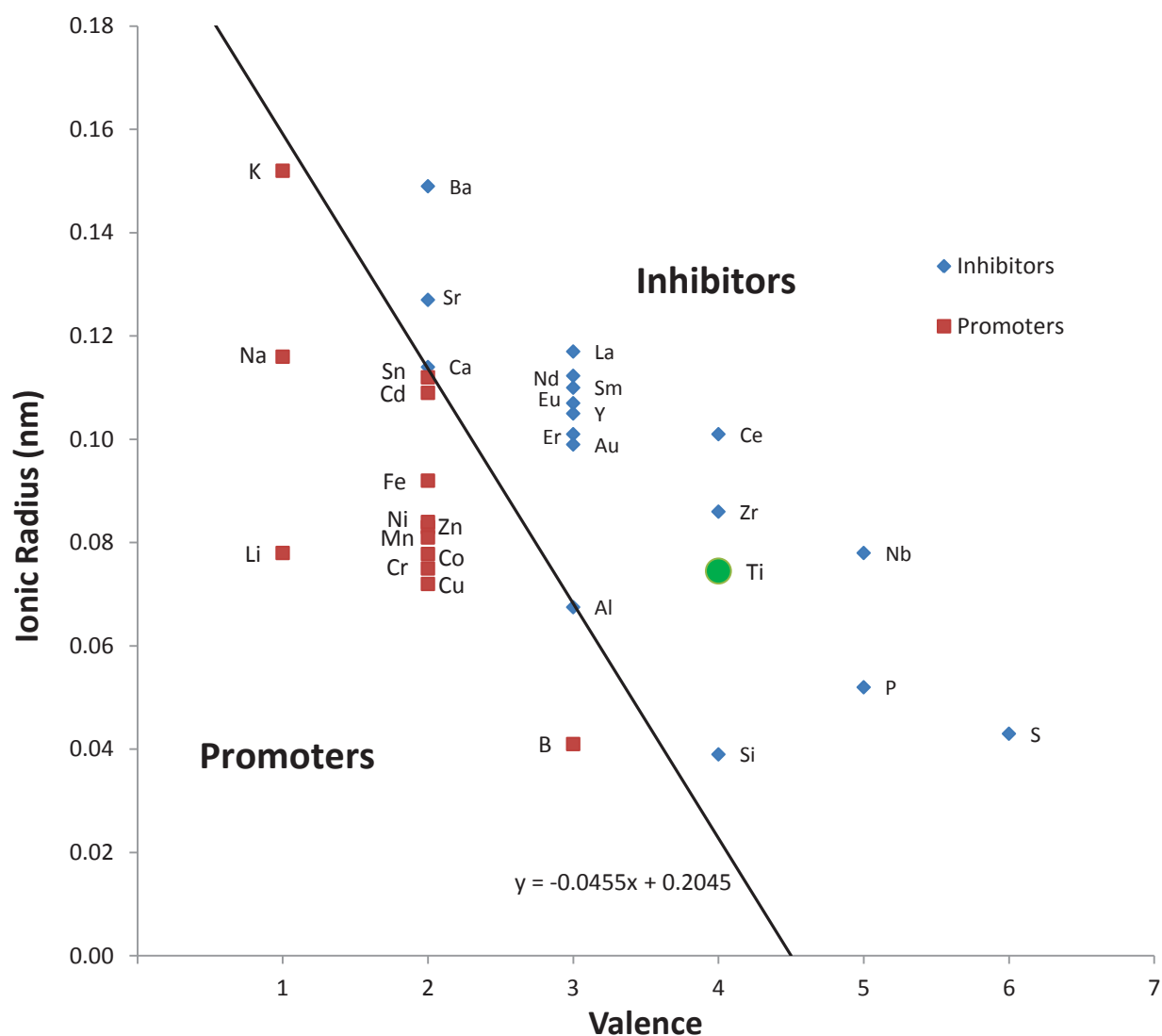


Fig. 3.11 Comprehensive valence/radius plot of anatase to rutile transformation, categorising inhibiting and promoting dopants, based on the published reports in Table 3.5.

The formula of the boundary line is:

$$y = -0.0455x + 0.2045 \quad (3.6)$$

where x = valence and y = ionic radius.

The data shown in Figure 3.11 should be considered indicative owing to the potential presence of impurities, the vagaries in the reported experimental procedures, and the assumptions stated above. For example, in 1960, Iida and Ozaki [128] reported findings which contrary to those of many other studies in that sodium was observed to inhibit the transformation. This seems likely to be due to the use of sodium in the form of a salt which only decomposed at 900°C.

3.4.1.2. Anionic dopants

Anions doping is of interest owing to its potential to improve the photocatalytic performance of TiO_2 [18]. There is limited discussion in the literature regarding the effects of foreign anions on the anatase to rutile transformation, probably owing to the uncertainty of whether doping actually occurs. It is reasonable to assume that doping by anions results in the filling of oxygen vacancies. The inhibition or promotion of the phase transformation is likely to depend on size and charge effects, which are as follows:

$$\text{Cl}^{1-} > \text{N}^{3-} > \text{O}^{2-} > \text{F}^{1-}$$

Nitrogen doping

Size Effects: According to Hume-Rothery [195], metal ion dopants whose ionic radii are within 15% of that of the host lattice, which typically is closest packed, can show appreciable solubility. It is assumed that the oxygen sublattice, which also is closest packing, can be considered similar to that of most metals. Unfortunately, the only comparable ionic radii for the two anions are for fourfold coordination [S-P], but the ionic radii of anions vary little across the different negative valences. Since nitrogen is only ~6% larger than oxygen, then substitution of nitrogen on the oxygen sublattice is possible. Hence, nitrogen is unlikely to destabilise the lattice and so would be expected to be an inhibitor of the phase transformation.

Charge Effects: If N^{3-} substitutes for O^{2-} , then the impossibility of establishing charge balance through the formation of Ti^{5+} means that oxygen must be removed from the lattice. Since the inclusion of two nitrogen ions is balanced by the removal of three oxygen ions, then the level of oxygen vacancies increases, the lattice can be expected to be destabilised, and the phase transformation is promoted. Accordingly, it has been reported that nitrogen doping increases the level of oxygen vacancies in anatase [118, 163] although there do not appear to be any reports on

the effect of chemical nitrogen (rather than physical nitrogen, as in the furnace atmosphere) on the phase transformation.

Fluorine doping

Size Effects: Fluorine in both fourfold and sixfold coordinations is ~6% smaller than oxygen, then fluorine replacement on the oxygen sublattice is possible. Hence, fluorine would be expected to be an inhibitor.

Charge Effects: If F^{1-} substitutes for O^{2-} , then anion charge balance requires the inclusion of two fluorine ions for each oxygen. This is extremely unlikely from size considerations. The other alternative is the inclusion of one fluorine ion in an oxygen vacancy site and the resultant reduction of the associated Ti^{4+} or Ti^{3+} , which would remain on the cation sublattice; the insertion of fluorine would decrease the level of oxygen vacancies. Further, the expansion of the titanium ionic radius upon reduction [s-p] would cause lattice constraint. Both of these mechanisms would be expected to inhibit the phase transformation. In agreement, fluorine has been reported to inhibit the phase transformation [65, 91].

The annihilation of an oxygen vacancy by fluorine doping is described by **equation 3.7**:



Here, $\square a$ denotes an anion vacancy.

Chlorine doping

Size Effects: Chlorine in sixfold coordination is ~33% larger than oxygen. Hence, it is very unlikely to enter (solid state) or be retained in (solution) the titania lattice .

Charge Effects: In light of the above, the inclusion of two chlorine ions for one oxygen ion is extremely unlikely. For the same reason, inclusion of one chlorine and titanium reduction also is unlikely. The preceding being said, chlorine has been reported to inhibit the phase

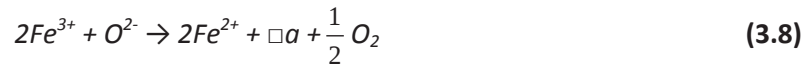
transformation [65, 91]. Conversely, atmospheric chlorine also has been reported to promote the phase transformation [3]

3.4.2. Valence changes

An important issue to consider is that certain cationic dopants may exhibit more than one valence and the associated potential for reduction-oxidation reactions [166, 170]. These can result in an increase in the level of oxygen vacancies (promotion of the phase transformation through increase in lattice relaxation) and/or the formation of Ti^{3+} interstitial (inhibition of the phase transformation through lattice constraint). The fact that Al^{3+} has only a single valence may explain why it inhibits the phase transformation as opposed to Fe^{3+} , which promotes the phase transformation, although being of similar size and valence to Al^{3+} .

This can be attributed to its likely valence change during heating:

Iron can undergo reduction creating an oxygen vacancy by the reaction in **equation 3.8**:



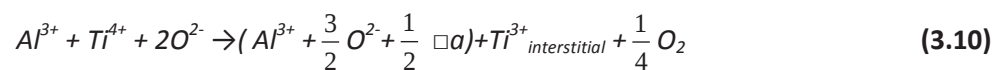
Here, $\square a$ denotes an anion vacancy

In the TiO_2 lattice the anatase to rutile phase transformation will be promoted by the formation of oxygen vacancies by the reduction of dopant iron 3+ following the reaction shown in **equation 3.9**:

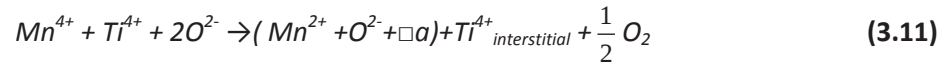


The anion vacancy, $\square a$, enhances the phase transformation.

In the case of aluminium doping of TiO_2 , the reaction is



In the case of doping of TiO₂ by Mn and its reduction from Mn⁴⁺ to Mn²⁺ which occurs spontaneously at temperatures above 400°C [170] the reaction is described by the following:



The creation of oxygen vacancies in TiO₂ through valence change in Fe was confirmed by Heald and Weiss [168] and Genarri and Pasquevich [194] who used haematite in solid state form as a dopant. In another study, after Fe was added in a 3+ oxidation state form and the doped TiO₂ was heated in air, electron paramagnetic resistance (EPR) showed that Fe was present in the 2+ oxidation state and that this promoted the phase transformation [196].

In contrast, the addition of Fe in the 2 valence, using FeCl₂ and firing in air, resulted in inhibition of the phase transformation [173]. Mössbauer spectroscopy revealed that iron was present interstitially in the 3 valence. If the 2 valence was retained during heating, then size and charge considerations support the view that Fe²⁺ would be unlikely to substitute for Ti⁴⁺. Further, the oxidation of Fe²⁺ to Fe³⁺ would require the annihilation of oxygen vacancies, in reverse of reaction 3.8. Hence, both of these phenomena would be expected to inhibit the phase transformation.

The preceding different outcomes from doping with the same metal highlight the importance of differentiating between the assumption of substitutional and interstitial solid solubility. Again, the same dopant in substitutional form may increase the oxygen vacancy level and promote the phase transition while, in the interstitial form, may enhance lattice constraint and inhibit the phase transformation. This applies to all dopants, although the transition metals of variable valence (*e.g.*, Mn, Fe, Ni), are most likely to be those that show mixed effects.

In contrast, the absence of the likelihood of valence change is more straightforward. In the case of substitution of Ti⁴⁺ by Al³⁺, half an oxygen vacancy and a Ti³⁺ interstitial are created (Equation 3.7), thereby promoting and inhibiting the phase transformation, respectively. Since, the

inhibition of the phase transformation by aluminium doping is well known [156, 177, 197], if substitution is the mechanism, then it can be concluded that the effect of lattice constraint is greater than that of lattice relaxation. However, if Al^{3+} enters the lattice interstitially, then only lattice constraint results, which inhibits the phase transformation and so no information about the relative importance of the two mechanisms is provided.

3.4.3. Predictive analysis

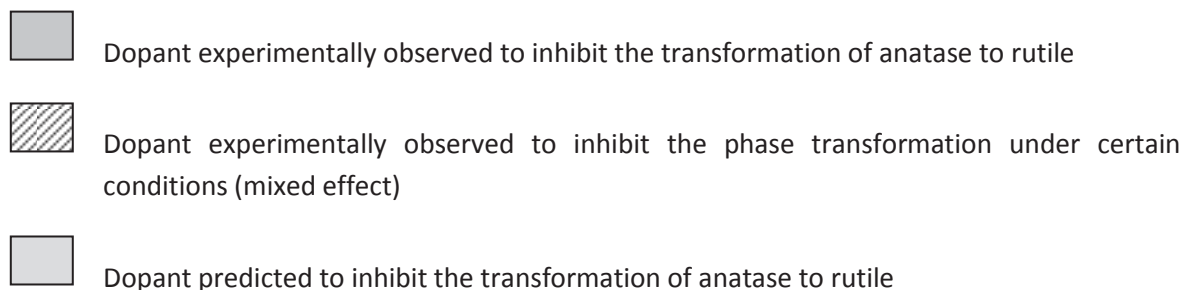
Using data from the literature, it is in principle possible to make a subjective estimate of the potential effects of dopants for which no data are available. The four deductive considerations used to predict the effects of dopants on the anatase to rutile transition is:

- Most common valence and ionic radii of substitutional cationic dopants in conjunction with Equation 3.6. and the equivalent interpolated boundary in Figure 3.11.
- The potential for valence changes in dopant cations (*e.g.*, $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$)
- The potential for oxygen vacancy formation through reduction (*e.g.*, C- and N-doping)
- The known effects of anionic dopants (*e.g.*, F^- and Cl^-)

A summary of the reported and predicted effects of dopants on the phase transformation is given as follows:

3.4.3.1. Inhibitors

Fig. 3.12 Experimental and predicted inhibition of anatase to rutile transformation based on the preceding four considerations.



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt									

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

3.4.3.2. Promoters

Fig. 3.13 Experimental and predicted promotion of anatase to rutile transformation based on the preceding four considerations.

	Dopant experimentally observed to promote the transformation of anatase to rutile
	Dopant experimentally observed to promote the phase transformation under certain conditions (mixed effect)
	Dopant predicted to promote the transformation of anatase to rutile

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt
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Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Carbon doping

Carbon is an attractive dopant for titanium dioxide photocatalysts as it has been reported to reduce the band gap and improve photocatalytic performance in anatase [20]. Carbon 4+ has an ionic radius of 0.03 nm, which places it close to the line of Equation 3.6, making a prediction of its effects on the anatase to rutile transformation based on valence/size considerations uncertain. Moreover, there is an apparent absence of reported data regarding the effects of carbon on the transformation of anatase to rutile. This is a result of the likelihood of carbon oxidation at temperatures below the anatase to rutile phase transformation temperature. However, carbon is a very strong reducing agent and, when retained during firing in an inert atmosphere, it would be likely to enhance the transformation to rutile through the formation of oxygen vacancies. Further, the oxygen-deficient atmosphere created through the use of an inert gas overpressure also would enhance the transformation to rutile through defect formation. In the extreme case, a stable carbide could form by reaction. Effectively, all of these are reduction reactions that take place to different degrees, as indicated:

Defect Formation: $\text{TiO}_2 + x\text{C} \rightarrow \text{TiO}_{2-x} + x\text{CO}$

Suboxide Formation: $\text{TiO}_2 + \text{C} \rightarrow \text{TiO} + \text{CO}$

Carbide Formation: $\text{TiO}_2 + 2\text{C} \rightarrow \text{TiC} + \text{CO}_2$

Consequently, carbon is predicted to promote the phase transformation, as shown in **figure 3.13**.

It has been reported that nitrogen doping increases the levels of oxygen vacancies in anatase [118, 163], so it is likely to promote the transition to rutile. However, this has not been reported. In light of the preceding, nitrogen also is predicted promote the phase transformation in figure 3.13.

3.4.4. Importance of doping methods

The preparation technique of doped anatase is critically important because it impacts on the degree of equilibration achieved. There are three general methods by which dopants can be combined with anatase: Point contact, surface contact, and molecular level mixing. These are listed below in order of decreasing diffusion distance required for the dopant ions in order to enter the anatase lattice:

- **Dry Mixing:** This involves the blending of dry powders of anatase and dopant-bearing phases, such as oxides. Both large particle sizes and inhomogeneous mixing are associated with increased diffusion distances.
- **Wet Impregnation:** This method involves mixing dry anatase powder with a dopant-bearing solution, such as dissolved salts or metal-alkoxides [68, 190].
- **Molecular-Level Mixing:** This method offers the most intimate level of association and involves mixing of a soluble titanium-bearing compound, typically an organometallic, such as titanium isopropoxide, with a soluble dopant-bearing compounds in an organic or aqueous solution. This level of mixing often is obtained through the use of doped sol-gels or co-precipitation.
- **Ion Implantation:** This method involves the impacting of accelerated ions into solid TiO_2 . Most often used in semiconductor fabrication, this method is appropriate for the formation of localised doping and has been used in the fabrication of doped TiO_2 nanotubes [198] and F doped single crystal TiO_2 [199].

Doping methods that involve larger diffusion distances for the dopant compounds to enter the titania lattice may diminish the inhibiting or promoting effect of the dopant on the anatase to rutile phase transformation since this may take place before the dopant has entered the anatase lattice.

3.4.5. Oxide dopants

Alumina, silica, and zirconia and have been used to stabilise anatase [67, 109, 121, 176, 200]. It has been suggested that Al, Si, and Zr stabilise anatase by occupying interstices, thereby distorting the anatase lattice and restricting the lattice contraction involved in the transformation to rutile [121]. Conversely, Yang and Ferreira [177] have suggested that the observed contraction in lattice parameters upon SiO_2 and/or Al_2O_3 doping is evidence of solid solubility. Another study of the effects of SiO_2 doping on the lattice parameter of anatase [83] also suggested that Si^{4+} enters substitutionally, thereby decreasing the lattice parameter of anatase (and forming interstitial Ti^{4+}). Further, it is possible that the distortion of the lattice by the doping restricts the ionic rearrangement similarly to that of interstitial ions. Also, the presence of undissolved SiO_2 , possibly as a grain boundary glassy phase, has been suggested to inhibit diffusion and reduce anatase interparticle contact, thus reducing the number of available heterogeneous nucleation sites [83].

The use of solid-state dopants introduces the scope for heterogeneous rutile nucleation at the surfaces of the dopant material. This may be the case for tin oxide which has been suggested to facilitate epitaxial growth of rutile due to its similar lattice parameters [159, 201]. Such rutile nucleation has been reported to accelerate the transformation to rutile, causing it to take place rapidly so that coarsening does not have the time to occur. This study supports the view that the grain growth typically associated with the phase transformation is not a cause but an effect.

3.5. Other Considerations

3.5.1. Effects of Firing Atmosphere on the Anatase to Rutile Transformation

Rutile is reported widely to exhibit oxygen deficiency and can be described more appropriately as having the formula TiO_{2-x} [164, 202–204]. Such a stoichiometry requires, in principle, the

presence of titanium lattice ions, unintentional impurities, and/or intentionally added dopants of valences lower than 4 in order to maintain charge balance. This nonstoichiometry may be present in anatase as well, although this appears not to have been discussed in the literature. The oxygen vacancies in anatase can be expected to enhance the transformation to rutile owing to the facilitated rearrangement of ions.

In contrast to the use of dopants, the atmosphere used during heating of anatase may affect the probability and kinetics of the transformation to rutile. That is, inert (*viz.*, noble gases) or reducing atmospheres (*viz.*, hydrogen) can be expected to increase the number of oxygen vacancies in the anatase lattice (relative to heating in air), thereby promoting the transformation to rutile. Conversely, heating in air or O₂ can be expected to inhibit the transformation owing to the filling of vacancies. These effects have been observed in various reports [68, 110, 168, 194], typically through reporting the transformation temperature.

3.5.2. Formation of Crystalline TiO₂ from Solutions

Alternative methods of obtaining rutile, anatase, or brookite directly from solution at relatively low temperatures have been investigated using solvothermal processes [84, 95–97, 122, 201, 205–207]. These approaches involve the use of titanium-bearing solutions of varying pH. When titanium alkoxides undergo hydrolysis, the result is agglomerated titanium hydroxide groups which are often in the form of white amorphous precipitates [46, 96, 208]. Such solutions also can be synthesised using TiCl₄ [97, 100, 104, 105, 206] which can result in crystalline phases of high purity. The use of a low pH limits condensation reactions [201], imposes a repulsive charge and limits the size of these precipitates resulting in the presence of free $[\text{Ti}(\text{OH})_x(\text{OH}_2)_{6-x}]^{(4-x)+}$ octahedra in solution [201, 205], possibly also through dissolution of amorphous particles [205]. These octahedra can then link together to give crystalline TiO₂ phases. Higher pH levels are more

conducive to the formation of amorphous titania as octahedra are not free in solution and therefore less able to link together to form a crystalline phase.

Upon heating, the manner in which $[\text{Ti}(\text{OH})_x(\text{OH}_2)_{6-x}]^{(4-x)+}$ octahedra join determines the crystalline phase that precipitates. If the octahedra have sufficient time to join linearly, with two edges of each octahedron's being shared (see figures 3.3 and 3.4), the free energy is lowered resulting in the formation of the equilibrium phase rutile in the form of grains elongated in the [001] direction [205, 206]. Alternatively, if the crystallisation rate from the solution is increased, the octahedra may tend to join at right angles (see Figure 3.3), as there are more positions for linkage available in this manner, such crystallisation would result in anatase formation which is statistically favoured owing to the more flexible zigzag construction of this polymorph, with four edges of each octahedron's being shared (see Figures 3.3 and 3.4) [205].

Slower crystallisation will yield the rutile phase and more rapid crystallisation favours anatase. This reasoning may also explain why anatase is generally the product phase from most industrial titania manufacturing methods which tend to involve rapid crystallisation of titania through flame pyrolysis of TiCl_4 .

3.5.3. Morphological Effects

The grain morphology plays an important role in photocatalytic applications of titania. Nanocrystallinity has been shown to lower the material's densification temperature and enhance its photocatalytic activity [74, 77, 111, 209]. A common goal is to inhibit the grain growth of titania during heating as this gives a higher surface area and thus improved performance.

Bulk rutile is more stable thermodynamically than anatase at all temperatures and pressures (Figures 3.7 and 3.8) owing to its lower free energy [74, 77, 106, 111, 210]. However, the lower *surface* energy of the anatase planes relative to those of rutile [77] cause the former to be more

stable for crystallites of extremely small sizes and correspondingly high surface areas. In these cases, surface energy considerations outweigh those of bulk thermodynamics and so, for crystallites below a critical size (45 nm [172], 14 nm [77], and 11 nm [211]), anatase has a lower *total* (bulk and surface) free energy [74, 77, 210]. Further, the size above which rutile becomes more stable depends on stresses [77].

Despite this, it has been reported that larger anatase grains (*i.e.*, predominantly bulk thermodynamics) transform to rutile more slowly than finer grains (*i.e.*, predominantly surface thermodynamics). This probably is due to the lower surface energy and fewer interfaces at which rutile can nucleate. Thus, the transition to rutile and grain growth of anatase can be considered as competing phenomena [209].

Significant rutile grain growth is exhibited as the anatase to rutile transition proceeds [68, 74, 109, 159, 172, 178, 179, 212]. Rutile grains coarsen at the expense of neighbouring anatase during coalescence until the large rutile grains begin to impinge on each other [112, 115]. This increase in grain size causes a decrease in surface area and a consequent decrease in photocatalytic activity [56, 74, 132].

3.5.4. Grain Boundary Effects

Dopant oxides that do not dissolve and remain on the grain boundaries restrict the grain growth and reduce interparticle contact, thereby impeding the phase transformation [88, 172].

Also, the presence of a liquid or vitreous phase on the grain boundaries generally represents a hindrance to diffusion and so it is expected that titania contaminated with silica or another glass former would be likely to inhibit the phase transformation [213].

3.6. Summary

An understanding of the transformation of anatase to rutile is of great importance to those studying TiO_2 for photocatalysis or other applications. The phase composition of the material has significant consequences on its properties and performance and therefore it may be desirable to enhance or inhibit the transformation to give a particular phase or phase mixture subsequent to thermal treatment.

At all temperatures and pressures, rutile is the stable phase of TiO_2 . Anatase is metastable but it can be considered to be kinetically stabilised at lower temperatures. Although rutile is the more stable phase from a thermodynamic point of view, anatase frequently is the product phase in the synthesis of TiO_2 owing to its less constrained structure and consequent enhanced kinetics of formation. The phase transformation of kinetically stabilised anatase to thermodynamically stable rutile does not have a distinct transformation temperature. Rather, it shows a gradual onset, the temperature of which is highly dependent on numerous parameters pertaining to the nature of the material, the thermal treatment, and measurement method. The transformation rate to rutile increases exponentially as the temperature increases.

The transformation of anatase to rutile can be promoted, accelerating its kinetics and causing it to become observable at lower temperatures and to progress more quickly. Alternatively, the transformation can be inhibited, retarding the kinetics and causing it to become observable only at higher temperatures. The latter also can be referred to as the *stabilisation* of anatase even though it is the less stable phase.

The kinetics of the anatase to rutile transformation are affected strongly by oxygen defect levels, where oxygen vacancies enhance the transformation. The oxygen defect levels are influenced by atmospheric conditions, reduction or oxidation reactions, unintentional impurities, and intentional dopants.

Dopants are an effective method for influencing the kinetics of the anatase to rutile transformation. Various cationic dopants have been shown to have a strong influence on the phase transformation through the change in oxygen vacancies. This effect can be seen clearly in Fig 3.11, which separates inhibitors and promoters in terms of the combined effects of their ionic radii and valence. Substitutional cationic dopants can increase (promoters) or decrease (inhibitors) oxygen vacancy levels through valence effects, alteration in cation coordination, or reduction/oxidation effects. However, the presence of interstitial ions (lattice constraint) and the reduction of interparticle contact (grain boundary phases) in anatase act to inhibit the transformation. Most doping ultimately increases the thermal stability of anatase. The effects of anionic dopants have been reported to a lesser degree.

The consideration of the mechanisms by which the anatase to rutile transformation is inhibited or promoted can enable prediction of the effects that various dopants and experimental conditions are likely to have on the chemistry, mineralogy, and phase assemblage of the resultant titania, as shown in Figs. 3.12 and 3.13. This ultimately can assist in facilitating the optimisation of the activity of titanium dioxide photocatalysts.

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4. Morphology and photocatalytic activity of highly oriented mixed phase titanium dioxide thin films

This chapter reports the fabrication of mixed phase TiO₂ thin films on quartz substrates as published in the Journal of Surface Coatings and Technology, volume 205, issue 12, pages 3658–3664.

The fabrication of immobilised titanium dioxide materials in thin-film form was chosen as this type of fabrication approach is relevant for water purification applications as well as for the fabrication of self cleaning coatings. Furthermore the use of materials in thin-film form on highly optically transparent single crystal quartz substrates allowed for the use of transmission UV-vis spectrometry for materials characterisation.

The work presented in this chapter explores the used of dopants and attempts to explain the effects of these dopants, as well as the quartz support materials, on the anatase to rutile phase transformation in light of the review paper presented in the preceding chapter. The information presented in Chapter 3 is also of value in understanding the mechanisms through which a high degree of orientation is imparted to the films prepared as part of this work.

A breakdown of the contributions of the individual authors is presented in the table below:

	Primary Author	Manuscript Preparation	Literature Research	Experimental Work	Data Analysis	Editing and Revision	Supervisory Role	Formatting and Layout	Advice and Support	
Dorian A. H. Hanaor	✓	✓	✓	✓	✓	✓		✓		
Charles C. Sorrell						✓	✓	✓	✓	
Gerry Triani									✓	

Key Findings

- The anatase phase exhibits greater thermal stability when immobilised on quartz substrates relative to unsupported TiO₂
- In undoped thin films rutile was found to form as parallel bands in anatase which broadened to consume the parent phase
- Films were observed to exhibit a high degree of orientation based on XRD analysis, likely as a result of interfaces with the single crystal substrates
- Cu doped films exhibited an enhanced anatase to rutile phase transformation relative to undoped films
- Doped films exhibited poorer photocatalytic performance as determined by the photo-oxidation of methylene blue

Morphology and Photocatalytic Activity of Highly Oriented Mixed Phase Titanium Dioxide Thin Films

D.A.H. Hanaor ^{[1]*}, G. Triani ^[2], and C.C. Sorrell ^[1]

[1] University of New South Wales, School of Materials Science and Engineering, Sydney, NSW 2052, Australia

[2] Australian Nuclear Science and Technology Organisation, Institute of Materials and Engineering Sciences, Menai, NSW 2234, Australia

*Corresponding Author: Email dorian@student.unsw.edu.au Ph: +61404188810

Abstract: Thin TiO₂ films on quartz substrates were prepared by spin coating of undoped and metal-ion-doped Sol-gel precursors. These films were characterised by Scanning Electron Microscopy, Laser Raman Microspectroscopy, X-ray Diffraction and UV-vis Transmission. The photocatalytic performances of the films were assessed by the photo-degradation of methylene-blue in aqueous solution under UV irradiation. Films exhibited a high degree of orientation and a thermal stabilization of the anatase phase as a result of substrate effects. In the absence of dopants, the rutile phase formed as parallel bands in the anatase which broadened as the transformation progressed. TiO₂ films doped or co-doped with transition metals exhibited the formation of rutile in segregated clusters at temperatures under ~800°C as a result of increased levels of oxygen vacancies. Photocatalytic activity of the films synthesised in this work was low as likely result of poor TiO₂ surface contact with dye molecules in solution. The presence of transition metal dopants appears detrimental to photocatalytic activity while the performance of mixed phase films was not observed to differ significantly from single phase material.

Keywords: TiO₂; Rutile; Anatase; Photocatalysis; Thin Films; Morphology

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4.1. Introduction

TiO₂ photocatalysts have attracted a significant volume of research interest during the last 30 years owing to the various environmentally beneficial applications of such materials. While thin films of TiO₂ exhibit poorer surface area, and thus lower photocatalytic activity in comparison with suspended powders, the synthesis of durable thin film coatings of TiO₂ is attractive as such materials eliminate the requirement for catalyst recovery processes and can be applied to impart beneficial qualities to existing surfaces. The various applications of such TiO₂ photocatalytic coatings include

Self cleaning coatings [1–4]

Self sterilising (antimicrobial) coatings [5–7]

Water purification [8–10]

Photocatalysed reactions on TiO₂ surfaces take place through the generation of electron-hole pairs, known as excitons, by radiation exceeding band gap of the material (~3.0eV for rutile and ~3.2eV for anatase [11–13]) and the subsequent formation of adsorbed reactive species. The performance of a TiO₂ photocatalyst is limited by the relative rates of photo-generation of excitons, generally by UV irradiation, and their recombination. Both of these competing phenomena are influenced by the morphology and phase composition of the material. It has been reported that TiO₂ of a mixed anatase-rutile phase assemblage exhibits superior photocatalytic performance as a result of improved charge carrier separation through the trapping of conduction band electrons in the rutile phase [14–17]. Morphologies of smaller grain size are reported to show superior photo-activity as a result of a higher surface area and thus greater levels of adsorbed reactive species [18, 19].

While rutile is the more thermodynamically stable phase of TiO₂ at all pressures and temperatures [20–22], anatase is frequently the first phase formed in many synthesis routes due to a less constrained structural re-arrangement necessary to form this phase from an amorphous precursor and a lower surface energy in comparison with the rutile phase [23–25]. Upon heating in air, the phase transformation of anatase to rutile generally takes place around 650°C in the absence of dopants or impurities. Dopants influence the anatase to rutile phase transformation through a change in oxygen vacancy levels and the inhibition or promotion of the structural rearrangement involved in the transformation [26–29].

The performance of TiO₂ photocatalysts is often studied by the photo-degradation of sample pollutants in liquid, solid or gas phase. Such experiments are usually carried out under UV illumination although the use of natural sunlight is attractive due to the lower environmental impact involved. Methylene blue is frequently used to examine photocatalytic activity due to the ability to use spectrometric techniques to determine the concentration of the dye.

The present work examines the morphology, phase assemblage and photocatalytic activity of mixed phase thin-film TiO₂ photocatalysts. Although it has been reported that apart from the use of noble metals (Pt, Au and Ag) most metal doping is detrimental to photocatalytic activity of titania[30–32] , the present work included the use of metal dopants to examine the consequent effects of dopants on the phase assemblage of biphasic TiO₂ thin films and the prospect of increased photon absorption through inter-valence charge transfer between dopants of different valences.

4.2. Experimental procedure

4.2.1. Materials

The preparation of samples involved the following chemicals. Isopropanol (>99% Univar) Titanium-tetra-iso-propoxide or TTIP (97% Sigma Aldrich), 2M solution of reagent grade Hydrochloric Acid in distilled water, and reagent grade iron chloride (FeCl₃) and copper chloride (CuCl₂), both from Sigma Aldrich. 20x20x1 mm (100) quartz wafers were used as substrates. Quartz substrates were used rather than glass slides due to the increased thermal stability of quartz and due to the problems associated with increased diffusion of cations from glass [33, 34].

4.2.2. Preparation of sol

Undoped films were made using a 50ml 0.5 M solution of TTIP in isopropanol prepared under magnetic stirring. For hydrolysis purposes 2M HCl was added to this solution in a quantity calculated to give a 2:1 molar ratio of H₂O:Ti. An increase in the viscosity of the solution was observed subsequent to this addition. A copper doped sol was prepared using the same method with the addition of copper chloride to give 5 at% Cu (Cu:Ti ratio 1:20), a co-doped sol was prepared with the additions of iron chloride and copper chloride both at 2.5 at% (Cu/Fe:Ti ratio 1:40).

4.2.3. Thin film synthesis

A Laurell WS-650Sz Spin coater was used to fabricate thin TiO₂ coatings on 20mm x 20mm x1 mm quartz substrates. The substrate surfaces were covered with sol using a pipette followed by spinning at 1000RPM. This was repeated three times to increase film thickness. Films were fired in air in a muffle furnace at temperatures ranging from 600–1100 degrees for durations of 4 hours

using a 5°/min heating rate. These thermal treatments imparted good film-substrate adhesion as thin films were resistant to rubbing off. Using a Micropack NanoCalc-2000 thin film measurement system in reflection mode with an integration time of 400 mS, films were determined to have thicknesses between 50 and 70 nm.

4.2.4. Analysis of films

An Invia Laser Raman Microspectrometer was used in conjunction with a 514 nm laser for the purpose of phase analysis with respect to microscopically visible features in the films. Overall phase analysis was carried out by glancing angle x-ray diffraction using a Phillips MRD system, with a 1.5 ° glancing angle. Phase quantification was carried out using the method developed by Spurr and Myers [35]. This method is described by equation 4.1.

$$\frac{W_R}{W_A} = 1.22 \frac{I_R}{I_A} - 0.028 \quad (4.1)$$

Here W_R and W_A are respectively the weight fractions of rutile and anatase ($W_R=1-W_A$), I_R and I_A are respectively the intensity of the rutile (110) peak at 27.35° 2 θ and the anatase (101) peak at 25.18° 2 θ .

Optical transmittance of the films prepared in this work was determined using a Lambda-35 UV-vis Spectrophotometer in the wavelength range 300–800 nm.

Microstructure of films was examined using Hitachi S3500 and S900 scanning electron microscopes.

4.2.5. Photocatalytic activity

The decomposition of methylene blue (MB) was carried out in a cylindrical vessel containing 1 litre of MB with an initial molar concentration of 0.107 mMol/litre. The quartz substrate was

supported on a platform in the solution and the solution was irradiated with a 15 W UV lamp with an emission peak at 350 nm wavelength placed 100mm above the film. The irradiance at the film surface was determined to be 2.14 Wm⁻² using a Digitech QM1587 light meter. Irradiation was applied intermittently for alternating intervals of 15 minutes to avoid significant heating of the solution. Experiments were carried out under magnetic stirring and air sparging. Optical absorbance of the methylene blue solutions were carried out after a cumulative 10 hours and 20 hours of irradiation had been achieved. MB concentrations were calculated using the measured absorbance peak at or around $\lambda = 663\text{nm}$ in conjunction with a prepared calibration procedure similar to analytical methods reported in the literature [36–38].

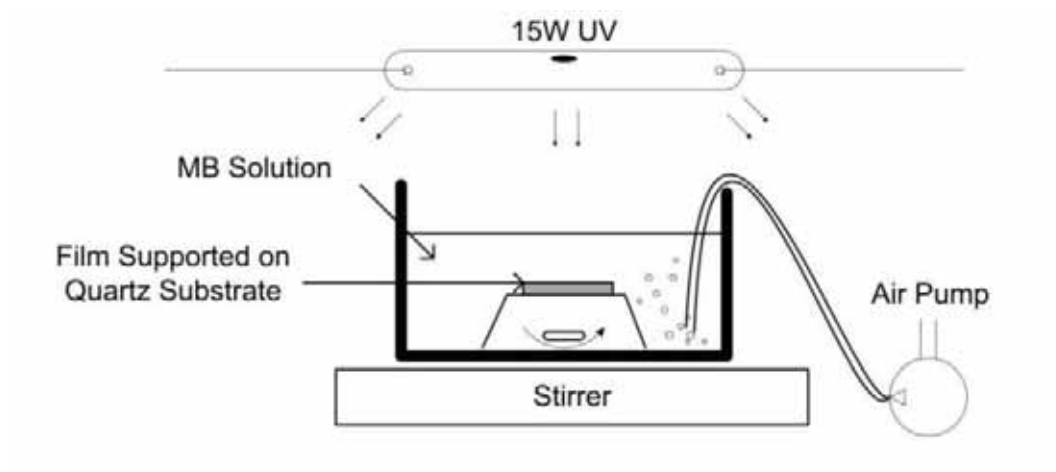


Fig. 4.1. Reactor for the photo-degradation of methylene blue by thin film TiO₂ photocatalysts .

4.3. Results

4.3.1. XRD

XRD patterns were gathered from undoped, Cu doped and Cu/Fe co-doped films fired at different temperatures. The resultant XRD spectra are shown in figure 4.2. The dominance of the anatase

(101) and rutile (110) peaks suggest a high degree of grain orientation. The Lotgering orientation factor was not calculated owing to the high noise to signal ratio in the XRD patterns gathered. Using the method of Spurr and Myers, these XRD spectra were interpreted to give anatase and rutile phase proportions which are plotted in figure 4.3. The presence of phases other than anatase or rutile was considered negligible in these calculations and thus the sum of anatase and rutile fractions was assumed to be unity.

Undoped films showed a biphasic composition when fired at temperatures between 800°C and 1000°C. At 1100°C the transformation was complete and only the rutile phase was observed. In comparison with undoped films, the anatase to rutile transformation was promoted by Cu doping as evident in figures 4.2b and 4.3, showing a predominantly rutile phase after firing at 800°C. Cu/Fe co-doped films also exhibited enhanced anatase-rutile transformation showing complete transformation to the rutile phase after firing at 1000°C.

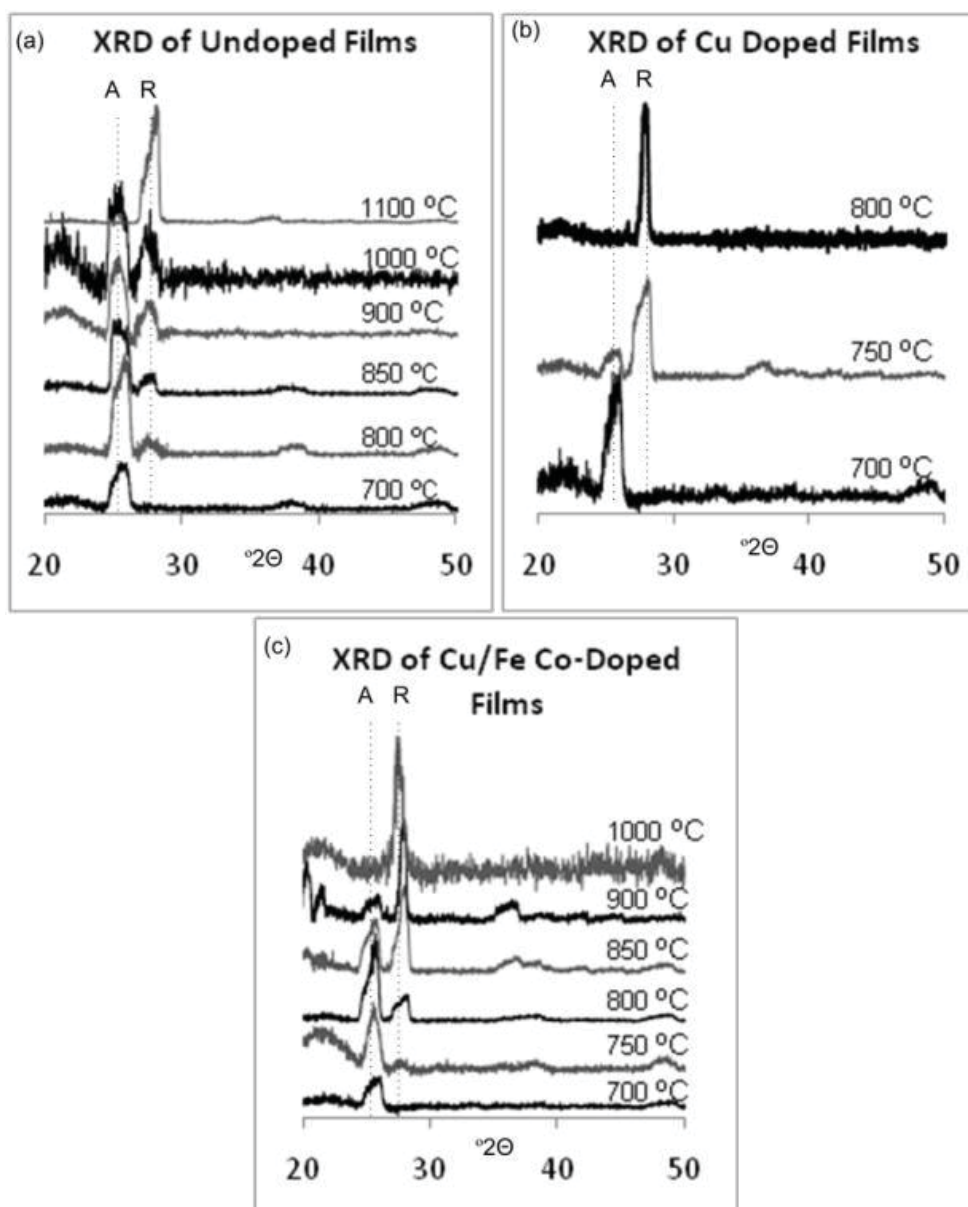


Fig. 4.2. Glancing angle XRD spectra of (a)Undoped TiO_2 films (b) Cu(ii) doped thin films and (c) Cu(ii)/Fe(iii) Co-Doped films fired at different temperatures with anatase (101) (A) and rutile (110) (R) peaks labelled.

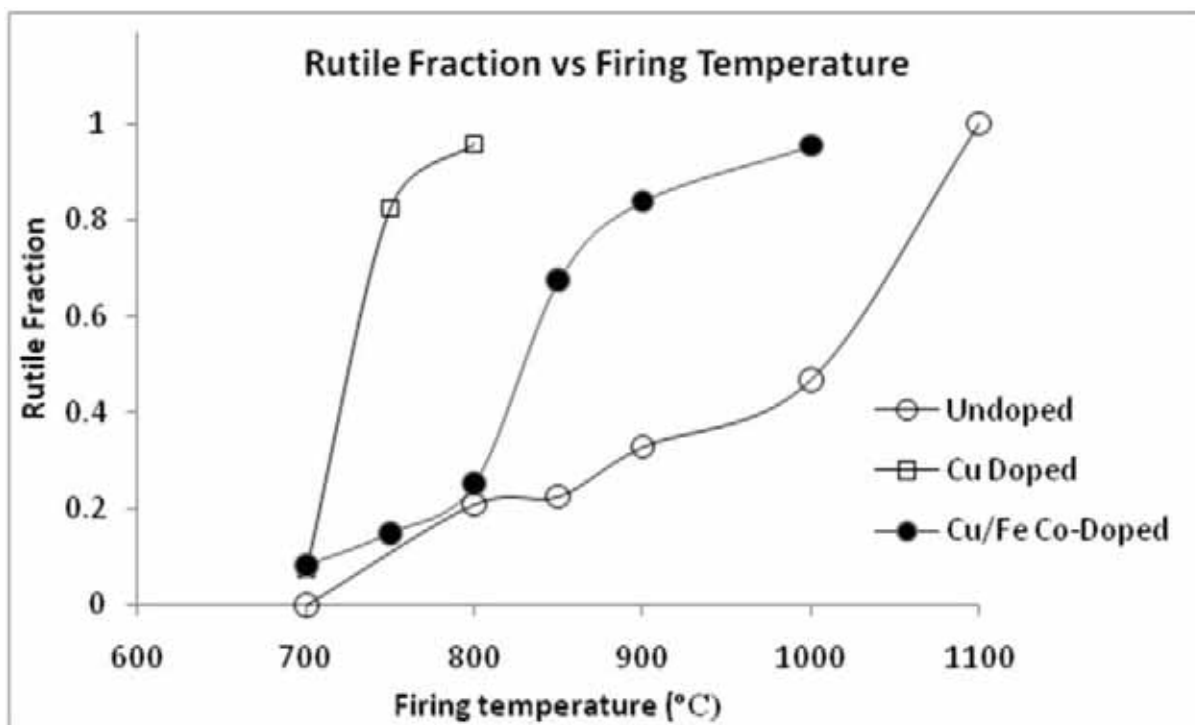


Fig. 4.3. Rutile content as a function of firing temperature for undoped, Cu(ii) doped and Cu(ii)/Fe(iii) Co-Doped TiO₂ thin films fired for 4h.

4.3.2. Raman microspectroscopy

The use of laser Raman microspectroscopy in conjunction with an optical microscope allows the differentiation of TiO₂ phases with respect to microscopically visible features. Figs. 4.4–4.6 show micrographs of thin films alongside Raman spectra gathered from the regions of different appearance apparent in the images. It was found that undoped samples exhibit the formation of rutile as parallel bands in anatase (Figure 4.4) these bands showed a consistent orientation throughout the film. Rutile bands became wider and anatase bands more narrow as the phase transformation progressed. In contrast, doped films showed segregated clusters of rutile as spots of varying dimensions in the parent anatase (Figures 4.5 and 4.6). It should be noted that the dominance of the anatase peak at 141 cm⁻¹ does not infer that this is the dominant phase rather

this is a result of the interaction area of the laser and the particularly strong Raman shift of anatase at this wave-number.

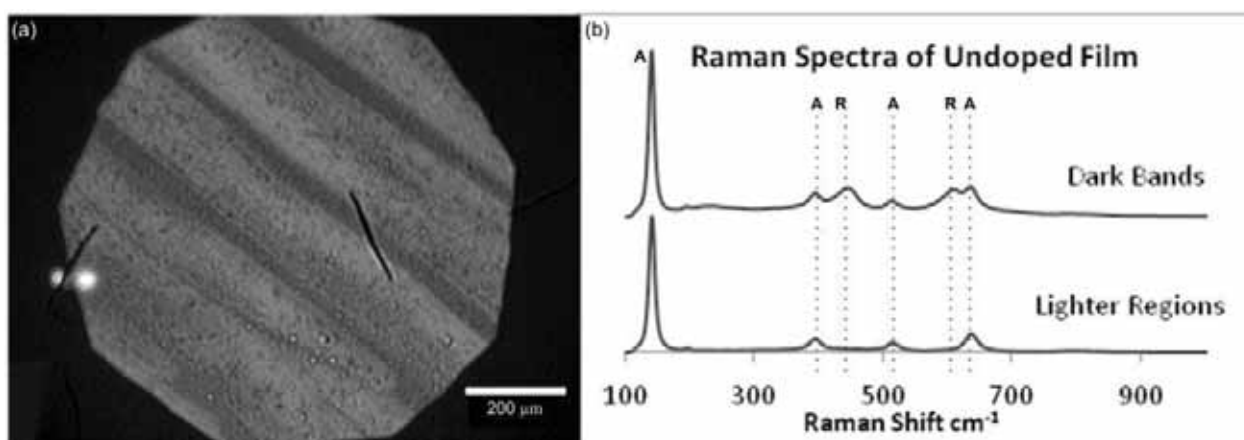


Fig. 4.4. (a) Optical micrograph of a 30% Rutile undoped TiO_2 thin film (b) Raman spectra gathered from spots in darker and lighter bands.

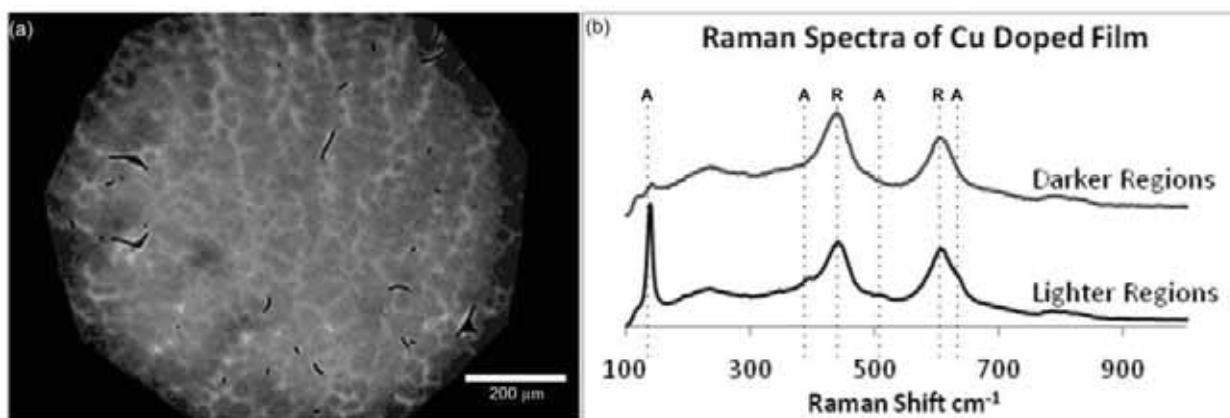


Fig. 4.5. (a) Optical micrograph of an 82% Rutile Cu(II) Doped TiO_2 thin film (b) Raman spectra gathered from dark spots and from lighter regions between spots.

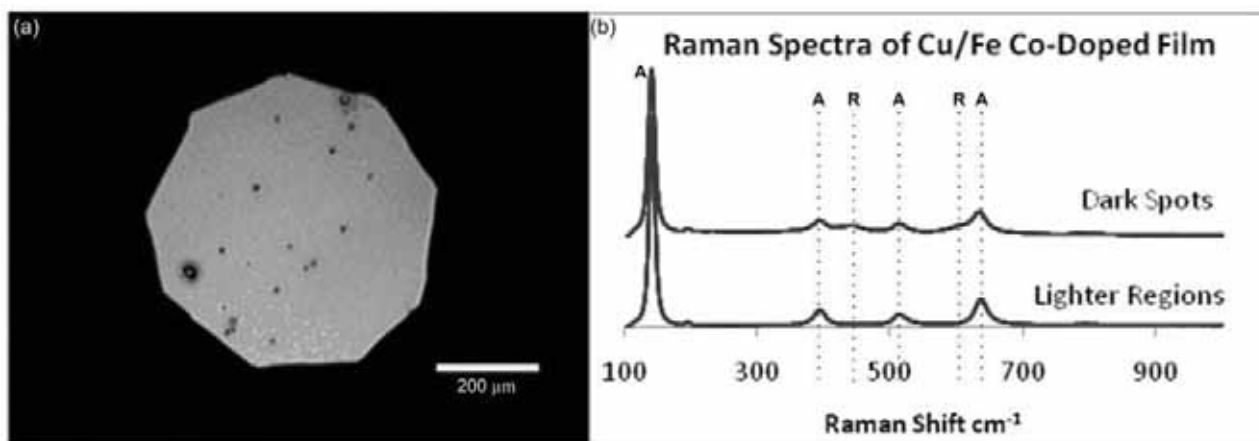


Fig. 4.6. (a) Optical micrograph of a 15% Rutile Cu(ii)/Fe(iii) Co-Doped TiO_2 thin film (b) Raman spectra gathered from dark spots and from lighter regions.

4.3.3. SEM analysis

Scanning electron microscope images of undoped films show an increase in grain size with the transformation to rutile (Fig. 4.7). It was found that films formed in this work were fully dense, the anatase phase showed a grain size of approximately 40–50 nm and rutile exhibited larger grains of 200–400 nm. Little to no porosity was observed however some shrinkage cracking was present. Grain morphology was similar in doped and co-doped anatase films, however less grain coarsening takes place in the transformation to rutile as evident from the absence of large consolidated grains in figure 4.8. The smaller crystallites visible in figure 8(b) are likely to be from the sputtered chromium coating applied to the sample prior to SEM analysis.

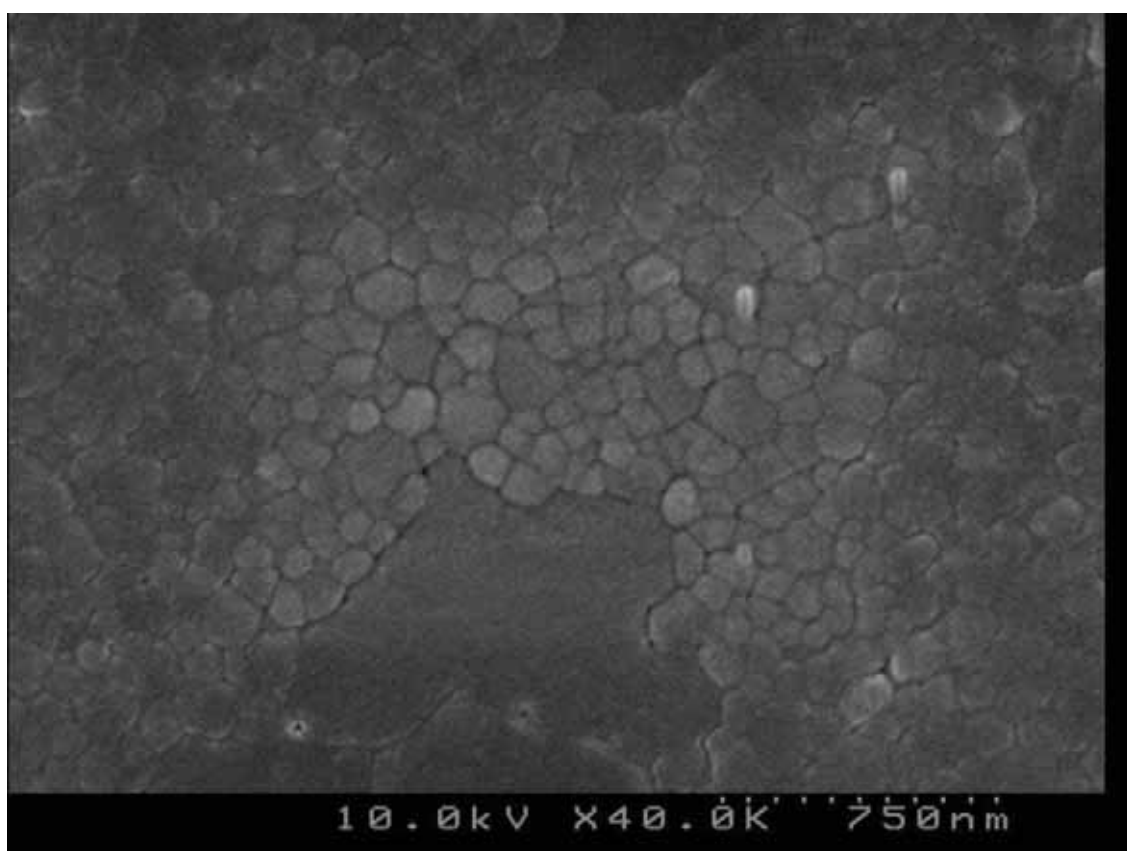
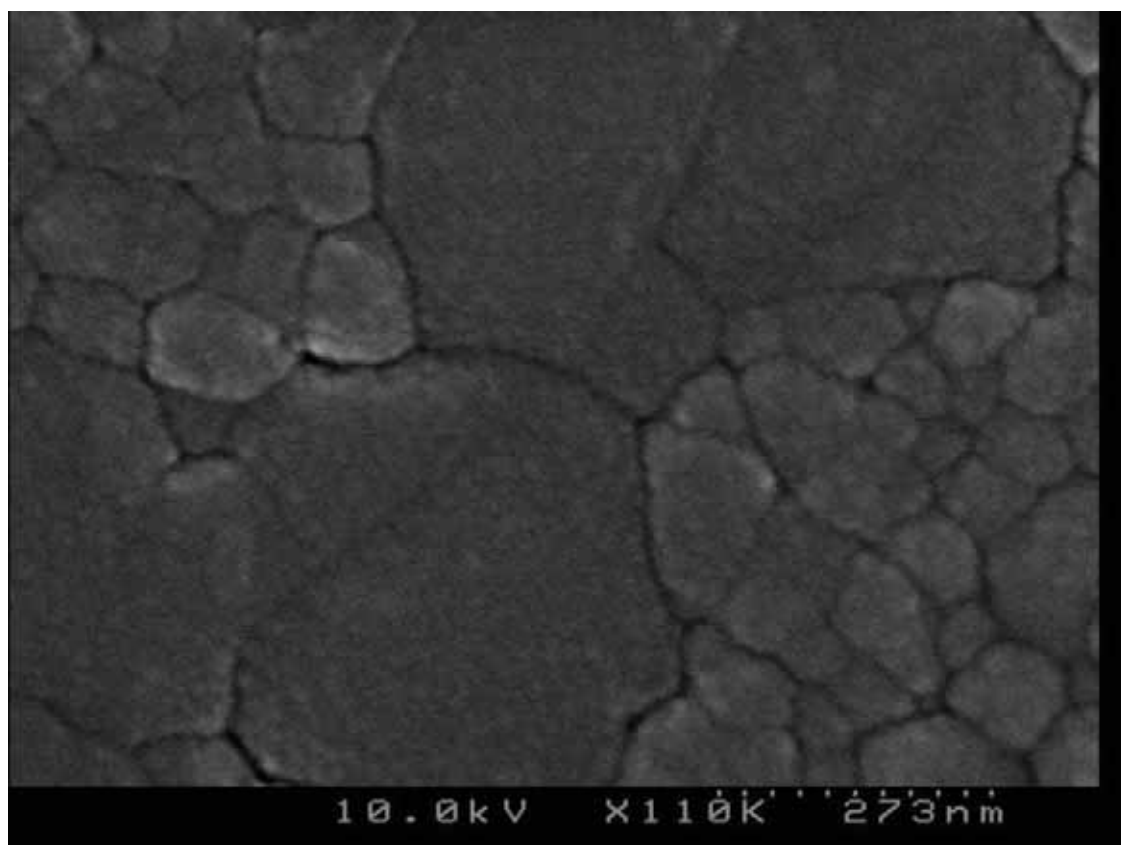


Fig. 4.7. Two SEM micrographs showing rutile grains alongside untransformed anatase in undoped films.

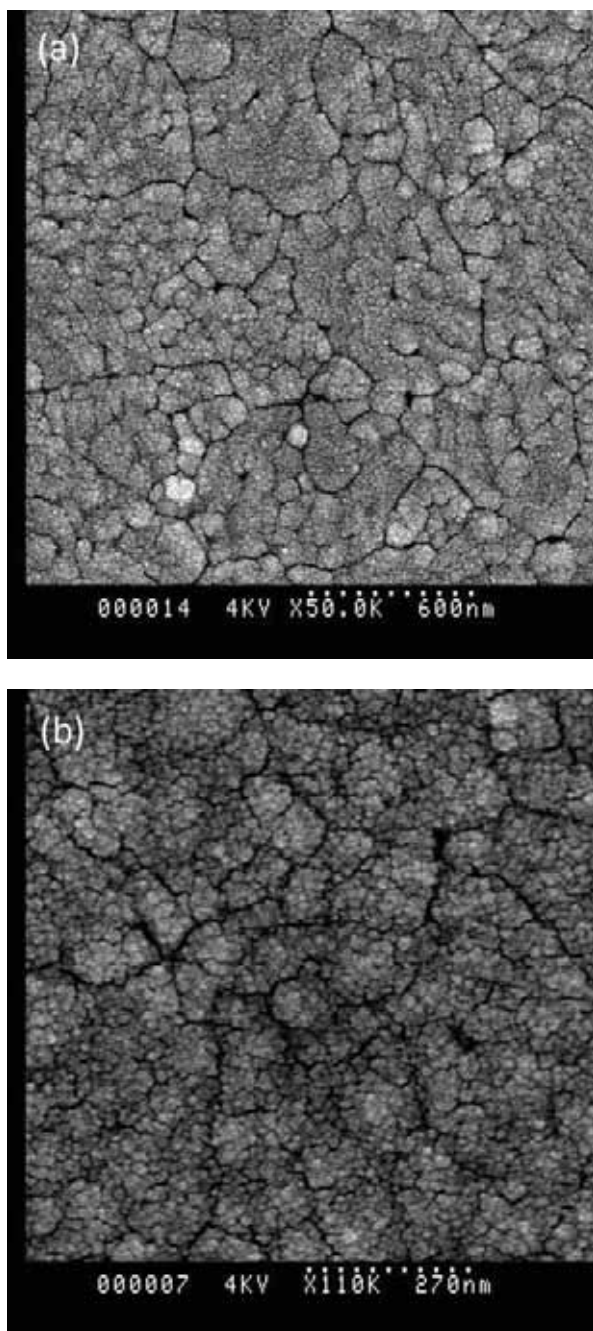


Fig. 4.8. (a) Cu/Fe co-doped mixed phase film (b) Cu doped rutile film.

4.3.4. Optical properties

UV-vis transmittance measurements were carried out to ascertain the effects of dopants and phase assemblage on the optical properties of the thin films synthesised in this work. It can be seen that doped films show lower transmittance levels compared with undoped films. Films

containing rutile phase, even at low phase proportions, showed an adsorption edge at higher wavelengths and lower overall transmittance in comparison with anatase films.

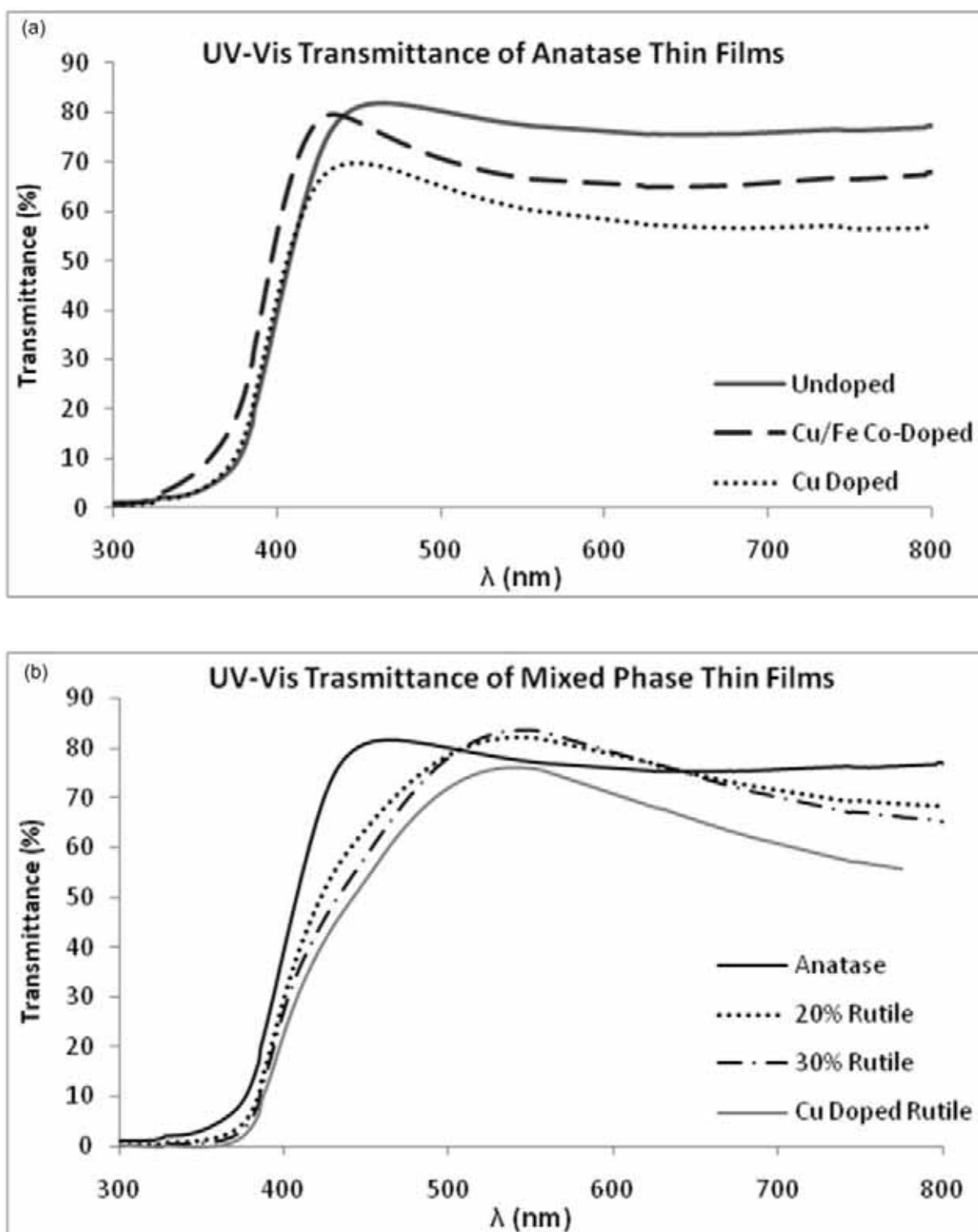


Fig. 4.9. (a) UV-vis transmittance of anatase films (b) UV-vis transmittance of mixed phase films.

4.3.5. Photocatalytic activity

The photocatalytic activity of the quartz supported thin films synthesised in this work was examined by the photo-degradation of methylene blue in aerated solutions using undoped films of 100% anatase and 70% anatase/30% rutile, Fe/Cu co-doped films of 100% anatase, Cu doped anatase films and Cu doped rutile films. An uncoated quartz substrate was used to establish the baseline photo-degradation of the dye, which had an initial concentration of 0.107 mM/L, in the absence of a photocatalyst. The UV-vis absorbance spectra of the MB solutions, subsequent to 10h and 20h of irradiation, were interpreted using the calculated slope of calibration curve shown in Figure 4.10 to establish the concentration of methylene blue in solution. The resultant dye concentrations are shown in Figure 4.11. It can be seen that the degradation of dye takes place to a significant extent without the presence of a TiO₂ film. While the photo-activity was poor in all films, it can be seen that the presence of TiO₂ enhances the degradation of the dye under UV light to a greater extent in undoped films than in doped films.

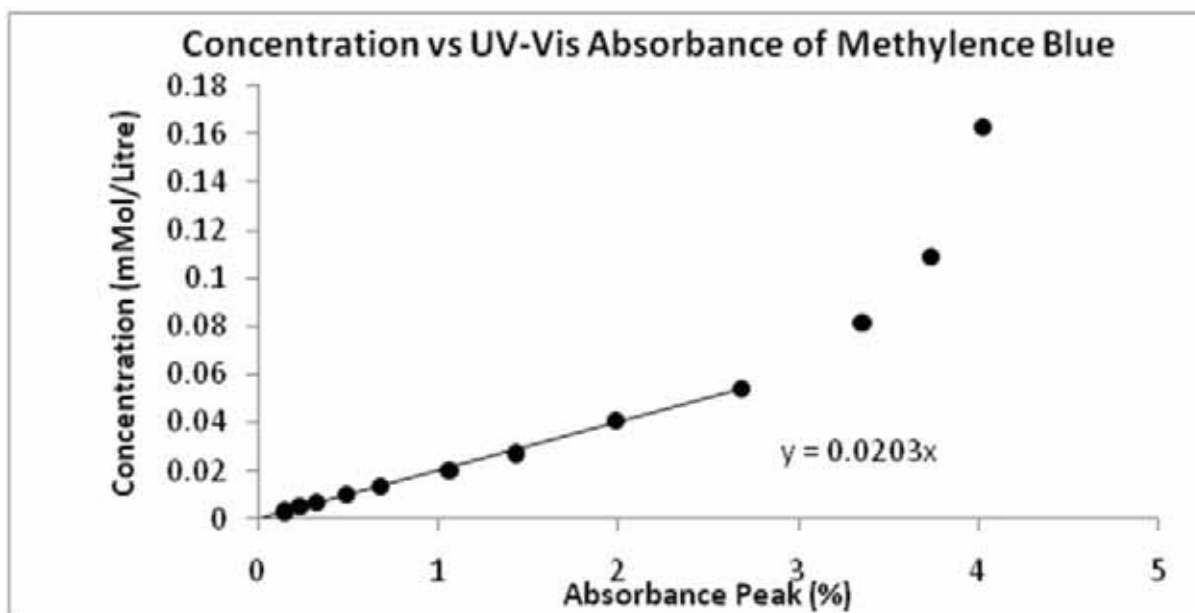


Fig. 4.10. Calibration curve used to determine dye concentration from optical absorbance data.

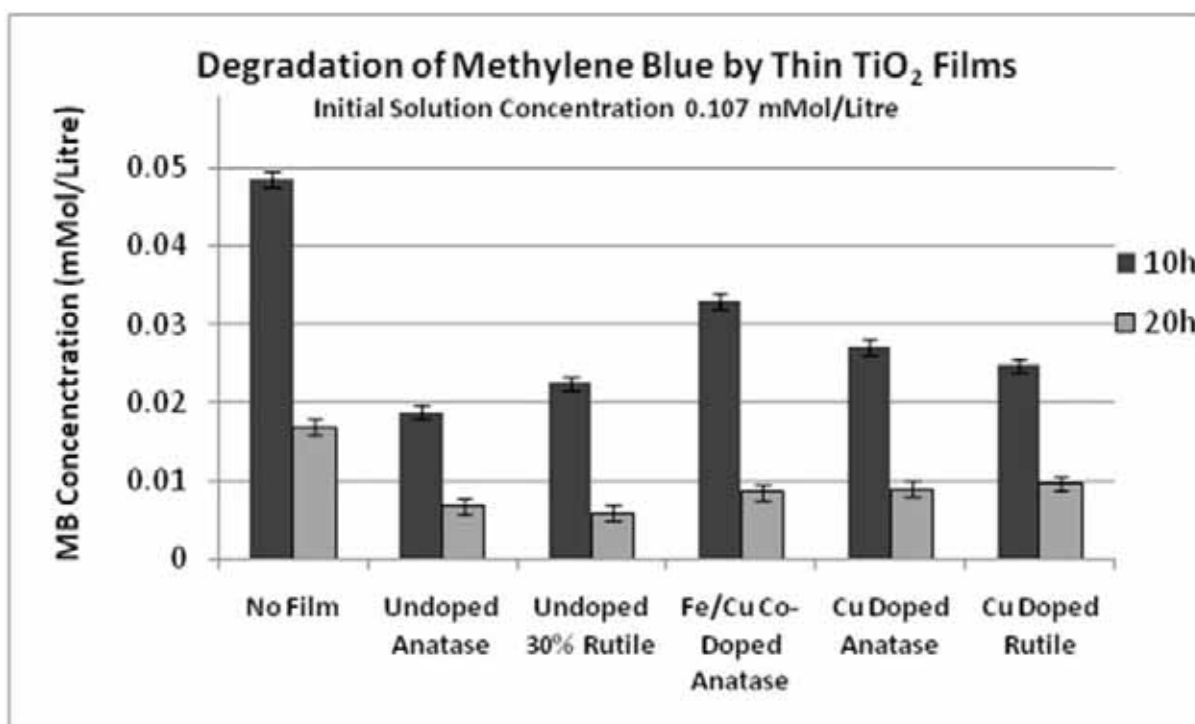


Fig. 4.11. TiO₂ photocatalyzed degradation of methylene blue.

4.4. Discussion

4.4.1. Phase transformation behaviour

From the glancing angle XRD patterns shown in Fig. 4.2, it can be seen that the anatase phase of TiO₂ films immobilised on quartz substrates shows improved thermal stability in comparison with unsupported TiO₂ powders. Undoped TiO₂ powder typically transforms to rutile at temperature of 600–700°C [39–41]. In contrast, undoped films synthesised in this work show the phase transformation onset only at 800°C. While it is possible that smaller temperature intervals and greater firing durations would reveal rutile formation at lower temperatures, the stabilisation of the anatase phase on quartz substrates due to diffusion of Si atoms is consistent with results published elsewhere [28, 42, 43]. The reconstructive anatase to rutile transformation involves the rearrangement of the TiO₂ lattice and an overall volume contraction of ~8% [44–46]. The presence of interstitial Si atoms is reported to hinder this structural rearrangement through lattice constraint [47] and it is further possible that the structural rearrangement is constrained further due to grain boundary pinning at the film-substrate interface.

In comparison with undoped TiO₂ thin films, the addition of Cu(II) through the use of CuCl₂ additive to the precursor sol brought about a marked enhancement of the anatase to rutile transformation. The enhancement is evident from a more rapid transformation at lower temperatures shown in Fig. 3. This is likely to be a result of increased oxygen vacancies brought about by the substitution of Ti by lower valence Cu ions as reported elsewhere [29, 48, 49]. The presence of these oxygen vacancies reduces lattice constraint and facilitates the reconstructive phase transformation. The co-doping of films with Fe/Cu additives introduced using CuCl₂ and FeCl₃ results in a weak enhancement of the phase transformation possibly due to the larger Fe³⁺

ions occupying interstitial lattice positions and impeding the structural rearrangement involved in the phase transformation.

4.4.2. Phase morphology

In all XRD patterns (Fig. 4.2) the anatase (101) and rutile (110) peaks are clearly dominant with other peaks being difficult to detect, in part due to a high noise signal ratio. Although the determination of the Lotgering orientation factor was not possible due to the aforementioned high background signals, the dominance of the anatase (101) and rutile (110) peaks suggest films synthesised in this work are highly oriented. This is a natural consequence of very thin films being deposited on single crystal substrate and is similar to the high degree of orientation observed in thin TiO₂ films on single crystal substrates reported elsewhere [18, 50].

Raman microspectroscopy shown revealed that undoped TiO₂ films exhibited the formation of banded phase segregation (Fig. 4) with narrow parallel rutile bands widening to consume the parent anatase as the phase transformation progressed. The Parallel bands exhibited a single dominant orientation across the entire film area. The morphology of rutile formation observed in this work has not been reported in the literature to date.

In undoped titania, rutile has been reported to nucleate at twin interfaces and form as lathes in the parent anatase with rutile {110} planes parallel to anatase {112} planes [51–53]. Based on these reports rutile formation as parallel plates within anatase grains may be possible however in the case of phase transformation in films of isotropic anatase grains no overall dominant rutile would be expected. For this reason the banded appearance of undoped films suggests that the high degree of orientation in the film as observed by XRD patterns plays a role in governing the orientation of rutile growth. Such preferential orientations are likely to be the result of the

interface with the single crystal quartz substrate. Consideration of film thickness and SEM micrographs suggests films synthesised in this work are likely to be of single grain thickness, particularly in the case of larger rutile grains, and this layer is likely to show significant substrate effect on crystallographic orientation.

The presence of continuous alternating bands of rutile and anatase as observed in undoped films was entirely absent from doped films. In doped films the rutile phase formed in segregated clusters or spots, shown in Figs. 5 and 6. This is likely to be due to the localisation of regions of increased oxygen vacancy levels owing to the segregation of anatase to rutile transformation enhancing dopants. As doped films were of similar thickness to undoped films we would expect similar substrate orientation effects as seen in undoped films, however anisotropic rutile growth was not observed in such films. This suggest localised effects of dopants outweigh crystallographic orientation effects in influencing the phase transformation behaviour in thin films.

4.4.3. Film morphology

SEM analysis of mixed phase undoped films revealed the presence of large consolidated grains alongside smaller grains shown in Fig. 4.7. This is likely to be the result of the significant grain coarsening which takes place as anatase transforms to rutile. In both phases little or no porosity is evident. The coarsening is significant as anatase grains of ~40nm transform to rutile of 300–400 nm size. This grain coarsening is consistent with reports in the literature and is generally considered detrimental to photocatalytic performance of titania as larger grains exhibit lower surface area [18, 48, 54, 55]. Phase transformation in doped samples was enhanced by the presence of low-valence species. This led to a more rapid transition to rutile and a smaller grain size of this phase in comparison with undoped films as seen in figure 8. The absence of larger consolidated grains in doped films is likely the result of a more homogeneous and rapid transformation brought on by the presence of diffused transformation-promoting dopants rather than the nucleation of rutile at twin interfaces as is the case with undoped material. It is further

possible that segregated dopants at grain boundaries impede the ionic rearrangement in the titania lattice and restrict grain coarsening in the course of the phase transformation. The transformation of anatase to rutile without significant grain growth as a result of doping has been reported elsewhere [55,56]. As films in this work are fully dense, the effect of grain growth on effective surface and adsorption of reactive species to the catalyst substrate is likely to be less significant in comparison with the use of powders in suspension or porous materials.

4.4.4. Optical properties

While the optical properties of thin films of TiO₂ are of significant importance in photocatalytic applications, UV-vis transmittance cannot be used to evaluate the photonic efficiency of such photocatalytic films as light that is not transmitted may be scattered or reflected. Furthermore an increase in optical absorbance does not necessarily infer an increase in exciton photo-generation. Thus it would be erroneous to make any assumptions regarding the merit of films as photocatalysts based on the measurement of optical properties.

From examination of Fig. 4.9 it is apparent that dopants bring about a reduction in optical transmittance. This effect is likely to be due to colour effects of the transition metal dopants used. These effects would be greater however the film thickness is less than the wavelength of the light used in UV-vis transmittance measurements. Co-doped films did not exhibit a notable change in optical properties suggesting that intervalence charge transfer between Cu²⁺ and Fe³⁺ does not take place to a significant extent.

The presence of rutile in the films altered the optical transmittance of the films shifting the absorption edge to higher wavelengths (lower photon energies). This change in optical absorption is a result of the lower band gap of rutile TiO₂ in comparison with anatase (~3.0eV vs. ~3.2eV) [11–13]. The presence of even a small level of rutile phase is sufficient to significantly alter the UV-vis transmittance, this is evident in the similarities between the transmittance of a 20% rutile film

and a 100% rutile film. This suggests that a small quantity of rutile may be sufficient to bring about a ~0.2 eV reduction in the band gap of TiO₂.

4.4.5. Photocatalytic performance

As demonstrated by the results from the control sample (a quartz substrate without a TiO₂ film), shown in Fig. 4.11, methylene blue concentrations are reduced by exposure to UV in the absence of a photocatalyst. The presence of TiO₂ only brings about a minor reduction in dye concentration in comparison with uncoated quartz suggesting poor photocatalytic activity. This low photocatalytic activity could be due to low TiO₂ surface area which results from the high density of the film evident in the SEM images shown in Fig. 4.7 and 4.8, and possible lack of dye molecule adsorption to the film surface.

Fig. 11 shows that photocatalytic photo-degradation of methylene blue was not noticeably enhanced in biphasic films and a comparison of the dye photo-degradation by single phase and mixed phase films does not show a significant variation despite the lower band-gap suggested by reduced optical transmittance of the mixed phase films in comparison with single phase anatase films. The presence of dopants appears to have negative effects on the performance of thin film photocatalysts this is likely to be due to dopants acting as charge carrier recombination centres as reported elsewhere. Photo-luminescence may be used in future experimentation to ascertain the effects of transition metal dopants on exciton lifetime.

4.5. Conclusions

- Sol-gel Synthesis of TiO₂ thin films on single crystal quartz substrates yielded highly oriented and thermally stable anatase.

- The addition of Cu enhances the transformation of anatase to rutile through an increase in oxygen vacancies in the TiO₂ lattice
- Undoped thin TiO₂ films on quartz substrates show the formation of rutile as oriented parallel bands in anatase.
- Transition metal dopants segregate in TiO₂ thin films and bring about a localised isotropic formation of the rutile phase.
- The presence of low levels of rutile is sufficient to alter the optical transmittance of TiO₂ thin films
- Transition metal doping and co-doping is detrimental to the photocatalytic performance of TiO₂ thin films

Acknowledgements

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5. Anodic aqueous electrophoretic deposition of titanium dioxide using carboxylic acids as dispersing agents

This chapter presents the published work which resulted from a collaborative research project carried out at the School of Materials and Environmental Engineering at the University of Modena and Reggio Emilia in Modena, Italy and at the School of Materials Science and Engineering at the University of New South Wales in Sydney Australia. This chapter as presented here has been published in the Journal of the European Ceramic Society, volume 31, issue 6, pages 1041–1047.

The work presented in this chapter, reports a novel approach for the immobilisation of titanium dioxide for photocatalytic applications. In contrast to the approach to TiO₂ immobilisation taken in the preceding chapter (Chapter 4), the use of electrophoretic deposition methods can be carried out at lower costs and enables the utilisation of prefabricated TiO₂ powders such as those which are reported in Chapter 8 of the present thesis.

A breakdown of the contributions of individual authors is shown in the table below:

	Primary Author	Manuscript Preparation	Literature Research	Experimental Work	Data Analysis	Editing and Revision	Supervisory Role	Formatting and Layout	Advice and Support	
Dorian A. H. Hanaor	✓	✓	✓	✓	✓	✓		✓		
Marco Michelazzi				✓					✓	
Charles C. Sorrell						✓		✓	✓	
Christina Leonelli							✓		✓	
Paolo Veronesi							✓			
Marcello Romagnoli							✓			

Key Findings

- The use of carboxylic acids (citric and oxalic) imparted strongly negative surface charge to TiO_2 particles in aqueous suspensions
- The electrokinetic properties of TiO_2 suspensions were analysed as a function of pH variation
- High absolute values of zeta potential and good dispersion of particles were achieved through the use of carboxylic acids
- The use of citric acid and oxalic acid facilitated anodic aqueous electrophoretic deposition at low pH levels
- Consistent thick films of TiO_2 exhibiting lower levels of bubble damage resulting from water electrolysis were achieved using carboxylic dispersion

Anodic Aqueous Electrophoretic Deposition of Titanium Dioxide Using Carboxylic Acids as Dispersing Agents

Dorian Hanaor,^{a,*} Marco Michelazzi^b, Paolo Veronesi^b, Cristina Leonelli^b, Marcello Romagnoli^b, Charles Sorrell^a

a: University of New South Wales, School of Materials Science and Engineering, Kensington NSW 2052, Australia

b: University of Modena and Reggio Emilia, Department of Materials and Environmental Engineering, 41100 Modena, Italy

* email: dorian@student.unsw.edu.au

Abstract: The dispersion of anatase phase TiO_2 powder in aqueous suspensions was investigated by zeta-potential and agglomerate size analysis. The iso-electric point (IEP) of anatase was determined to be at pH 2.8 using monoprotic acids for pH adjustment. In comparison, it was found that the use of carboxylic acids, citric and oxalic, caused a decrease in zeta-potential through the adsorption of negatively charged groups to the particle surfaces. The use of these reagents was shown to enable effective anodic electrophoretic deposition (EPD) of TiO_2 onto graphite substrates at low pH levels with a decreased level of bubble damage in comparison with anodic EPD from basic suspensions. The results obtained demonstrate that the IEP of TiO_2 varies with the type of reagent used for pH adjustment. The low pH level of the IEP and the ability to decrease the zeta-potential through the use of carboxylic acids suggest that the anodic EPD of anatase is more readily facilitated than cathodic EPD.

Keywords: Electrophoretic deposition; TiO_2 ; Zeta potential; Suspension; Microstructure-prefiring

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5.1. Introduction

Titanium dioxide is distinct in its ability to function as a photocatalyst due to the particular levels of its valence and conduction bands[1]. Titanium dioxide photocatalysts are of great interest owing to their ability to facilitate various reactions of environmental benefit. In recent years applications for which TiO_2 photocatalysis has been investigated include:

- Generation of hydrogen [2–6]
- Dye sensitised solar cells [7–9]
- Destruction of bacteria [10–14]
- Removal of contaminants from water [15–19]
- Self-cleaning coatings [20–23]

Titanium dioxide photocatalysts have been used in various forms including powders, thin films and thick films. Although powders often show higher performance than immobilised films, the significant disadvantage in using powders is the associated difficulty in catalyst recovery [24]. It is for this reason that the immobilisation of TiO_2 is often carried out. Immobilised TiO_2 is often synthesised by the use of precursor chemicals such as titanium alkoxides or titanium tetrachloride or through the use of pre synthesised TiO_2 powders.

Electrophoretic deposition, EPD, is a useful technique to immobilise powders from suspensions. In the process of EPD, charged particles move towards an oppositely charged electrode and form a stable deposit. EPD is generally followed by a densification process through thermal treatment. The process of EPD has been used with suspensions of TiO_2 in the past [25–27]. EPD synthesis of materials has several advantages:

- Cost effectiveness

- Ability to utilise fine powders
- Homogeneity of resultant coatings
- Ability to utilise suspensions of low solids loadings
- Simple apparatus requirements
- Binder-free process

EPD has been used to fabricate thick films on a variety of conductive and non-conductive substrates as well as being used to synthesise free-standing objects. The migration and deposition of suspended particles on to a positive electrode (anode) is known as anodic deposition while EPD on to a negative electrode (cathode) is known as cathodic deposition.

Charged particles in suspension are generally surrounded by an increased concentration of ions of opposite charge. During the process of electrophoresis, a layer of these ions migrate along with the particle. The potential at the slipping plane, between the layer of counter-ions which moves along with the particle and the bulk liquid, is known as the zeta (ζ) potential. Negative zeta potentials are used for anodic depositions while positive zeta potential values are necessary for cathodic EPD. Zeta potentials near zero give rise to agglomeration which is detrimental for either type of EPD.

The kinetics of electrophoretic deposition have been studied and various formulae are used in the analysis of electrophoretic processes. The Hamaker equation (Eq. 5.1) is a widely used kinetic model for EPD in planar geometries.

$$m = C_s \mu S E t \quad (5.1)$$

Here C_s is the solids loading (g cm^{-3}), μ is the electrophoretic mobility ($\text{cm}^2 \text{s}^{-1} \text{V}^{-1}$), S is the deposition area (cm^2), E is the electric field (V cm^{-1}) and t is time (s) [28–31].

The electrophoretic mobility represents the velocity at which a particle moves under the influence of an applied field and is generally expressed as shown in equation 5.2.

$$\mu = v/E \quad (5.2)$$

The velocity at which a particle moves is determined by the zeta potential. Equation 5.3 shows how the zeta potential can be used to express the electrophoretic mobility [29].

$$\mu = \frac{2\varepsilon_0\varepsilon_r\zeta}{3\eta} f(\kappa r) \quad (5.3)$$

Here ε_0 is the permittivity of free space, ε_r and η are respectively the permittivity and viscosity of the suspension medium, ζ is the zeta potential of particles in suspension and $f(\kappa r)$ is the Henry coefficient, which relates the thickness of the double layer to the radius of the suspended particle.

For a situation where the double layer is thin in comparison with the particle size, this can be approximated as equation 5.4 [28, 32]:

$$\mu = \frac{\varepsilon_0\varepsilon_r\zeta}{\eta} \quad (5.4)$$

As the Hamaker equation assumes 100% adhesion, i.e. all particles reaching the electrode remain in the EPD-formed deposit, it is appropriate to add an adhesion factor α , which accounts for the fraction of the deposit which remains on the electrode subsequent to extraction from the liquid medium. Therefore, if we assume a constant solids loading and electric field strength in the suspension, the Hamaker equation can be written as shown in equation 5.5.

$$m = \frac{\alpha C_s \varepsilon_0 \varepsilon_r \zeta S E t}{\eta} \quad (5.5)$$

It can be seen from equations 5.4 and 5.5, that for a given experimental setup, suspension medium and suspended powder, variation of the zeta potential can be used to control the electrophoretic mobility and thus the EPD rate. This can be achieved by acidity regulation. Typically, the zeta potential increases with increasing pH, and pH modification can be used to control the performance of EPD processes. Zeta potential behaviour is generally consistent regardless of the acids or bases used to modify the pH, and there exists a specific pH at which the

zeta potential equals zero. This pH level is widely known as the iso-electric point (IEP), or point of zero charge.

The use of citric acid and other carboxylic acids has been reported to give rise to a lower zeta potential, bring the IEP down to a lower pH, and enhance dispersion of alumina particles in suspension [33, 34] this behaviour can be explained by the adsorption of negatively charged groups on the particle surface.

The IEP of titanium dioxide has been reported to be around pH 6 [35–37]. This would imply that suspensions most suitable for electrophoretic depositions are on either side of this value. Several studies have investigated cathodic deposition of TiO_2 onto conductive substrates [25, 38, 39]. And the use of basic pH levels to facilitate anodic EPD has also been reported [40]. Many studies into electrophoretic deposition have used non-aqueous suspension media, typically organic media such as alcohols or acetone [31]. Water is problematic as a suspension medium due to the parasitic process of water electrolysis which takes place during the deposition and can cause gas bubbles to accumulate at the electrode surfaces to the detriment of the electrophoretically deposited coating. Despite this phenomenon, using water as a suspension medium is attractive as it has a lower environmental impact than organic media and is easier to upscale to an industrial size process.

5.2. Materials and methods

High purity anatase powder (>99%) supplied by Merck Chemicals was used in all experiments in this work. The powder was washed with distilled water and recovered by centrifugation to remove surface contamination that may have imparted a surface charge. Suspension parameters of agglomerate size, zeta potential and electrophoretic mobility were measured using a Malvern

Instruments Nano Series Zetasizer. All suspensions were made using distilled water as a suspension medium. Due to the high opacity of anatase suspensions, for zeta potential and agglomerate size analysis suspensions of 0.05 wt% ($5 \times 10^{-4} \text{ g cm}^{-3}$) were used. To determine the typical effect of acidity on zeta potential and agglomeration, pH levels were varied with nitric acid / ammonium hydroxide and hydrochloric acid / sodium hydroxide. The effects of carboxylic acids on suspension properties were investigated by the use of citric and oxalic acids as pH varying agents. To achieve basic pH levels, solutions of the carboxylic acids with NaOH at a 1:4 molar ratio were employed to give basic pH levels while maintaining levels of carboxylic groups in solution sufficient to saturate particles surfaces [33].

Anodic electrophoretic depositions were carried out onto 25 x 25 x 2 mm graphite substrates immersed in the suspensions to a depth of 10 mm. Prior to depositions, the graphite substrates were ultrasonically cleaned in acetone of purity >99.5%, from Sigma Aldrich (<0.5% H_2O , <0.05% isopropanol, <0.05% methanol, <0.001% evaporation residue). Subsequent to acetone cleaning, substrates were dried at 110°C and adhesive tape was applied as an insulating backing. It is possible that residues resulting from acetone cleaning have a detrimental effect on the adhesion of thick films to the graphite substrates, however as the evaporation residue of the acetone used is reported at <0.001% this is unlikely to be a significant factor in the current work. Graphite substrates were chosen for the EPD of TiO_2 as carbon diffusion into TiO_2 coatings may improve photocatalytic performance as suggested by results of other work [41]. Furthermore the graphite may act as a reducing agent and increase oxygen vacancy levels in the anatase thus lowering the anatase to rutile transformation temperature and enabling the formation of mixed anatase/rutile TiO_2 photocatalysts at temperatures lower than what would otherwise be possible on metallic substrates [42]. The formation of such a mixed- phase composition may too be favourable for photocatalytic performance based on previous publications [43–45].

Anodic EPD experiments used aqueous suspensions of 1 wt% (0.01 g cm^{-3}) anatase solids loadings. Depositions utilised the same pH adjustment reagents used for zeta potential and agglomerate size analysis. Electrophoretic depositions lasting 10 minutes were carried out using a 10 V DC power supply with a strip of gold foil as a cathode (counter electrode) and the graphite substrates as anodes (working electrodes). These electrodes were separated by 20 mm. Electrical contact to the electrodes was made with alligator clips. The applied voltage was maintained during the slow extraction of the working electrode from the suspension to minimise coating removal during extraction.

The quality of the coatings achieved by EPD was assessed by optical microscopy and scanning electron microscopy (SEM) using a Hitachi S3400 microscope.

5.3. Results

5.3.1. Suspension properties

Standard variation of zeta potential was investigated by varying pH levels with commonly used monoprotic acids and bases. This is shown in **figure 5.1**. The resultant variation of zeta potential with acidity appears consistent for both sets of reagents and it can be seen that the IEP appears to be around pH 2.80. This figure is lower than what has been reported previously as the IEP of TiO_2 . Values for electrophoretic mobility were also recorded from the apparatus used. These values were found to show a linear relationship with the values recorded for zeta potential. This is expected as parameters in equation 5.4 remain constant apart from ζ potential.

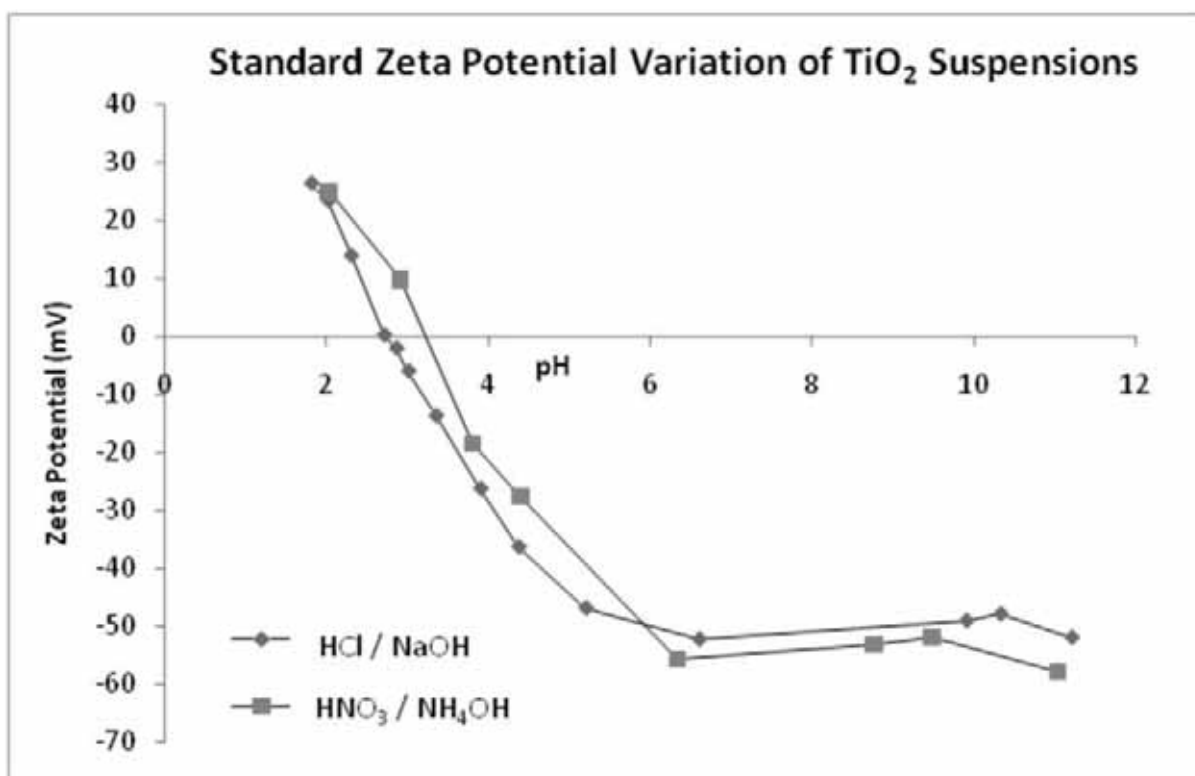


Fig. 5.1. Zeta potential of TiO_2 as a function of pH value adjusted with typical acids and bases.

Figure 5.2 shows the typical agglomeration behaviour of TiO_2 suspensions using nitric acid and ammonium hydroxide as pH adjusting agents. Due to equipment limitations non-agglomerated suspensions were found generally to return a value of 300–400nm for agglomerate size. This is not necessarily a true indication of particle size in non-agglomerated suspensions.

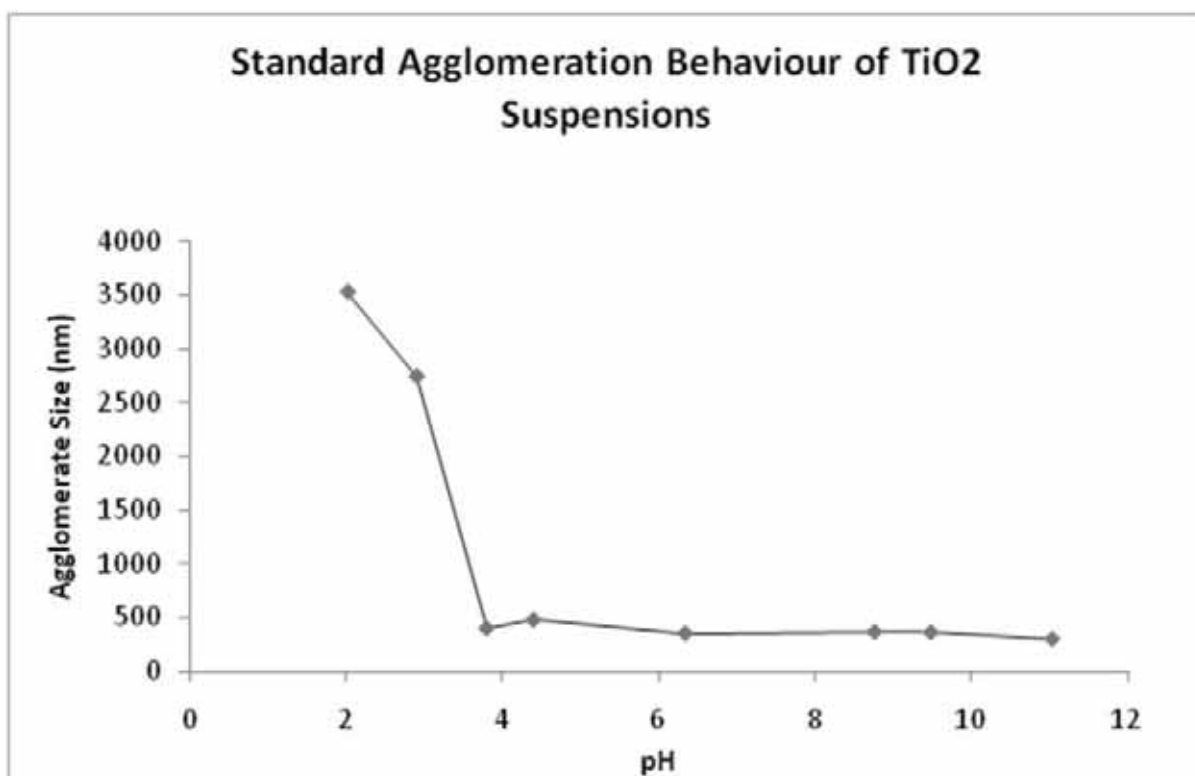


Fig. 5.2. Agglomerate size of TiO_2 suspensions as a function of pH value adjusted with nitric acid and ammonium hydroxide.

In contrast to the use of monoprotic acids, the use of citric acid resulted in a negative zeta potential at all pH levels. The zeta potential rises as pH decreases however when using citric acid for pH adjustment, the suspension did not appear to reach a point of zero charge (IEP). Flocculation was observed to take place at lower pH levels despite the negative zeta potential values recorded.

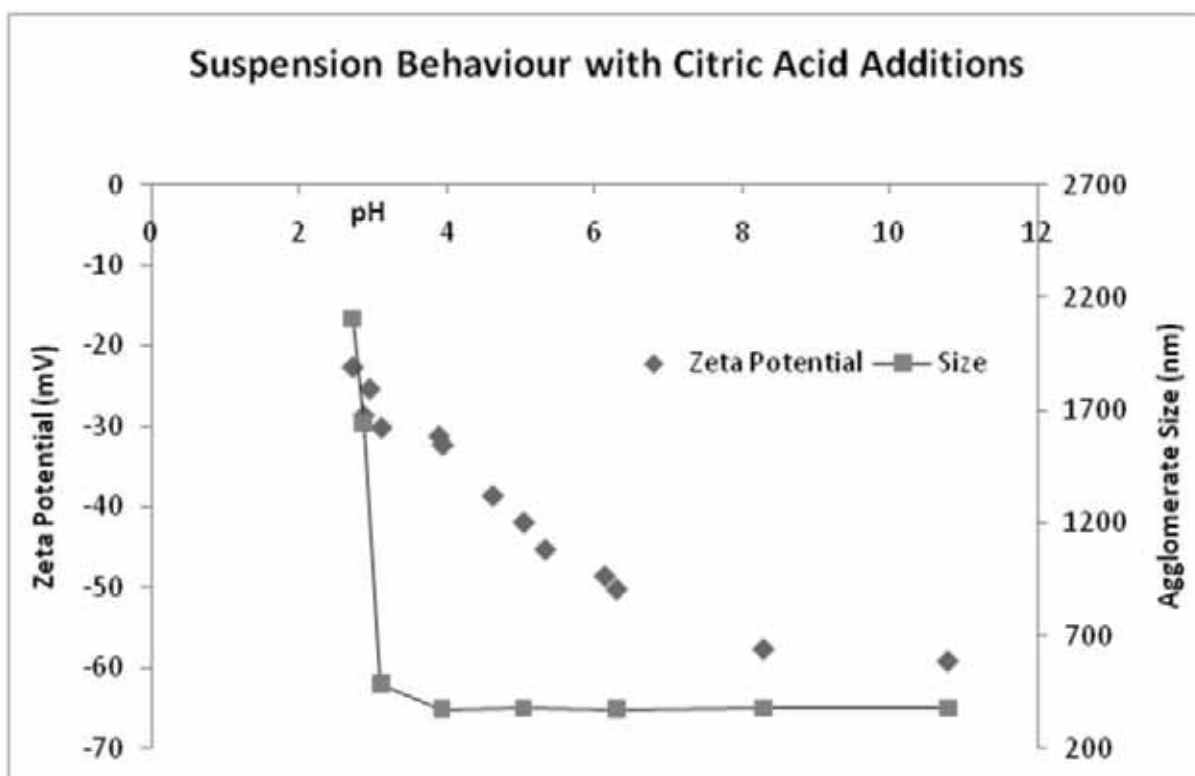


Fig.5.3. Zeta potential and agglomerate size as a function of pH value adjusted with citric acid.

The use of oxalic acid resulted in negative zeta potential values slightly lower than those obtained with the use of citric acid. Again a point of zero charge was not reached. In similarity to the case of citric acid, flocculation occurred in suspensions of low pH showing negative zeta potentials.

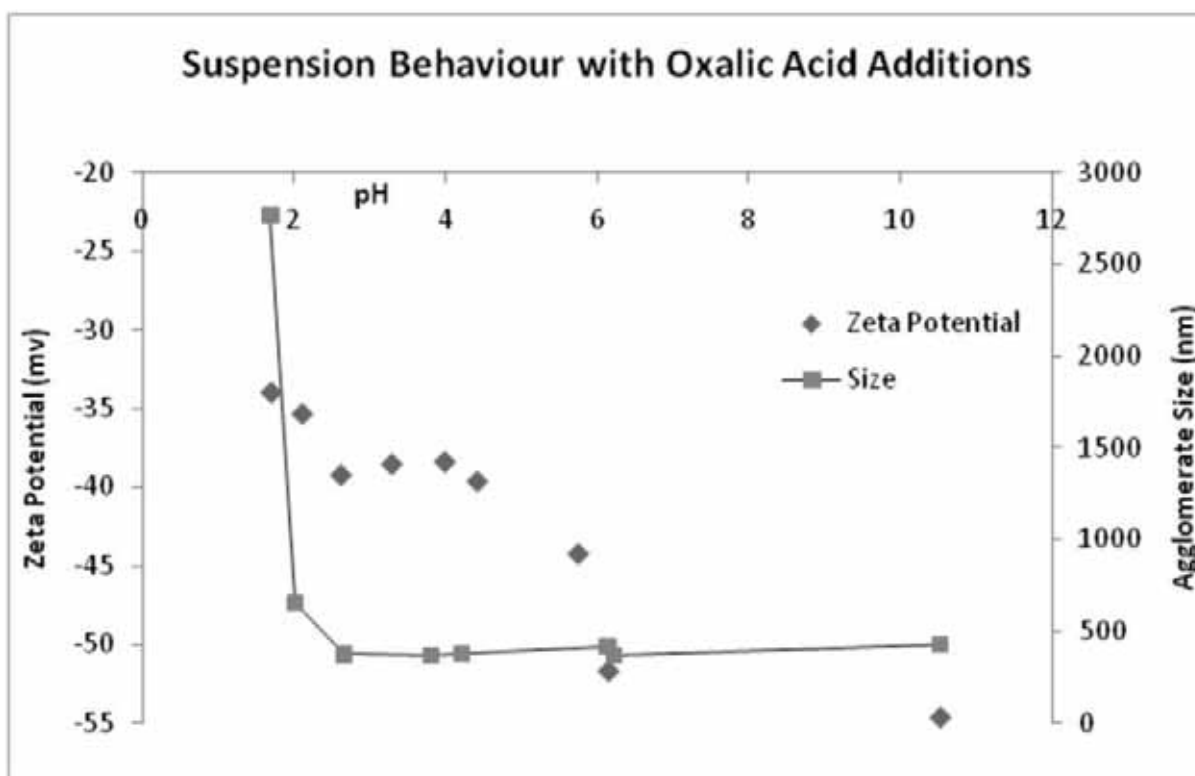


Fig. 5.4. Zeta potential and agglomerate size as a function of pH value adjusted with oxalic acid.

5.3.2. EPD coatings

Electrophoretic depositions were carried out using the same reagents described in the preceding section to impart acidic and basic pH levels to the suspensions. The weight of the graphite substrate before and after the deposition along with the dimensions of the coated area was used to determine the deposited mass per unit area, reported in mg cm^{-2} . The calculated mass was determined using the Hamaker equation (eq. 5.1) in conjunction with electrophoretic mobility readings. This calculation did not take into consideration the insulation effects of the coating on the electrical field strength, which was taken as 5 V cm^{-1} , and the decrease in the solids loading of the suspension as deposition proceeded. The results of electrophoretic depositions are outlined in Table 5.1.

Table 5.1. Electrophoretic deposition data.

	Reagent	pH	ζ potential (mv)	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) $\times 10^{-4}$	Deposited Mass (mg cm^{-2})	Calculated Mass (mg cm^{-2})
Acidic	Nitric Acid	3.62	-10.86	-0.85	0.88	2.54
	Citric Acid	3.80	-33.73	-2.63	4.14	7.89
	Oxalic Acid	3.30	-38.73	-3.02	7.82	9.06
Basic	NaOH	10.71	-59.88	-4.67	8.18	14.01
	Citric + NaOH	10.57	-59.28	-4.66	8.52	14.00
	Oxalic + NaOH	11.80	-56.92	-4.43	12.36	13.32

The comparison of the calculated deposit mass according to eq. 5.1 with the measured deposit mass resulting from anodic electrophoretic depositions from acidic suspensions using different pH adjustment agents is illustrated in figure 5.5. The use of carboxylic acids significantly raised the deposition rate at lower pH levels. At basic pH levels the use of carboxylic acids had a less marked effect on deposition rates although some effect was observed, this can be seen in figure 5.6.

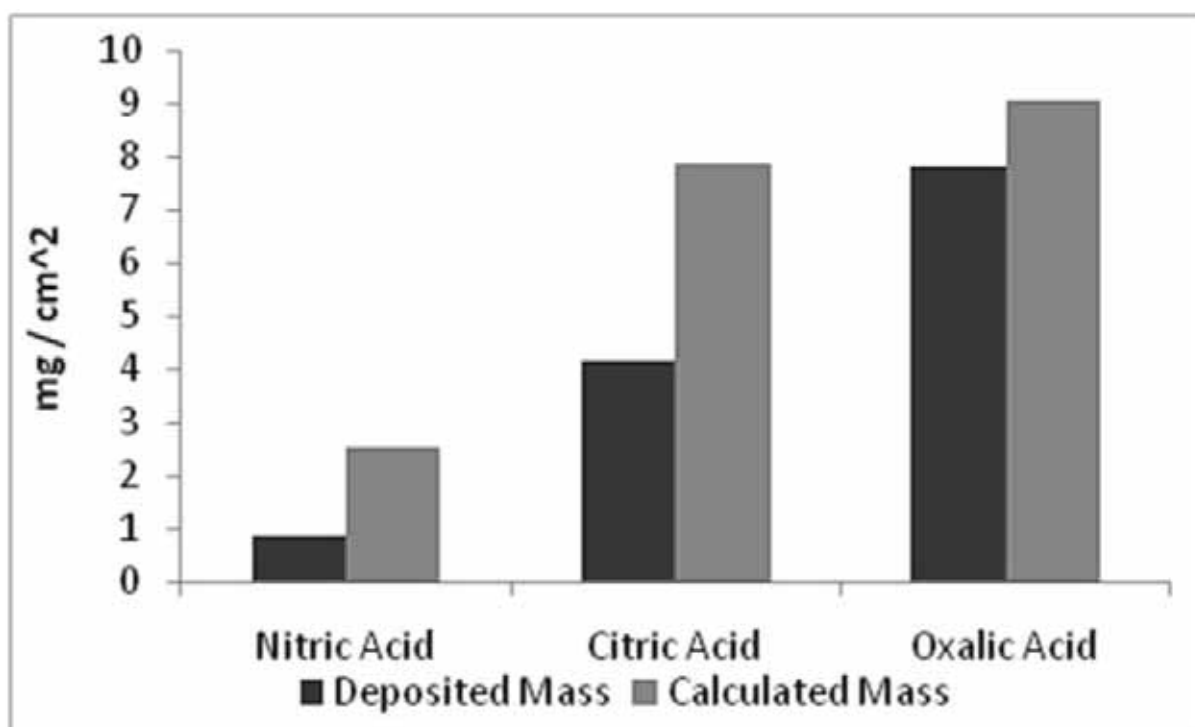


Fig. 5.5. Comparison of actual deposit mass with calculated deposit mass from acidic suspensions using different pH adjusting agents

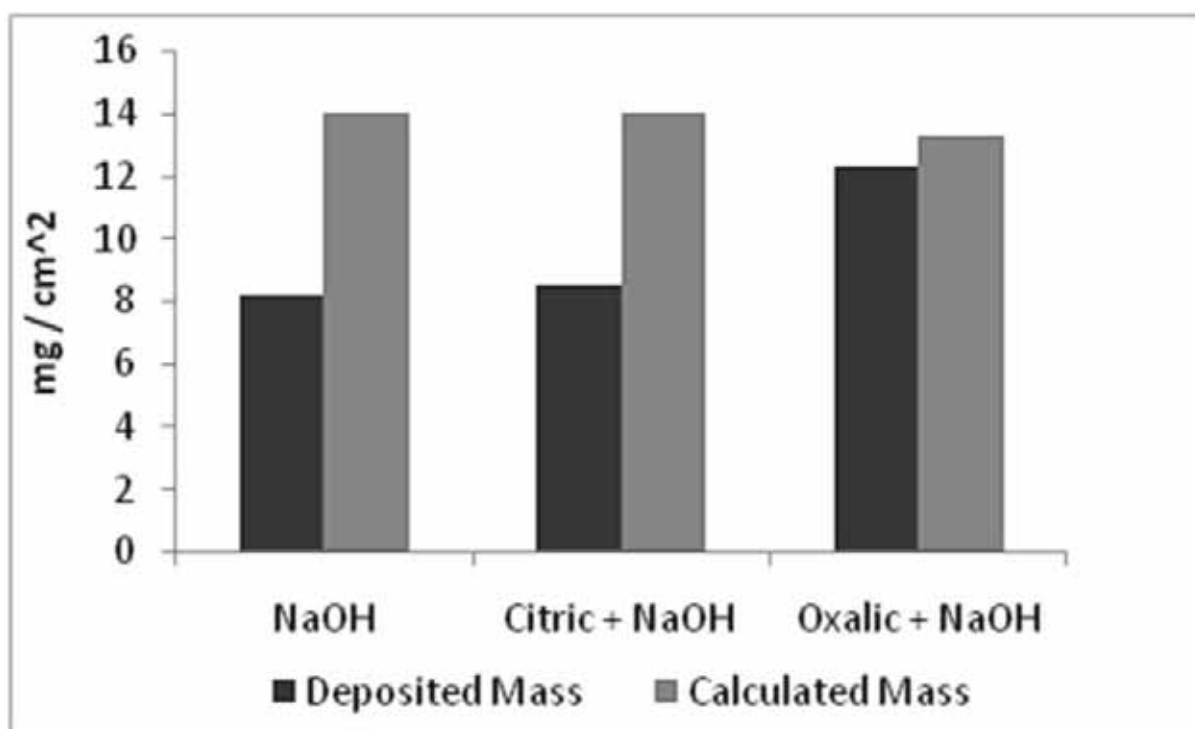


Fig. 5.6. Comparison of actual deposit mass with calculated deposit mass from basic suspensions using different pH adjusting agents.

Images of the deposited material were taken by optical microscopy and scanning electron microscopy. These images show surfaces marked with pinholes resulting from gas bubbles trapped in the coating. These gas bubbles are likely to be the result of the electrolysis of water, a parasitic process discussed earlier. Coatings made with acidic pH levels adjusted by oxalic and citric acids were fairly consistent with many small pinholes of 5–10 μm in size (Figure 5.7). Coatings made from acidic suspensions with nitric acid were irregular and coverage was poor (Figure 5.8). This is consistent with the low level of deposited mass per unit area measured. Coatings made from basic suspensions showed more extensive evidence of gas bubble damage to the electrophoretically deposited coating, with holes or craters ranging from 20–50 μm in size as

seen in Fig. 9, suggesting greater levels of water electrolysis or larger gas bubbles at the electrode / suspension interface.

The microstructure of the deposit can be seen in the SEM micrograph in Fig. 10. The grains are in the region of 200 nm in size. This is due to the morphology of the anatase powder used in the EPD processes this structure was consistent across all samples fabricated.

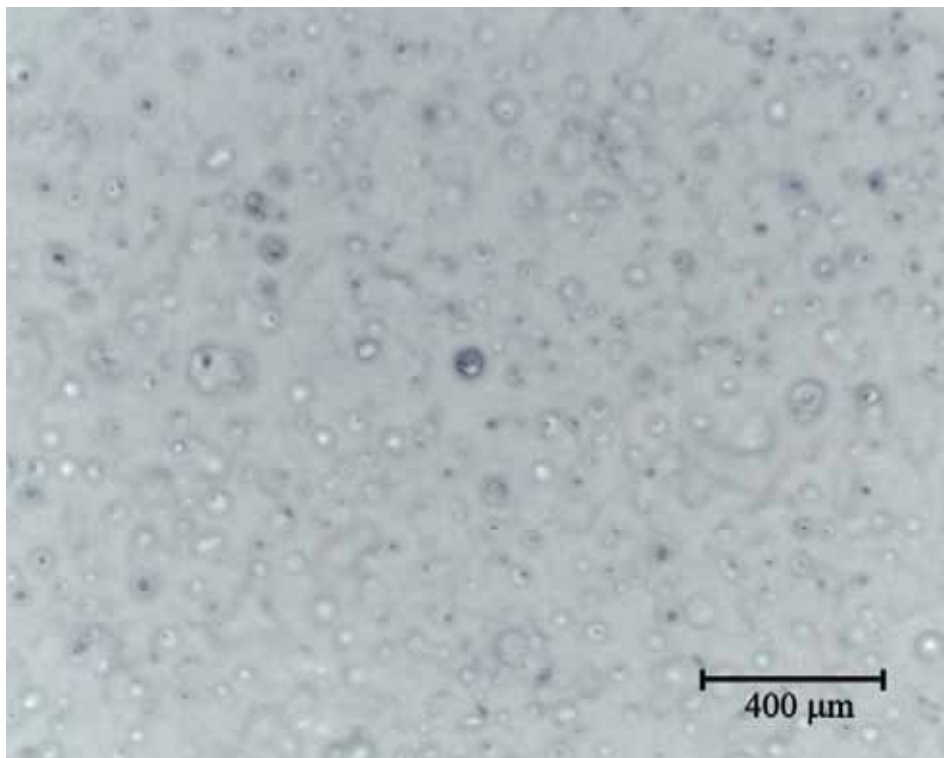


Fig. 5.7. EPD coating typical of those produced from acidic suspensions with pH adjustment by carboxylic acids.

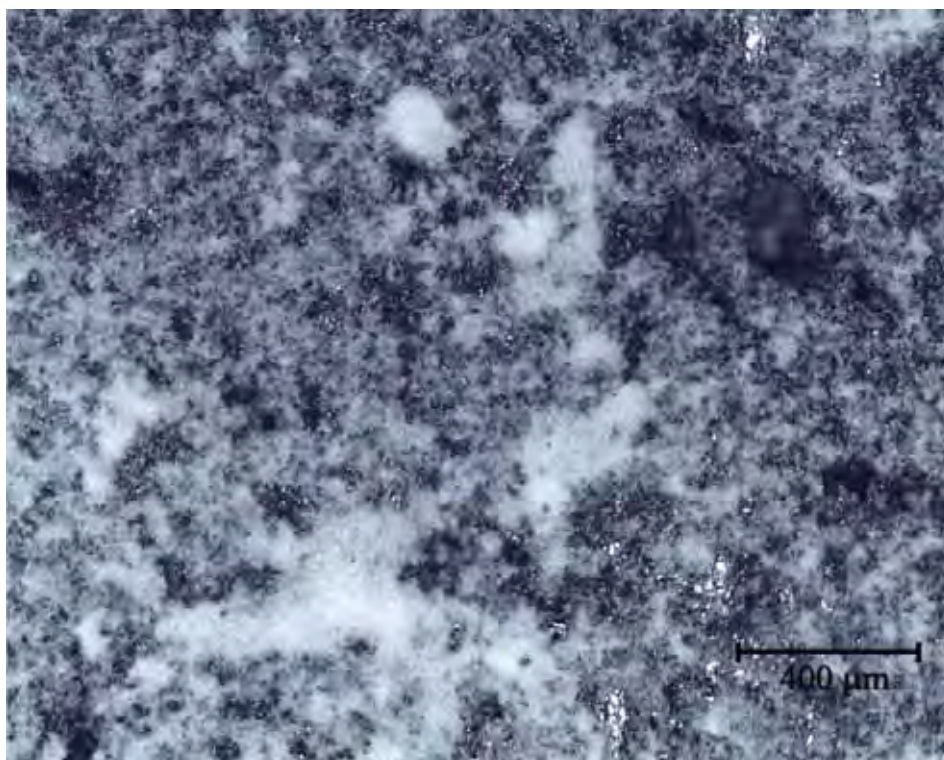


Fig. 5.8. EPD coating produced from an acidic suspension with pH adjustment by Nitric Acid.

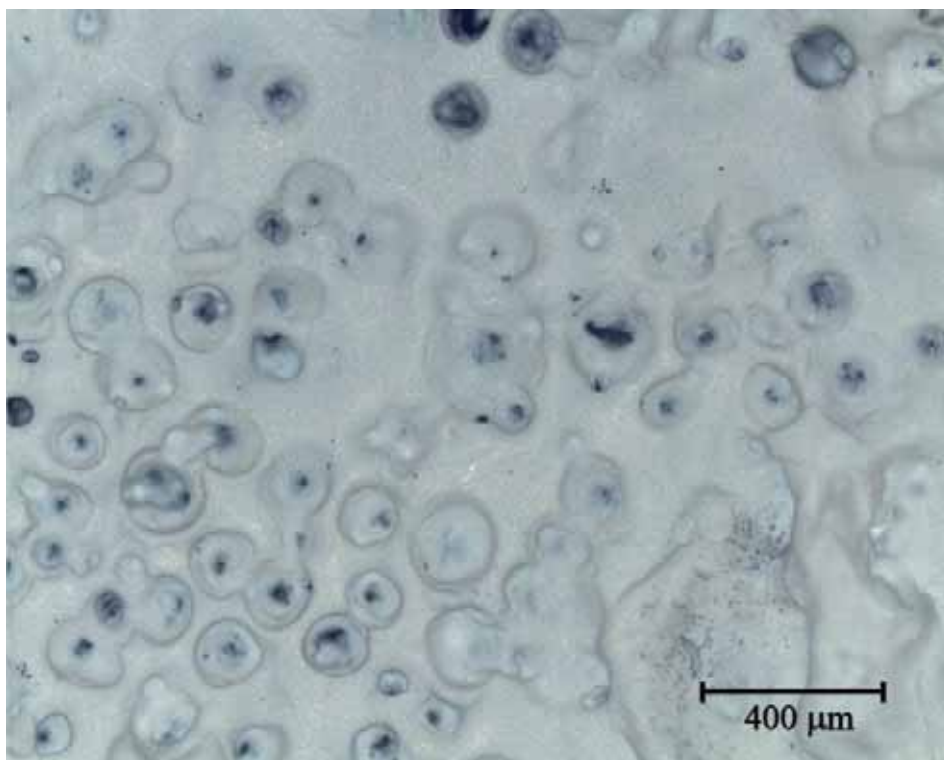


Fig.5.9. EPD coating typical of those produced from basic suspensions with pH adjustment by sodium hydroxide.

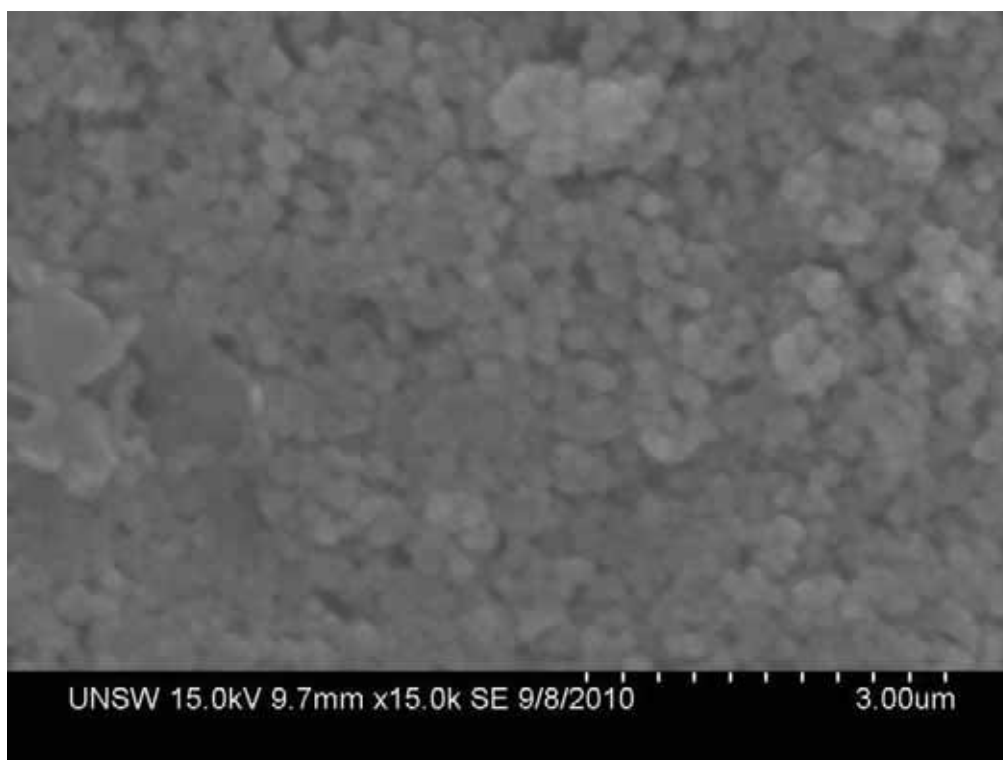


Fig.5.10. Microstructure of deposited anatase.

5.4. Discussion

The variation of the zeta potential of aqueous TiO_2 suspensions with conventional pH adjustment showed typical behaviour with positive values at low pH values decreasing to negative values at higher pH levels. The behaviour of such suspensions appeared to be divergent from what has been reported previously in that the IEP was determined to at pH 2.8. This is a lower figure than what has been observed in other work and suggests that anodic EPD is more readily facilitated than cathodic EPD with aqueous suspensions of TiO_2 . The discrepancy between IEP valued from this work and those obtained elsewhere could be due to impurities in the material used as low levels of impurities in the suspended particles or in the suspension medium can profoundly affect the zeta potential [46, 47]. Although the anatase used in this work was of high purity and had

undergone washing, it is possible that the presence of acidic groups on the surface brought the IEP down to lower levels as reported elsewhere [48, 49].

In comparison with pH adjustment by monoprotic acids, hydrochloric and nitric, the use of citric and oxalic acids, tri-carboxylic and bi-carboxylic acids respectively, was shown to bring about significantly lower zeta potential values and thus lower electrophoretic mobility values in suspensions of TiO_2 across all pH levels these values remained negative even at low pH levels. This phenomenon is likely to be due to negative citrate and oxalate ions adsorbed on the TiO_2 surfaces and imparting a negative charge to these particles. It has been reported that negative monovalent citrate ions show stronger adsorption to surfaces in comparison with the fully protonated citric acid and this preferential adsorption may occur with the use of other carboxylic acids [50]. This preferential adsorption of negatively charged groups may explain the negative zeta potential values imparted by the carboxylic acids used in this work at lower pH values. Similar observations of lowered zeta potential values were reported from experiments using citric acid as a low molecular weight dispersant for Al_2O_3 particles in aqueous suspension where it was reported that two of the three carboxylic groups of the citric acid coordinate to the alumina surface [33].

Despite the negative zeta potential values, acidic TiO_2 suspensions adjusted by means of carboxylic acids used in this work exhibited agglomeration at pH levels around 2. As citric and oxalic are weak acids, high concentrations of these reagents were necessary to achieve low pH levels. It is likely that the high levels of protonated citric and oxalic groups in aqueous solution lead to a decrease in the volume of the liquid sphere which moves along with the particle in suspension and thus allows the particles to approach each other, facilitating agglomeration [27, 32, 33].

Citric and oxalic acids were successfully used to facilitate anodic electrophoretic depositions of TiO_2 onto graphite substrates at low pH levels. The negative zeta potential achieved through the use of these reagents enabled high deposition rates in comparison with depositions which utilised

monoprotic nitric acid to impart acidity. While the measurement of the deposited mass per unit area is likely to vary due to experimental inaccuracies associated with weighing the substrates before and after deposition, it was clear that the use of carboxylic acids to impart low pH levels was advantageous for anodic EPD from acidic suspensions. Anodic EPD from basic suspensions were fairly rapid with and without the use of carboxylic acids. Although the use of carboxylic acids along in basic suspensions did seem to bring about a higher deposit mass, this improvement was less significant than in the case of acidic suspensions. The good levels of deposit mass in EPD from all basic suspensions are likely to be a result of low zeta potential levels associated with high pH suspensions, however the apparent drawback of such depositions was the apparent increased extent of water electrolysis that was evident through the presence of large craters due to gas bubbles in the deposited thick films achieved from basic suspensions. This phenomenon can be explained by the increased electrolysis of water at high pH levels that has been reported elsewhere [51]. This highlights the advantages of the use of lower pH suspensions for aqueous electrophoretic depositions and the use of carboxylic acids as low molecular weight dispersants to achieve such depositions.

The use of polyelectrolyte dispersants such as poly-acrylates is a widespread method to enhance the dispersion of ceramic particles in suspension [52, 53]. The use of carboxylic acids as alternative lower molecular weight dispersants has advantages over the use of long-chain molecules of due to higher adsorption ability, greater chemical stability, lower cost and a lower environmental impact than such high molecular weight additives [34, 54, 55].

Further work may investigate the sintering of TiO_2 coatings such as those synthesised in this work and the resultant photocatalytic performance of these materials.

5.5. Conclusions

Citric and oxalic acids, compounds with multiple carboxylic groups bind to TiO_2 particle surfaces, and impart strongly negative zeta potential values and a greater electrophoretic mobility to these particles in aqueous suspensions. Thus such reagents can be used as low molecular weight dispersants for aqueous suspensions of TiO_2

Effective anodic electrophoretic deposition from acidic suspensions can be facilitated through the use of carboxylic acid additions. This may improve the quality of the electrophoretically deposited coating in comparison with the use of basic suspensions through lower levels of water electrolysis and associated gas bubbles in the deposits.

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6. The effects of firing conditions on the properties of electrophoretically deposited titanium dioxide films on graphite substrates

This chapter presents an article published in the Journal of the European Ceramic Society, volume 31, issue 15, pages 2877–2885. The research project reported in this paper builds on the fabrication methods developed as part of the collaborative effort reported in Chapter 5 and explores the effects of different firing atmospheres and temperatures on the properties of thick graphite supported TiO₂ films.

Phenomena investigated in Chapter 3 are highly relevant to the observed phase transformation behaviour reported in this chapter. As expected based on the predictive analysis carried out in Chapter 3, the presence of reducing effects from the carbon substrate and a nitrogen firing atmosphere bring about an enhancement of the anatase to rutile phase transformation relative to unsupported powder and the formation of a mixed phase composition at lower temperatures.

The single and mixed phase materials fabricated in the course of the work presented in this chapter were evaluated in water purification applications by the inactivation of *E. coli* bacteria. This approach is highly relevant to the application of such materials in real world scenarios, where bacterial contamination prevents the safe usage of water resources.

	Primary Author	Manuscript Preparation	Literature Research	Experimental Work	Data Analysis	Editing and Revision	Supervisory Role	Formatting and Layout	Advice and Support	
Dorian Hanaor	✓	✓	✓	✓	✓	✓		✓		
Marco Michelazzi									✓	
Charles C. Sorrell						✓		✓	✓	
Christina Leonelli							✓		✓	

Key Findings

- Thick electrophoretically deposited films on graphite substrates fired in nitrogen exhibited superior photocatalytic performance relative to air fired samples as determined by the photocatalysed inactivation of bacteria
- Graphite substrates enhance the anatase to rutile phase transformation relative to unsupported commercially available TiO₂ powders, likely through increased oxygen vacancy levels
- Nitrogen doped films exhibited higher levels of excitation as determined by photoluminescence
- Significant grain growth occurs in the transformation of anatase to rutile

The Effects of Firing Conditions on the Properties of Electrophoretically Deposited Titanium Dioxide Films on Graphite Substrates

Dorian Hanaor,^{a,*} Marco Michelazzi^b, Jeremy Chenu^c, Cristina Leonelli^b, Charles Sorrell^a

a: University of New South Wales, School of Materials Science and Engineering, Kensington NSW 2052, Australia

b: University of Modena and Reggio Emilia, Department of Materials and Environmental Engineering, 41100 Modena, Italy

c: University of New South Wales, School of Chemical Engineering, Kensington NSW 2052, Australia

**Corresponding author, email: dorian@student.unsw.edu.au Ph: 61-404-188810*

Abstract: Thick anatase films were fabricated on graphite substrates using a method of anodic aqueous electrophoretic-deposition using oxalic acid as a dispersant. Thick films were subsequently fired in air and in nitrogen at a range of temperatures. The morphology and phase composition were assessed and the photocatalytic performance was examined by the inactivation of *Escherichia coli* in water. It was found that the transformation of anatase to rutile is enhanced by the presence of a graphite substrate through reduction effects. The use of a nitrogen atmosphere allows higher firing temperatures, results in less cracking of the films and yields superior bactericidal performance in comparison with firing in air. The beneficial effects of a nitrogen firing atmosphere on the photocatalytic performance of the material are likely to be a result of the diffusion of nitrogen and carbon into the TiO₂ lattice and the consequent creation of new valence band states.

Keywords: Photocatalysis; Films; TiO₂; Substrates; Sintering

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6.1. Introduction

The development of novel approaches to water purification is of increasing importance as population growth and climate change place a growing strain on water resources [1, 2]. Photocatalysis is an attractive approach to water treatment as this technique does not involve the consumption of chemical reagents, enables the removal of a variety of pollutants, is effective across a wide range of pollutant concentration levels and can be achieved using solar irradiation as the sole energy input [3–5].

Owing to the distinct levels of its valence and conduction bands, TiO₂ has emerged as the leading material in photocatalytic applications [6, 7]. TiO₂ photocatalysis takes place through the photo-generation of an electron-hole pair, an exciton, by irradiation exceeding the band gap of the material. This leads to the generation of surface adsorbed radicals and subsequent oxidation of organic pollutants on TiO₂ surfaces [8]. The two phases of titanium dioxide most commonly used in photocatalysis are anatase and rutile. Despite the slightly larger band gap of anatase (~3.2eV vs. ~3.0eV), this phase is widely considered to exhibit superior photocatalytic activity as a result of greater levels of surface adsorbed radicals [9–12]. It has been frequently reported that mixed-phase TiO₂ exhibiting low levels of rutile alongside anatase exhibits enhanced performance through reduced electron-hole recombination [13–17].

As photocatalyzed destruction of pollutants takes place at close proximity to TiO₂ surfaces, a high surface area is advantageous for effective rates of pollutant removal [18]. For this reason studies of water purification by TiO₂ photocatalysts are often carried out using aqueous suspensions of powder [19, 20]. The disadvantage of using TiO₂ in the form of a powder suspended in the treated

water is the required catalyst recovery processes, for this reason the immobilisation of TiO₂ is frequently carried out [21–24].

Electrophoretic deposition (EPD) is a practical method for immobilising TiO₂ photocatalysts as it enables rapid sample fabrication from suspensions of low solids loading [25–27]. The current work examines the effects of firing conditions on the microstructure and performance of thick films prepared by anodic electrophoretic deposition of anatase TiO₂ onto graphite substrates. As carbon has been reported to enhance the anatase to rutile phase transformation and lower the band gap in TiO₂[28–30], this method of fabrication may improve photocatalytic performance by yielding bi-phasic TiO₂ at lower temperatures and through carbon doping of the photocatalyst layer.

6.2. Experimental procedure

6.2.1. EPD

Thick TiO₂ films were prepared through anodic EPD from acidic aqueous suspensions adjusted to pH~ 3 using oxalic acid. As reported elsewhere, the use of oxalic acid imparts a negative zeta potential to TiO₂ particles in suspension and thus facilitates anodic EPD from acidic aqueous suspensions with lower levels of water electrolysis [31]. Using a solids loading of 1%, a deposition voltage of 10 V and a deposition time of 10 min, TiO₂ anatase powder (>99%, Merck Chemicals) with a BET evaluated surface area of ~10 m²g⁻¹, was deposited on 25 x 25 x 2 mm graphite substrates (GrafTech International, Ohio, USA). The average density of 8 thick films prepared was evaluated to be 64.5 gm⁻² with a standard deviation of 12.2 gm⁻² and from cross sectional examination the thickness was found to be ~80 µm.

6.2.2. Sintering

Anatase films deposited on graphite substrates were fired in air using an electric muffle furnace in the range 500°–700°C. Graphite substrates were completely burnt off at 700°C when fired in air, while samples fired at lower temperatures exhibited poor adhesion and substrate deterioration. Samples fired in nitrogen were fabricated in a tube furnace at temperatures 500–900°C with high purity nitrogen flowing through the tube at 1 l min⁻¹. Subsequent to firing, no substrate deterioration was observed in nitrogen fired samples and films showed good adhesion to substrates, although some loosely adhered particles were present.

- -

6.2.3. Microstructural analysis

Scanning electron microscopy (SEM) and optical microscopy were employed to examine the microstructure of films synthesised in this work. SEM analysis was facilitated using a FEI Nova-230 SEM. Phase identification by laser Raman microspectroscopy was facilitated using a Renishaw inVia Raman microscope with laser excitation at 514 nm wavelength. Quantitative phase analysis by X-ray Diffraction was carried out using a Phillips MPD unit. Phase fractions were calculated from XRD peaks using the method of Spurr and Myers according to the following equation [32].

$$X_A = (1 + 1.26 \frac{I_R}{I_A})^{-1} \quad (6.1)$$

In this equation X_A is the phase fraction of anatase (assumed $X_A=1-X_R$) and I_R and I_A are respectively the intensity of the rutile (110) peak at 27.35° 2θ and the anatase (101) peak at 25.18° 2θ.

6.2.4. Bactericidal activity

Bactericidal activity of the samples fabricated in this work was assessed by the inactivation of *Escherichia coli* (*E. coli*) AN180 (School of Biotechnology and Biomolecular Sciences, UNSW, Australia) in aerated water, a common approach to evaluating the bactericidal activity of TiO₂ photocatalysts. A diagram of the bactericidal reactor is shown in Fig. 6.1.

Bactericidal evaluation was carried out by adding 2 ml of overnight-incubated *E. coli* culture in Tryptone Soy Broth (Oxoid, Basingstoke, UK) to 300 ml of autoclaved distilled water in which photocatalyst samples were placed. The system was irradiated by two 15W UV lamps with emission peaks at $\lambda=350$ nm. Using a Digitech QM1587 Light Meter, irradiance was evaluated to be 4.42 Wm⁻¹ at the photocatalyst surface.

The destruction of bacteria was evaluated by determining the concentration of colony forming units (CFUs) in the treated water according to ASTM D5465. 1 ml aliquots of water were taken at fixed time intervals and serially diluted at 1:9 ratios in sterile 0.1% peptone water (Oxoid). Subsequently, 0.1 ml aliquots of the appropriate dilutions were spread-plated on Tryptone Soy Agar (Oxoid) and the plates were incubated for 24 hours at 37°C. After incubation, colonies were enumerated and counts converted to log₁₀ CFU/ml, representing the concentration of bacteria in the reactor water.

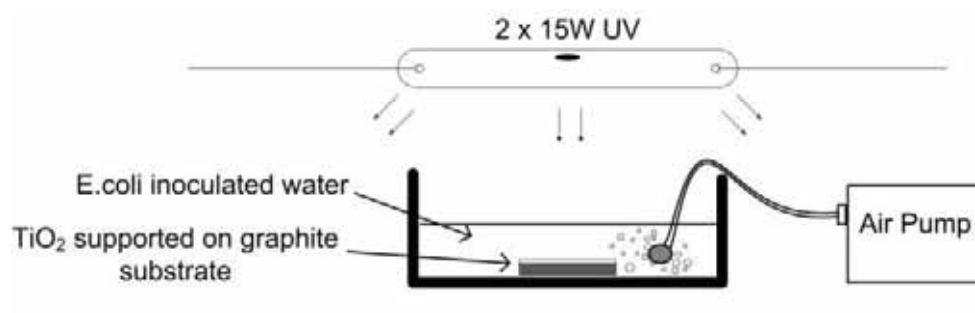


Fig. 6.1. Diagram of bactericidal reactor.

6.2.5. Spectroscopy

The radiative recombination of photogenerated electron-hole pairs in the different samples was studied by examining the intensities of photoluminescence (PL) emission spectra. This was carried out by gathering diffuse spectra in the range 350–900 nm (~3.5–1.4 eV) using a Kimmon 20 mW 325 nm He-Cd laser in conjunction with a Renishaw inVia Raman microscope.

UV-visible absorbance spectra were gathered to examine the shift in the absorption edge and overall absorbance between the different samples. These spectra were gathered using a Perkin-Elmer Lambda-35 UV-vis spectrometer with a Labsphere RSA-PE-20 integrating sphere of 50 mm diameter. Scans were carried out in the wavelength range 200–700 nm with a 2 nm slit width.

6.3. Results

6.3.1. Microstructure

The prefiring microstructure of all thick films prepared in this work exhibited gas-bubble damage resulting from the parasitic process of water electrolysis as shown in Fig. 6.2. Holes resulting from bubble damaged ranged from ~5 to ~50 μm in size. Samples fired in air at 700°C exhibited complete oxidation of the graphite substrate, leaving behind a fragile unsupported TiO₂ film. Samples fired in air at 500 and 600°C exhibited substrate deterioration through partial oxidation, resulting in spalling and poor adhesion of deposited films. Samples fired in nitrogen did not exhibit substrate deterioration and resulted in well adhered films showing less cracking as evident from the comparison of Fig. 6.3a and 6.3b. For samples fired at 600°C the grain size consisted of

anatase grains of ~ 150 nm size, increasing with firing temperature, as Shown in Fig. 6.4. Films fired at 900°C showed large $\sim 1\ \mu$ coalesced grains of rutile.

Porosity was evident in films fired at all temperatures, a feature likely to be beneficial for photocatalytic applications through the increase in available surface area.



Fig. 6.2. Typical microstructure showing gas-bubble damage on the surface of a thick film fired in nitrogen at 600°C .

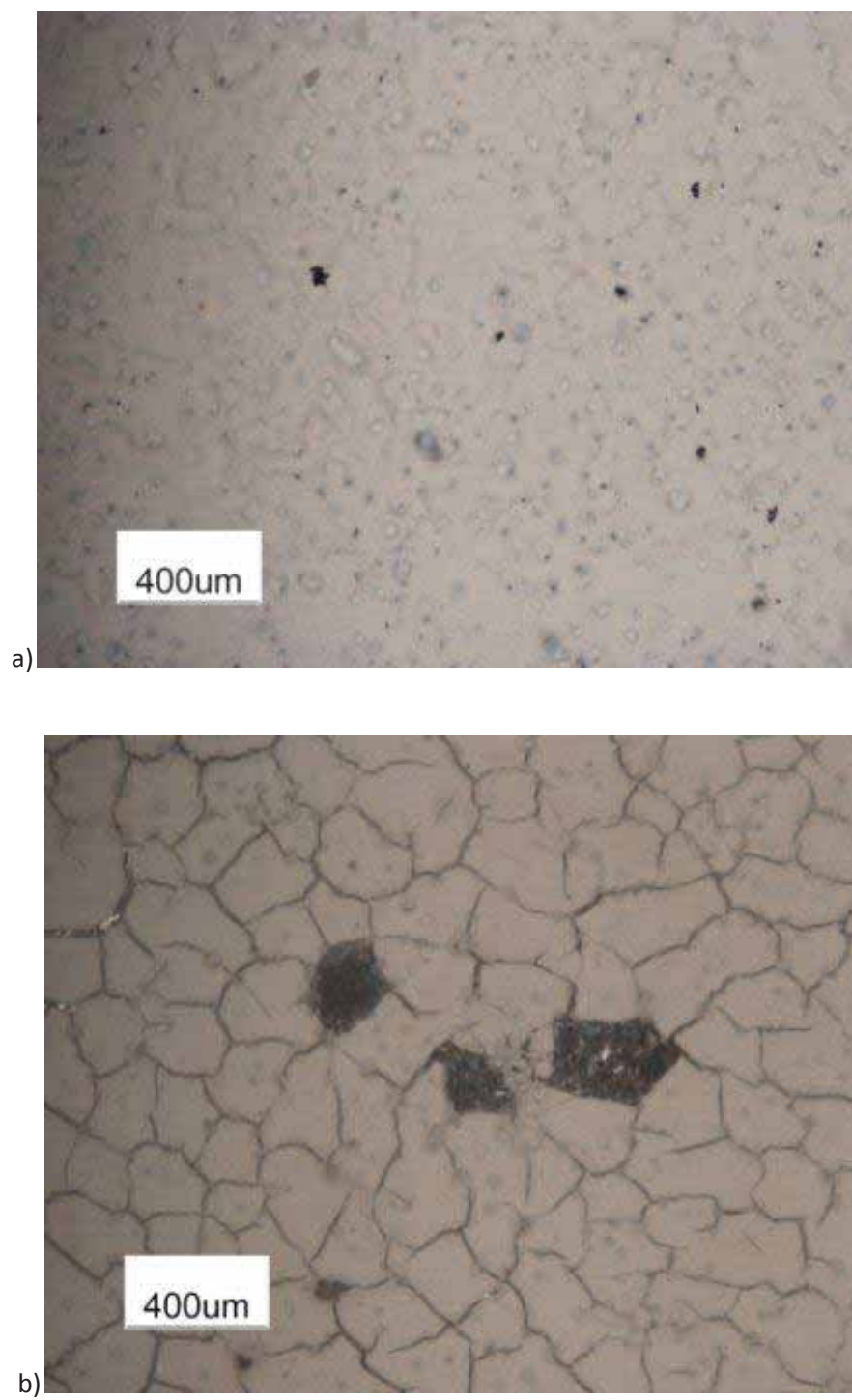
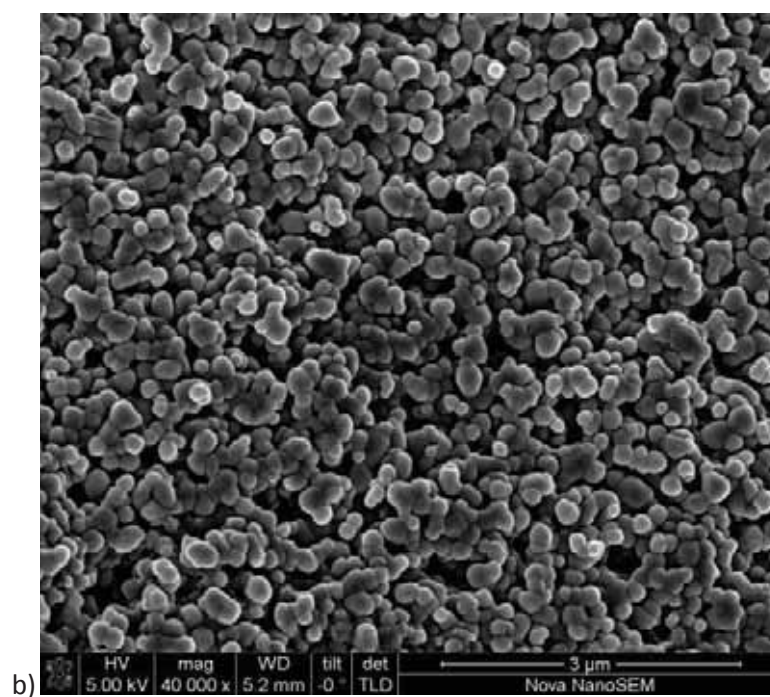
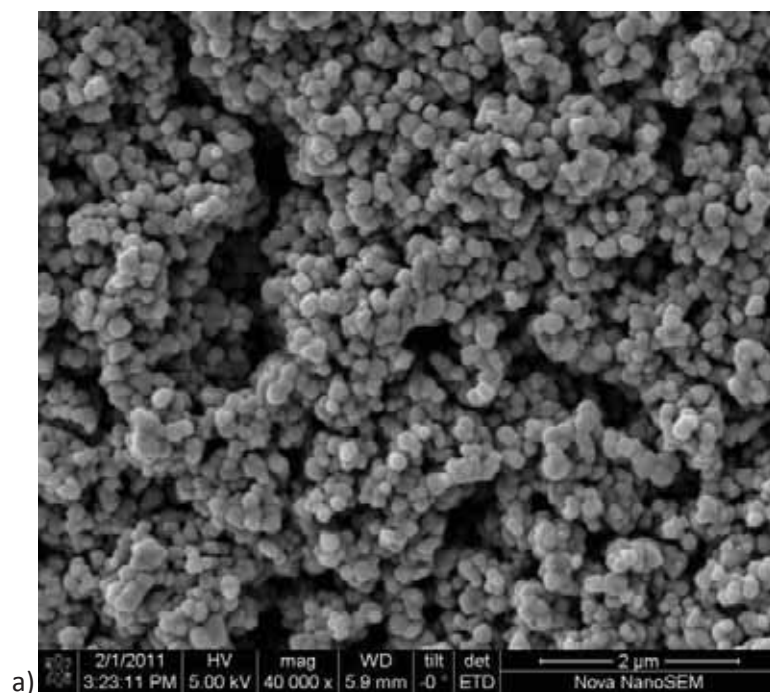


Fig. 6.3. EPD films fired at 600°C (a) in nitrogen (b) in air.



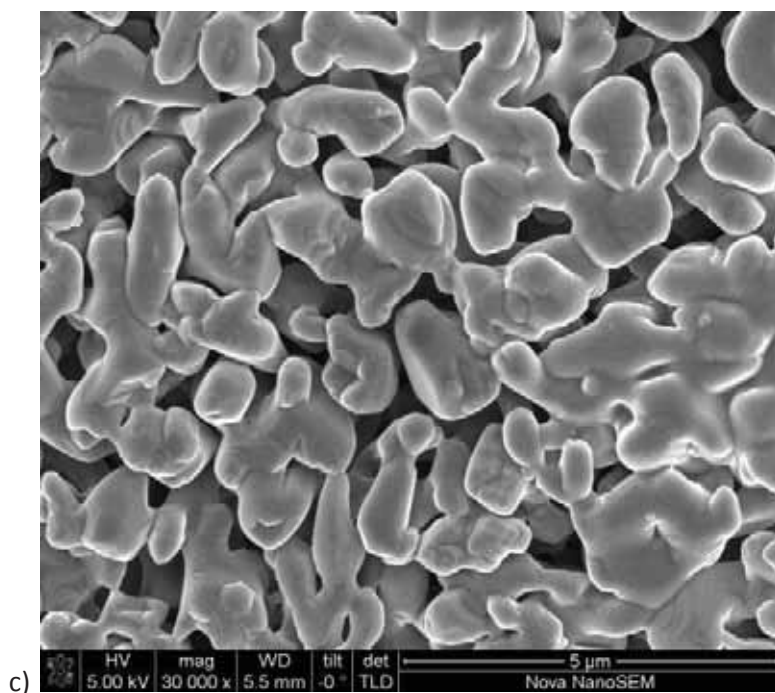


Fig.6.4. Microstructure of film fired in nitrogen at (a) 600°C (b) 800°C and (c) 900°C.

6.3.2. Phase composition

XRD and Raman patterns, shown in Fig. 6.5. and Fig. 6.6. respectively, show the presence of rutile in EPD films fired in nitrogen at 800°C with near complete transformation to rutile at 900°C. No significant effect of firing atmosphere on phase transformation was observed as all samples fired in air showed only the anatase phase of TiO_2 . Unsupported anatase exhibited greater thermal stability and showed only anatase peaks after firing at 800°C in air and nitrogen.

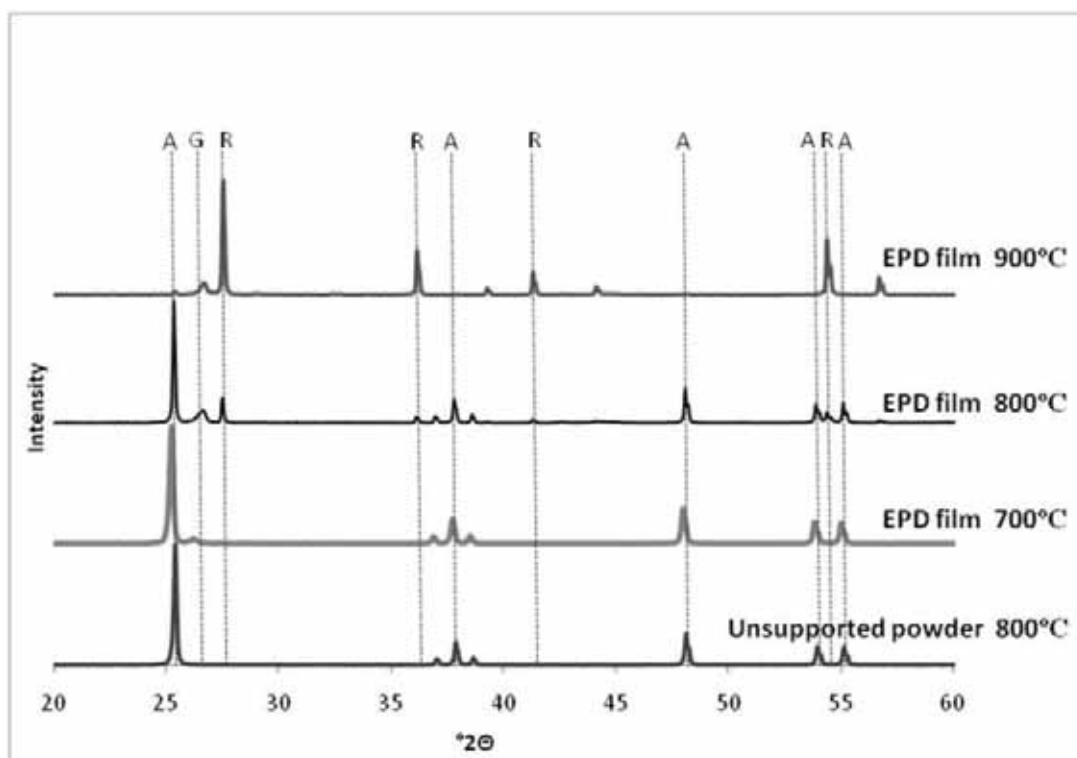


Fig. 6.5. XRD patterns of samples fired in nitrogen. A, R and G represent anatase, rutile and graphite respectively.

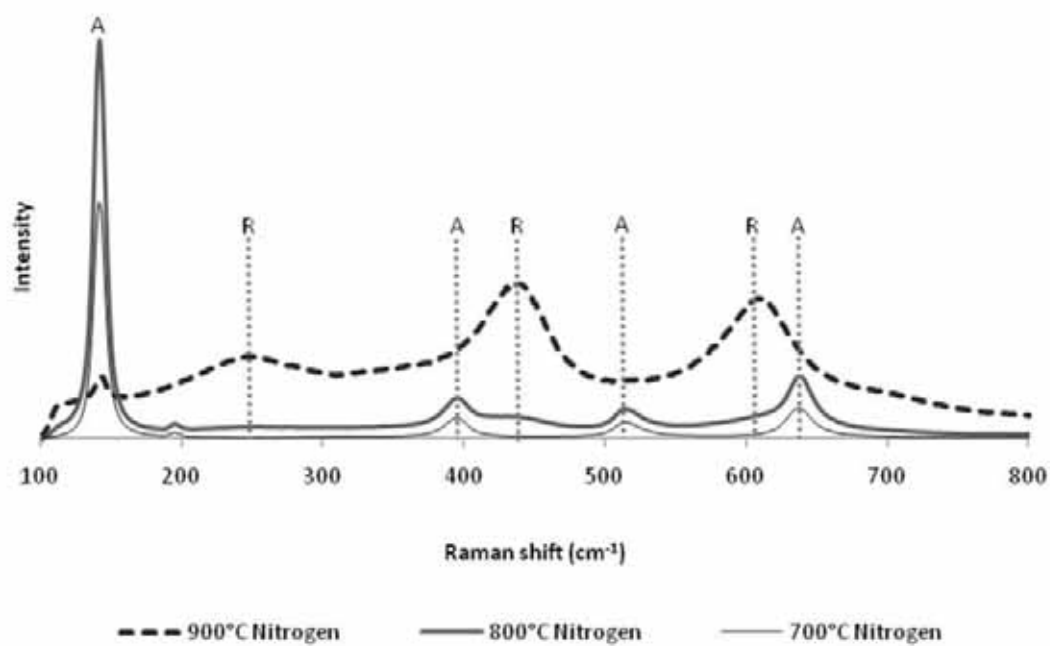


Fig. 6.6. Raman spectra of EPD films fired in nitrogen with anatase (A) and rutile (R) peaks marked.

XRD patterns were interpreted to calculate phase fractions using the method of Spurr and Myers. The quantitative analysis of phase composition is shown in Fig. 6.7. The enhanced anatase to rutile transformation in graphite-supported thick films is evident from the larger rutile fraction in these samples in comparison with isothermally fired unsupported powder.

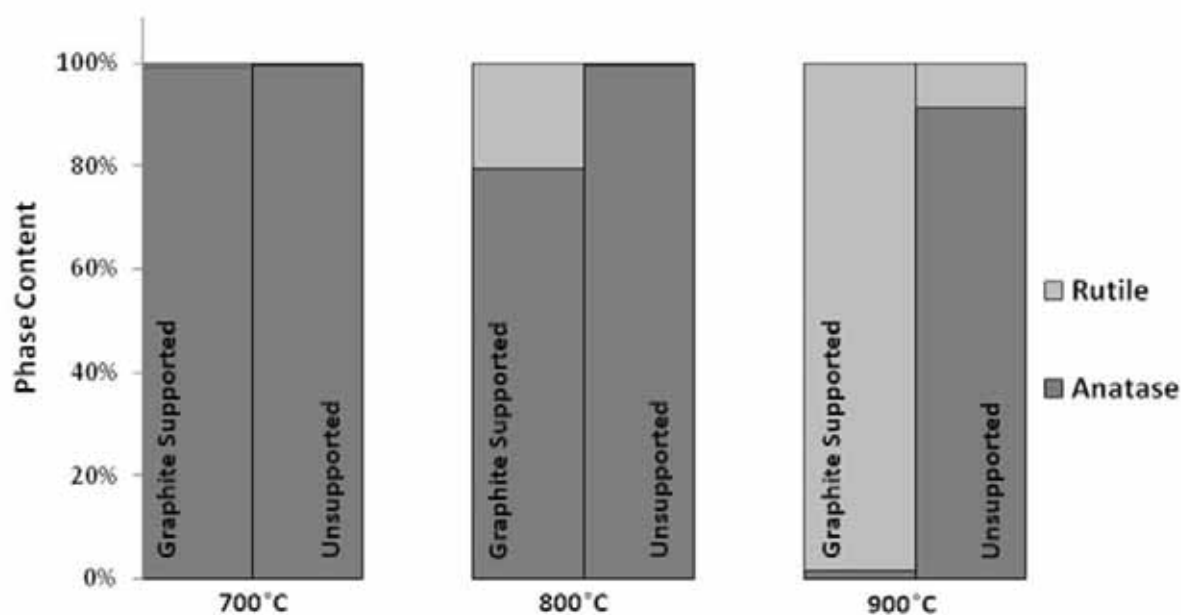


Fig.6.7. Quantitative analysis of phase composition in graphite supported TiO_2 thick films and unsupported TiO_2 .

6.3.3. Bactericidal activity

The changes in the concentration of *E. coli* AN180 CFUs under UV illumination are shown in Fig. 6.8. An uncoated graphite substrate was used to evaluate the baseline inactivation of bacteria under UV illumination in the absence of a photocatalyst and it can be seen that only a minor decrease in CFU concentration takes place under such conditions.

Samples fired in nitrogen exhibited superior bactericidal activity than samples fired in air. Nitrogen fired TiO₂ thick films facilitated a > 90% inactivation rate within 20 minutes of UV irradiation while air fired samples did not achieve similar results. The effects of firing temperature on bactericidal activity are not unequivocal from the results, however it appears that sample fired at lower temperature exhibits a higher initial rate of bacteria inactivation.

Complete sterilisation of the water was not achieved within the timeframe of the experiments, rather the microbial concentration reached a sustainable level at which the rate of bacteria inactivation was offset by their natural multiplication.

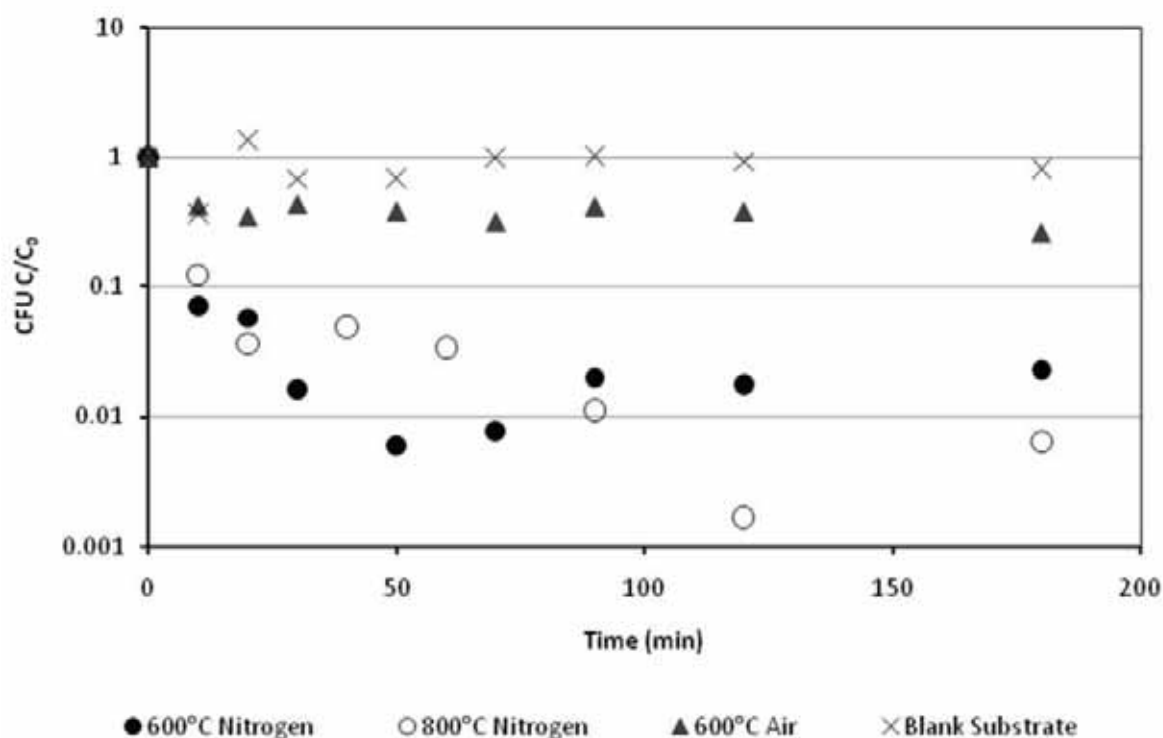


Fig. 6.8. Concentration of *E. coli* AN180 CFUs as a function of time in bactericidal experiments using TiO₂ thick films.

6.3.4. Spectroscopy

Photoluminescence emission spectra gathered at room temperature from different films are shown in Fig. 6.9. The emission peak at ~ 2.3 eV is consistent with the reported PL spectra of anatase [33–35]. Thick films fired in nitrogen at 600° C exhibit higher levels of PL emission which decrease with increasing firing temperature. Consistent with reported data, the decrease in PL emission is particularly significant as the anatase to rutile transformation takes place [34, 35]. A sample fired in air exhibited lower PL emission in comparison with sample isothermally fired in nitrogen. This may be a result of lower charge carrier recombination (owing to lower excitation levels or improved electron-hole separation) or a consequence of increased scattering of the 325nm UV laser used for photoexcitation.

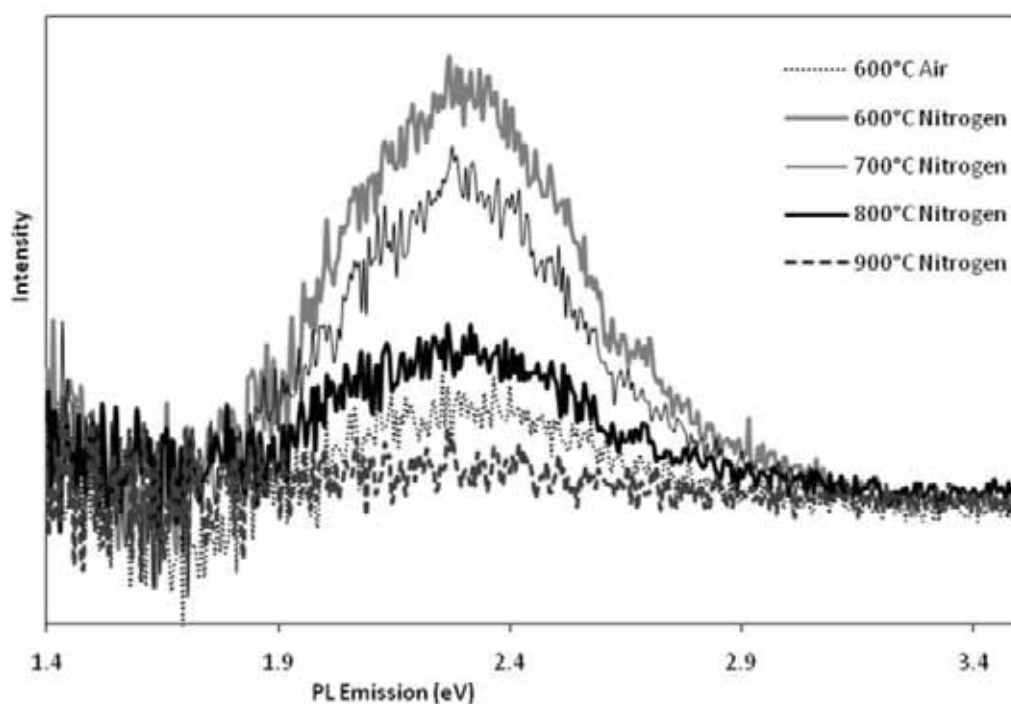


Fig. 6.9. Photoluminescence emission spectra of samples excited by 325 nm irradiation.

UV-visible absorption spectra are shown in Fig. 6.10. An absorption edge at around 380–390 nm corresponds to the band gap of anatase TiO₂ of ~3.2 eV. It can be observed that samples fired in nitrogen exhibit higher overall absorption and a more moderate slope at the absorption edge. These results cannot be interpreted to determine the photocatalytic performance of the material as increased absorption does not necessarily imply increased photogeneration of electron-hole pairs. Furthermore the differing levels of exposure of the graphite substrates bring about a shift in the absorption levels of the films. The step at 326 nm is a result of the irradiation lamp changeover at this wavelength.

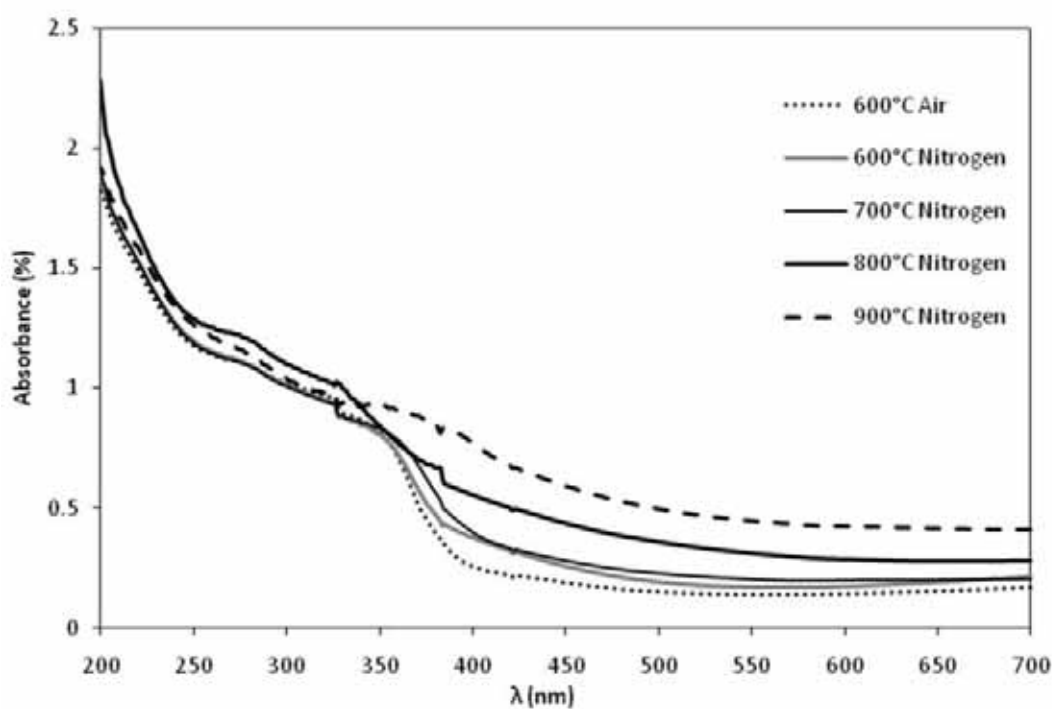


Fig. 6.10. UV-visible absorption of TiO₂ thick films fired at different temperatures in air and nitrogen.

6.4. Discussion

6.4.1. Effect of firing conditions on microstructure

Graphite is generally reported to exhibit rapid oxidation in air around 700°C [36, 37] and thus the oxidation of the substrates fired at 700°C in air in this work was anticipated. As would be expected, the oxidation of the graphite substrate for films fired in air has a detrimental effect on the structure and adhesion of the deposited thick film. This is evident from increased spalling and cracking, shown in Fig. 6.3, and the low resilience of the air-fired films to abrasion, suggesting firing in air is an unsuitable treatment for EPD films on graphite substrates, even at temperatures below the ignition temperature of graphite. In contrast, EPD thick films fired in nitrogen did not show oxidation damage and exhibited superior adhesion. As shown in Fig. 6.4, grain size increased with increasing firing temperature, with a significant growth occurring between 800–900°C, as the phase transformation to rutile reached near completion. Significant grain growth is likely to be detrimental to the photocatalytic activity of the material due to a decrease in available surface area; however the partial transformation to rutile may be beneficial for the photocatalytic activity through improved charge carrier separation as reported elsewhere.

6.4.2. Phase composition

The anatase phase of the powder used in this work shows greater thermal stability to what is frequently reported in the literature. While anatase is typically reported to transform to rutile at temperatures between 600 and 700°C [30, 38–41], unsupported powder in this work remained entirely in the anatase phase after firing at 800°C. Similar commercially available anatase has shown thermally stable anatase phase in other work [42, 43], this thermal stability is likely to be due to low levels of silica impurities in the raw material [30]. The presence of the graphite substrate promotes the anatase to rutile transformation. This promotion of the phase

transformation, illustrated in Fig. 6.5. And Fig. 6.7., is most likely due to the increase in oxygen vacancies in the anatase lattice as reported elsewhere [30]. In a non-oxidising atmosphere, the carbon in the graphite substrate may cause a partial reduction of the TiO₂ film giving rise to the formation of oxygen vacancies and Ti⁺³ species, the presence of which enhances the anatase to rutile phase transformation by easing the atomic rearrangement involved in this transformation [44].

6.4.3. Bactericidal activity

From Fig. 6.8. it can be seen that samples fired in nitrogen exhibited superior photocatalytic performance in comparison with air fired material. Higher photocatalytic activity of TiO₂ fired in nitrogen has been reported previously [45]. A likely explanation of the enhanced photocatalytic performance observed in samples fired in nitrogen is that this treatment enables the diffusion of nitrogen atoms from the firing atmosphere and carbon atoms from the substrate, into the TiO₂ lattice which facilitate an increase in exciton photo-generation. As reported elsewhere [28, 29, 46], the substitution of oxygen with nitrogen and carbon atoms in TiO₂ gives rise to new valence states and thus increases the optical response by a decrease in the band-gap of the material. It has also been reported that the substitution of carbon and nitrogen in place of oxygen in TiO₂ reduces charge carrier recombination [28]. Conversely, in samples fired in air, bactericidal activity was low, showing only moderate activity relative to an uncoated graphite substrate. The lower photocatalytic activity of air fired samples may be a result of substrate oxidation which inhibited the diffusion of carbon into the TiO₂ lattice and brought about deterioration in the quality of EPD films which resulted in a loss of photocatalyst in the bactericidal reactor.

The effect of increasing firing temperature on the bactericidal activity is not unequivocally clear from the results shown in Fig. 6.8. It appears the material fired at a lower temperature brings about a more rapid initial bacterial inactivation, however the sample fired at 800°C exhibits a lower final CFU concentration. The differences in bactericidal performance between the two samples fired in nitrogen at different temperatures are not of a significant magnitude, and the ambiguity may result from the mixed effect of grain size and phase composition. The lower-temperature fired material exhibits higher surface area owing to the finer grain size visible in Fig. 6.4, however the material fired at 800°C shows a secondary rutile phase, potentially improving charge carrier separation and consequently improving photocatalytic activity [13–17]. Furthermore the material fired at 800°C may exhibit greater levels of carbon and nitrogen diffusion in the TiO₂ lattice, giving rise to a lower band-gap.

In general, the bactericidal activity observed in this work was notably low in comparison with results reported elsewhere [19, 20, 47], and no complete sterilisation was achieved. The comparatively low rates of *E. coli* inactivation evident from Fig. 6.8. are likely to be the result of small catalyst area in comparison with the reactor dimensions, low irradiance levels, the use of air sparging rather than pure oxygen sparging, and the surface area of the commercially available material used which is lower than catalysts used in other work. Irradiance levels in the reactor used in this work were measured at 4.42 Wm⁻² while the UV irradiance of sunlight is up to 50 Wm⁻² [48]. This suggests that greater efficiencies can be achieved using natural solar irradiation rather than illumination by a UV lamp. The deposition of higher surface area TiO₂ powder in conjunction with nitrogen firing may yield improved performance than the samples prepared in this work.

6.4.4. Spectroscopy

The photoluminescence spectra of thick films fired in nitrogen shown in Fig.6.9 exhibit a decrease in PL emission intensity with increasing firing temperature. Increased PL emission in TiO₂ results

generally from increased radiative recombination of excitons [49, 50] and may indicate enhanced photo-generation of these electron-hole pairs, a faster rate of their recombination or a combination of both of these phenomena [51–53]. Intensity of PL emission may also vary as a result of surface properties and resultant variation in the scattering of the photoexciting UV [53]. Consequently, similar to UV-vis absorbance, PL emission intensity cannot be used to directly infer photocatalytic activity.

The spectra in Fig. 6.9 show higher levels of PL emission from samples fired in N₂ in comparison with a sample fired in air. An increase in PL emission in TiO₂ fired in an oxygen deficient atmosphere has been previously reported as a result of increased oxygen vacancies[34]. Additionally, the PL spectra from the sample fired in air at 600°C may be diffuse owing to increased surface roughness resulting from oxidation of the substrate and consequent deterioration of the thick TiO₂ film.

The similar levels photocatalyzed inactivation of *E. coli* exhibited by samples fired at 600°C and 800°C in nitrogen suggest that the lower PL emission intensity of the sample fired at 800°C in nitrogen can be attributed ,at least partly, to improved charge carrier separation in this sample resulting from a mixed anatase-rutile phase composition. If the lower PL emission intensity in the sample fired at 800°C was purely a result of lower levels of excitation, this material would exhibit markedly poorer photocatalytic activity in the inactivation of bacteria. Conversely if the lower PL emission intensity was solely the result of improved charge carrier separation, this material would be expected to exhibit noticeably higher activity.

UV-visible spectra shown in Fig. 6.10 show a more moderate slope at the adsorption edge in nitrogen doped samples with higher overall absorption. These spectra are consistent with the aforementioned formation of new valence states by nitrogen and/or carbon diffusion and the resultant increased optical response [54]. A further increase in overall absorption and broadening of the UV-vis absorption spectra can be seen as a result of rutile formation. This is consistent with

reports that the formation of rutile at low levels is sufficient to shift the absorption edge of TiO₂ to higher wavelengths[24].

6.5. Conclusions

Porous thick films of TiO₂ can be fabricated on graphite substrates by using a method of anodic aqueous EPD. When such fabrication methods are combined with firing in a nitrogen atmosphere a well adhered film exhibiting enhanced photocatalytic activity can be obtained.

The anatase to rutile transformation is enhanced in thick films on graphite substrates as a result of increased levels of oxygen vacancies created by the diffusion of carbon atoms into the TiO₂ lattice. The diffusion of carbon and nitrogen into the TiO₂ lattice may also explain the improved photocatalytic activity of material fired in nitrogen in comparison with air fired material. A mixed phase composition, achieved by firing at 800°C in nitrogen, further enhances photocatalytic activity through improved charge carrier separation.

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7. The effects of carboxylic acids on the aqueous dispersion and electrophoretic deposition of ZrO_2

This chapter presents a paper accepted for publication with the Journal of the European Ceramic Society. As with the previous chapters of this thesis involving carboxylic dispersion of oxide particles, the research presented in this paper is a result of collaboration between the School of Materials and Environmental Engineering at the University of Modena and Reggio Emilia in Modena, Italy and the School of Materials Science and Engineering at the University of New South Wales in Sydney Australia.

The paper which comprises the present chapter is a phenomenological investigation into the aqueous dispersion of zirconium dioxide particles using carboxylic acids. Although this work does not directly involve the fabrication of titanium dioxide photocatalysts, the research presented here is highly relevant to the development of EPD fabrication methods for TiO_2 as reported in the papers presented in Chapters 5 and 6.

The results of the research reported in this chapter elucidated the mechanisms through which carboxylic acids at low levels of addition can effectively disperse oxide particles in aqueous suspensions, inhibiting sedimentation and facilitating EPD fabrication methods from suspensions which would otherwise be unsuitable for use with such fabrication techniques.

	Primary Author	Manuscript Preparation	Literature Research	Experimental Work	Data Analysis	Editing and Revision	Supervisory Role	Formatting and Layout	Advice and Support
Dorian Hanaor	✓	✓	✓	✓	✓	✓		✓	
Marco Michelazzi				✓					✓
Charles C. Sorrell						✓		✓	✓
Christina Leonelli							✓		✓

Key Findings

- Carboxylic acids were found to impart electrosteric stabilisation to aqueous ZrO_2 suspensions
- A sharp drop in zeta potential occurs at distinct reagent addition levels corresponding to surface saturation by negatively charged carboxylate groups
- Adsorption cross section areas of EDTA, citric acid and oxalic acid were determined
- The use of carboxylic acids was shown to facilitate effective aqueous EPD of ZrO_2
- Adsorption and dispersion phenomena were discussed in terms of speciation, size and structure of the reagents used

The Effects of Carboxylic Acids on the Aqueous Dispersion and Electrophoretic Deposition of ZrO_2

Dorian A. H. Hanaor,^{a,*} Marco Michelazzi^b, Cristina Leonelli^b, Charles C. Sorrell^a

^a*School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia*

^b*Department of Materials and Environmental Engineering, University of Modena and Reggio Emilia, 41100 Modena, Italy*

* E-Mail: dorian@student.unsw.edu.au

Abstract: The agglomeration, electrokinetic properties and electrophoretic deposition behaviour of aqueous suspensions of ZrO_2 with carboxylic acid additives were studied in comparison with conventional pH adjustment. It was found that citric acid imparted negative zeta-potential values and electrosteric stabilisation to particles in suspensions at all pH levels. The examination of additions of carboxylic acids to ZrO_2 suspensions revealed that these reagents cause a sharp drop in zeta-potential at distinct addition levels, which correspond to surface saturation of the particles with negatively charged carboxylate groups. Adsorption cross sections of citric acid, EDTA and oxalic acid were evaluated from these results, showing that both citric acid and EDTA coordinate to ZrO_2 surfaces by two carboxylate groups while oxalic acid is coordinated by one group. The use of carboxylic acids was shown to facilitate superior electrophoretic deposition in comparison with zeta-potential modification by conventional pH adjustment through improved suspension stability.

Keywords: Suspensions; ZrO_2 ; Microstructure-prefiring; Carboxylic acid; Fuel cells

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7.1. Introduction

The electrokinetic properties of oxide particles in aqueous suspensions are of paramount importance in controlling the electrophoretic processes involving these materials. Such processes include the electrophoretic deposition (EPD) of thick ceramic films, [1–5] the filtration and separation of oxide particles, [6, 7] and the removal of solid contaminants from soil, [8, 9] Further, electrokinetic properties are important parameters in governing rheological properties of thick suspensions or slurries used for slip casting, screen printing, gel casting, direct coagulation casting (DCC), and extrusion. [10–13]

EPD in particular is of growing importance owing to the capacity of this method to be used to fabricate unique microstructures in a variety of forms from dilute suspensions of fine particles in a cost-effective manner. [1, 3, 14–16] EPD consists of the movement of charged particles under an electric field and their compact deposition on a substrate. Typically, this deposition is followed by a densification step through heat treatment. EPD often is conducted using organic suspension media owing to the occurrence of the parasitic process of water electrolysis in EPD from aqueous suspensions. Despite the associated problem of water electrolysis, the use of aqueous suspension media for EPD is attractive due to the lower environmental impact, greater simplicity, and lower cost that facilitate the application of such methods in larger scale processes.

The electrokinetic properties of a particle in suspension are governed by the electric charge distribution in the double layer that surrounds the particle. [17, 18] This double layer is formed when a surface-charge-carrying solid particle suspended in a liquid becomes surrounded by counter-ions of charge opposite to that of the particle surface. As the particle moves in the solution, the plane beyond which counter-ions do not migrate along with the particle is known as the slipping plane. The electrical potential at the slipping plane is known as the zeta potential (ζ) and typically is measured in mV.

As a result of increased electrostatic repulsion inhibiting agglomeration and settling, a suspension of particles showing a high absolute value of zeta potential is more stable in comparison to suspensions exhibiting lower zeta potential absolute values. In electrophoretic processes, a high zeta potential is desirable as it enhances the rate of particle movement under a given electrical field while inhibiting the sedimentation of the material. The point at which the potential at the slipping plane is zero is known as the isoelectric point (IEP). At this point electrostatic repulsion is minimised and Van der Waals forces facilitate agglomeration.

The rate of particle movement under an electrical field is known as the electrophoretic mobility, μ . This parameter is defined by equation 7.1. [1, 19]

$$\mu = v/E \quad (7.1)$$

Here, v = velocity and E = electric field. Electrophoretic mobility is the key parameter in governing the kinetics of EPD. Particle movement under an electric field is directly related to the magnitude of the zeta potential. This can be seen in the expression of electrophoretic shown in equation 7.2. [1, 15]

$$\mu = \frac{\epsilon_0 \epsilon_r \zeta}{\eta} \quad (7.2)$$

Here, ϵ_0 is the permittivity of free space, ϵ_r and η are the permittivity and viscosity of the suspension medium, respectively, and ζ is the zeta potential of the suspended particles. This equation is an approximation and it assumes that the double layer thickness is negligible relative to the particle diameter. It can be seen that, for a given suspension medium, the electrophoretic mobility is proportional to the zeta potential.

For given deposition conditions, the kinetics of EPD in planar geometries are governed by the electrophoretic mobility (or zeta potential) of the suspended particles as shown by the Hamaker equation in equation 7.3. [2, 20]

$$d = C_s \mu E t \quad (7.3)$$

Here d is the density of the deposit (g cm^{-2}), C_s is the solids loading (g cm^{-3}), μ is the electrophoretic mobility ($\text{cm}^2 \text{s}^{-1} \text{V}^{-1}$) (which can be expressed as a function of ζ as shown in Eq. 7.2.), E is the electric field (V cm^{-1}) and t is time (s).

Zeta potential is varied most commonly by pH adjustment. The zeta potential generally goes to more positive values with decreasing pH level. [1, 21] The point at which $\zeta=0$, the IEP of a particulate suspension, generally is discussed in terms of the pH at which this occurs. It should be noted that the IEP of a particular powder can occur at different pH levels through the use of dispersants or by the use of alternative pH adjustment agents. [22–24]

Organic additives often are used as dispersants to increase repulsive forces between ceramic particles in suspension. Typically, these additives are charge-carrying long-chain polyelectrolytes. These additives adsorb on particle surfaces and modify the surface charge of these particles in suspension and thus enhance the interparticle electrostatic repulsion while further providing a steric barrier to agglomeration. Commonly used polyelectrolyte dispersants typically have molecular weights in the range 6,000–15,000. [3, 10, 25–28] Dispersants of lower molecular weight may have advantages over such polyelectrolytes owing to their low costs, higher adsorption capacities, lesser effects on post-firing microstructure and lower environmental impact both in polar and non polar solvents. [11, 23, 24, 29] Carboxylic acids have been shown to act as low molecular weight dispersants for aqueous suspensions of alumina. [11, 22, 24] Such reagents are reported to impart negative surface charge on particles in suspension through the surface adsorption of the carboxylate anion (RCOO^-). Carboxylic acids have been used to facilitate anodic EPD with decreased levels of water electrolysis in acidic aqueous suspensions of TiO_2 . [20]

ZrO_2 is an oxide of considerable technical interest owing to its potential applications in structural ceramics, bioceramics, oxygen sensing materials and in electrolyte films in solid oxide fuel cells

(SOFCs). EPD of this oxide has been shown to be one of the most promising fabrication methods in the production of SOFCs. [18, 30–33] Studies of the zeta potential behaviour of undoped ZrO_2 have shown the IEP of this material to be at an pH level of ~ 5.5 [15, 34] while tetragonal zirconia doped with 3% yttria (as used for SOFCs) has been reported to exhibit an IEP at $\text{pH} \sim 7$. [35] The present work discusses the electrokinetic properties of aqueous suspensions of monoclinic ZrO_2 dispersed with the aid of carboxylic acids and the consequent effects of such dispersion methods on the electrophoretic deposition behaviour of this material.

7.2. Materials and methods

Commercial monoclinic zirconia powder (Colorobbia, Italy) was used for suspension preparation. The powder was hand-ground using an agate mortar and pestle for degglomeration. Surface area of the degglomerated powder was determined using N_2 adsorption isotherms at 77K in conjunction with BET calculation methods. A 0.1 wt% (0.001 g/mL) suspension of ZrO_2 in distilled water was stirred magnetically and sonicated in an ultrasonic bath for 10 minutes to achieve consistent dispersion of particles in suspension.

Zeta potential, electrophoretic mobility, suspension conductivity and agglomerate size distribution were measured using a Nano-Zetasizer (Malvern Instruments, Worcestershire, UK). Reagent-grade anhydrous citric acid (Sigma Aldrich, USA), oxalic acid, and ethylene diamine tetraacetic acid (EDTA) (both Univar, Germany) were used as carboxylic dispersants while nitric acid (70 %), ammonium hydroxide (25%) and sodium hydroxide (all Univar) were used for conventional pH adjustment.

Zeta potential and electrophoretic mobility variation with conventional pH adjustment of ZrO_2 suspensions was compared to data resulting from pH adjustment using citric acid and sodium hydroxide for pH adjustment. At all pH values, citric acid was a component of the solution in order to ensure that the citrate group was available for adsorption.

The dispersant effects of three carboxylic acids with differing numbers of carboxyl groups were investigated through additions of controlled small quantities of dilute citric acid, oxalic acid, and EDTA to suspensions which had at fixed pH levels adjusted by prior addition of nitric acid. This was done in order to examine the dispersion phenomena of ZrO_2 suspensions by determining the electrokinetic properties as a function of additive concentration. pH levels of the dilute additive solutions of carboxylic acid were measured as pH=3.2, pH=2.9 and pH=3.4 for Citric acid, oxalic acid and EDTA respectively. Owing to the small molar quantities of carboxylic additives, only a slight variation in ionic strength occurred as supported by the lack of significant variation in suspension conductivity.

The anodic electrophoretic deposition of ZrO_2 was facilitated at low pH levels using citric acid and oxalic acids for pH/ ζ modification, and at high pH levels using sodium hydroxide. Cathodic EPD was carried out using nitric acid for pH/ ζ modification. Electrophoretic depositions were carried out from suspensions of 0.01g cm^{-3} solids loadings onto graphite substrates (GrafTech International, Ohio, USA) cut to approximate dimensions 25X25x2 mm and masked to leave one side available for deposition. Depositions were carried out for 10 minutes at 10 V with an electrode separation of 20 mm. EPD results were evaluated by determining the weight of ZrO_2 deposited per unit of area.

7.3. Results

7.3.1. Characterisation of ZrO_2 Powder

Adsorption isotherms of N_2 at 77 K in conjunction with BET analysis methods revealed the deglommed powder to exhibit a surface area of $121.7\text{ m}^2\text{g}^{-1}$. The size distribution of dispersed ZrO_2 particles in aqueous suspension as determined by dynamic light scattering is shown in **Fig.**

7.1.

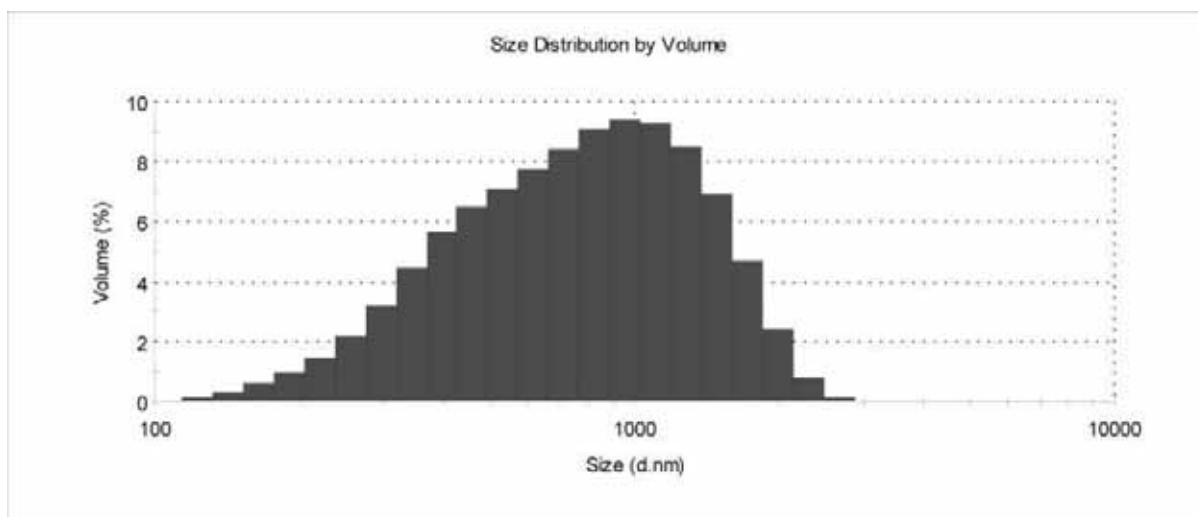


Fig. 7.1. Size distribution histogram by volume for dispersed monoclinic ZrO_2 powder.

7.3.2. Variation of zeta potential with pH

The conventional variation of zeta potential and a particle dispersion as a function of pH (without effects of surface adsorbed dispersants) in aqueous suspensions of ZrO_2 was determined using nitric acid and ammonium hydroxide for pH adjustment. This is shown in Fig. 7.2. These reagents are unlikely to adsorb on oxide surfaces due to the absence of functional groups which are able to substitute for the surface hydroxo groups.[36] In consistency with Eq. 7.2, data showed that zeta potential varied as a linear function of electrophoretic mobility, therefore μ values are not reported. The agglomerate sizes shown in the figure are approximate. The IEP occurs at pH ~ 5.5 , which is similar to values reported elsewhere for non-stabilized zirconia [15, 26]. Soft-agglomerate formation of the ZrO_2 particles in suspension was observed to occur when the absolute value of the zeta potential was less than ~ 30 mV, which is observed commonly in many oxide suspensions [37, 38]. As expected, agglomeration was maximised in the region of pH ~ 5.5 , which corresponds to the pH at which the zeta potential is minimal. At high (>9) and low (<4) pH levels a moderate decrease in zeta potential (absolute value) occurs. This is an anticipated consequence of the greater ionic strength imparted by higher reagent concentrations required to

adjust the pH values to strongly acidic and basic conditions and the resultant compression of the electric double layer. [39, 40]

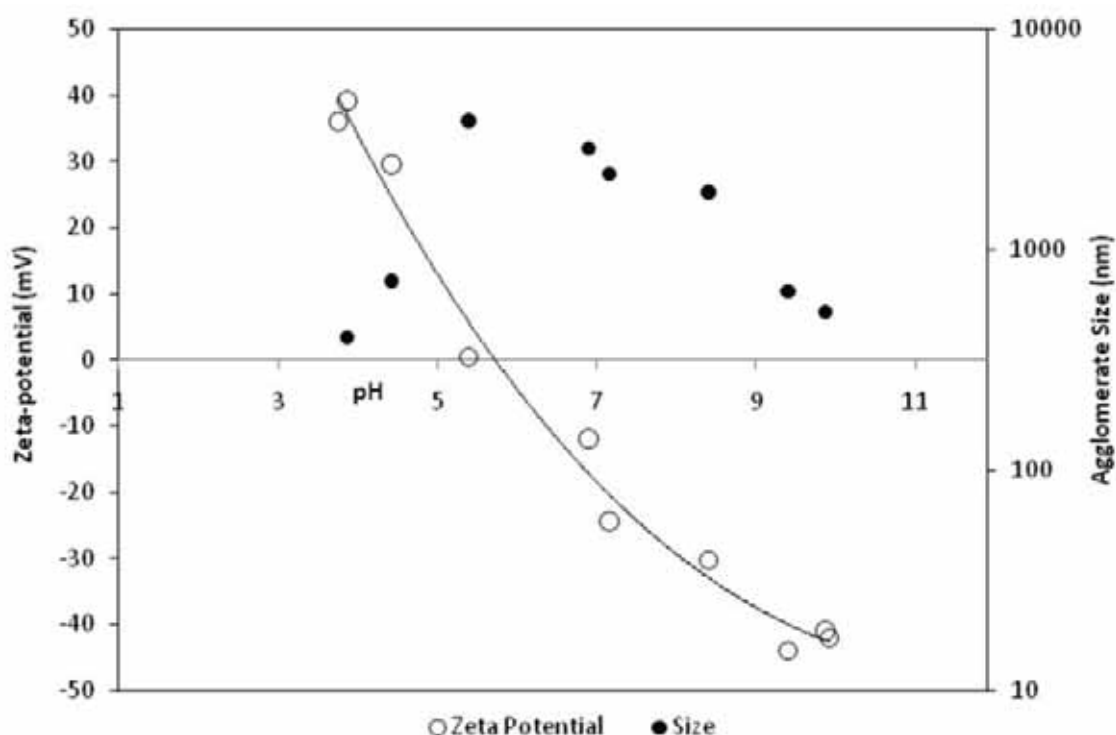


Fig. 7.2. Conventional zeta potential and agglomeration behaviour of monoclinic ZrO_2 as a function of pH.

In comparison to the zeta potential variation shown in Fig. 7.2, which is consistent with the variation in zeta potential with pH reported elsewhere, the use of citric acid led to a significantly different zeta potential variation as a function of pH, as shown in Fig. 7.3. It can be seen that the zeta potential remains negative even at low pH values. At all pH levels particle dispersion was maintained and no agglomeration of the suspended particles was observed, suggesting that a zeta potential in the region of only ~ 18 mV (as limited by the dissociation constant of citric acid pK_{a1}) is sufficient to maintain particle dispersion. The negative zeta potential values are consistent with previous observations of the dispersion of oxide suspensions using carboxylic acids. [11, 22, 24, 41]

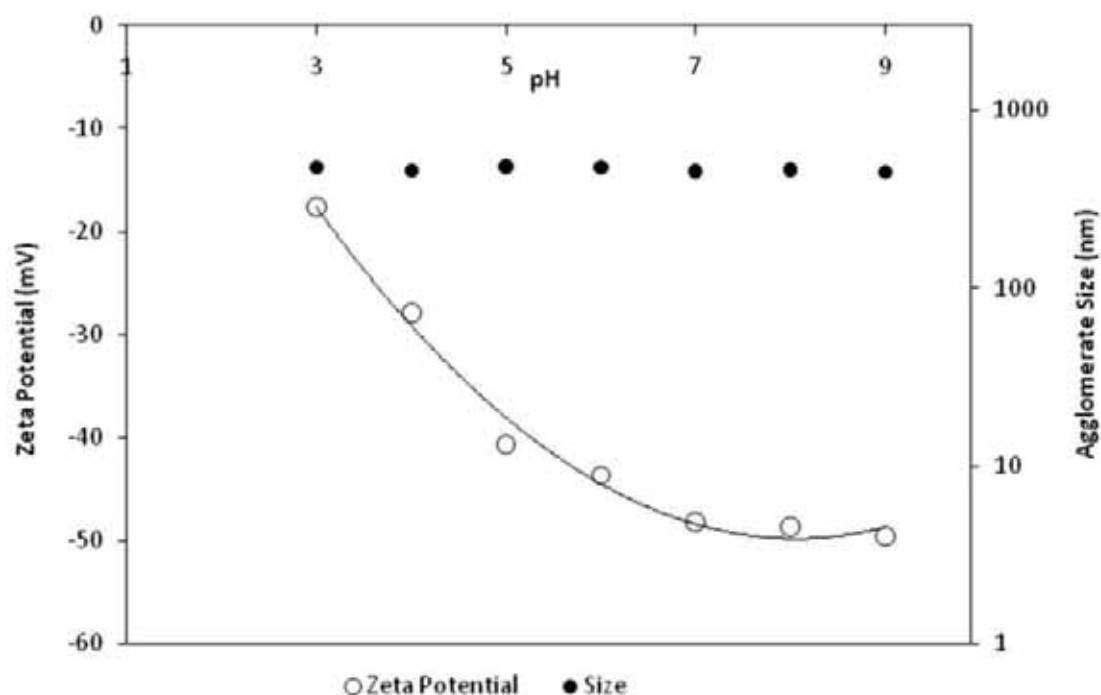


Fig. 7.3. Zeta potential and agglomeration behaviour of ZrO_2 as a function of pH varied with citric acid and sodium hydroxide.

7.3.3. Effects of carboxylic acids on zeta potential

The dispersant effects of different carboxylic acids on aqueous suspensions of ZrO_2 were investigated by measuring the zeta potential of acidified and native-pH suspensions with controlled additions of the three carboxylic acids oxalic acid, citric acid and EDTA, which exhibit two, three and four carboxyl groups respectively with symmetrical stereochemistry.

Aqueous ZrO_2 suspensions were adjusted to an initial acidity of pH=4 with nitric acid (in order to be able to lower an initially positive zeta potential across the IEP) and then treated with additions of dilute solutions of carboxylic acids. As shown in Fig. 7.4, the quantities of carboxylic acids added were sufficient to decrease the zeta potential significantly; this resulted in a pH change of only ± 0.2 . Repetition of these experiments confirmed these results. It can be seen that a higher concentration of oxalic acid is required to facilitate dispersion in comparison with citric acid or

EDTA. Citric and oxalic acids yielded similar and lower ultimate zeta potential values than that for EDTA.

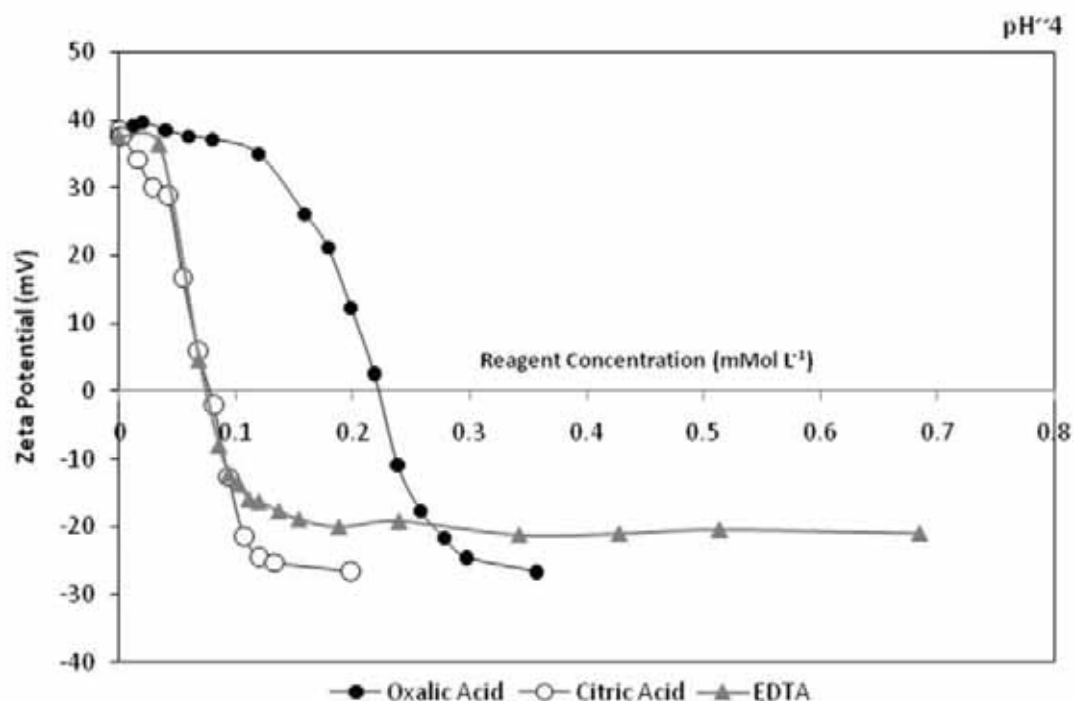


Fig. 7.4. The effects of carboxylic acid additions on the zeta potential of ZrO_2 at pH =4.

As shown in Fig. 7.5, similar additions of these carboxylic acids were made without pH standardisation (native-pH). The starting suspension, comprised only of ZrO_2 powder in distilled water, was found to have an initial pH of ~ 5.4 , which can be compared to the data point in Fig. 7.2 at which the zeta potential was close to zero (no addition of acid or base). The acidic native-pH for ZrO_2 has been observed elsewhere. [15, 26] The onset of the drop in zeta potential occurred immediately and at a lower concentration compared to the addition levels to ZrO_2 suspensions at pH=4. It also can be seen that the curves are not as smooth as those in Fig. 7.4. It is likely that both of these effects occurred because, as shown in Fig. 7.2, at pH=4, dispersion is optimised and so the suspension is more resistant to the small changes in pH that occur due to the additions while at the native pH level, dispersion is minimised as this pH value is close to the IEP and so the suspension responds more readily to small changes in pH.

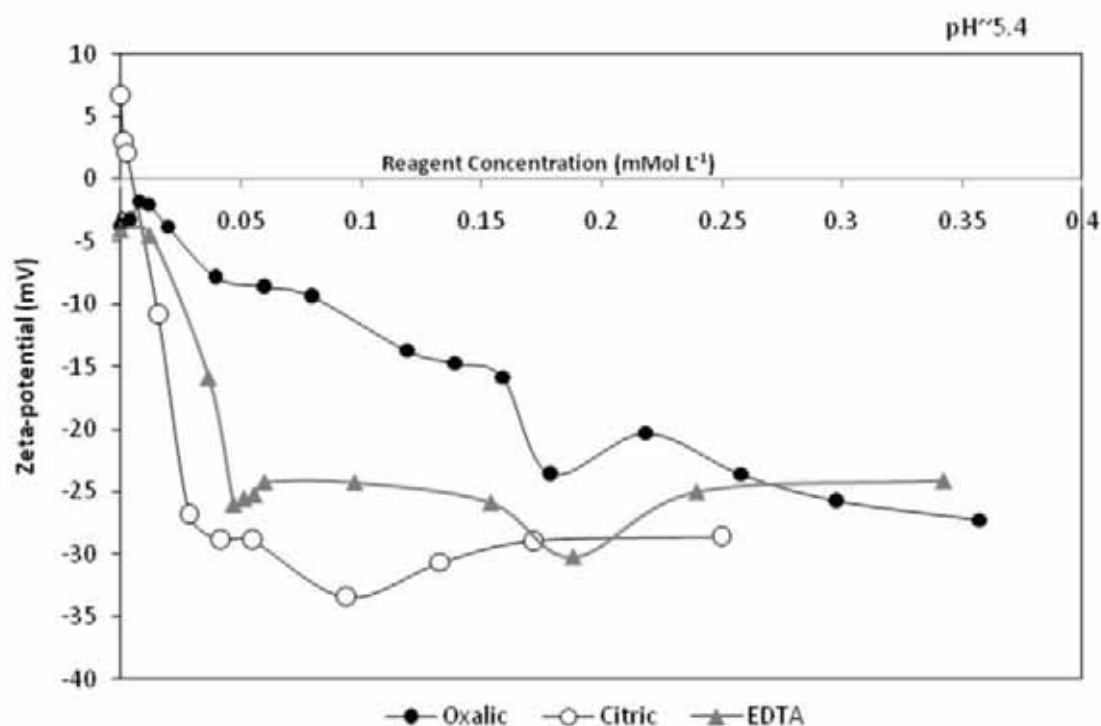


Fig. 7.5. The effects of carboxylic acids on the zeta potential of ZrO_2 at its native pH level of ~ 5.4 .

Citrate adsorption on ZrO_2 particles was further examined by measuring the variation in pH of a ZrO_2 suspension during controlled additions of dilute citric acid. Both the suspension and the citric acid additive were prepared at pH=4 to eliminate acid-base neutralisation effects. It was found that as the reagent was added an increase in pH occurred, reaching a maximum as the zeta potential reached a minimum as shown in Fig. 7.6. These results indicate that the change in pH of the suspension is a consequence of the interaction of citric acid with the suspended ZrO_2 particles.

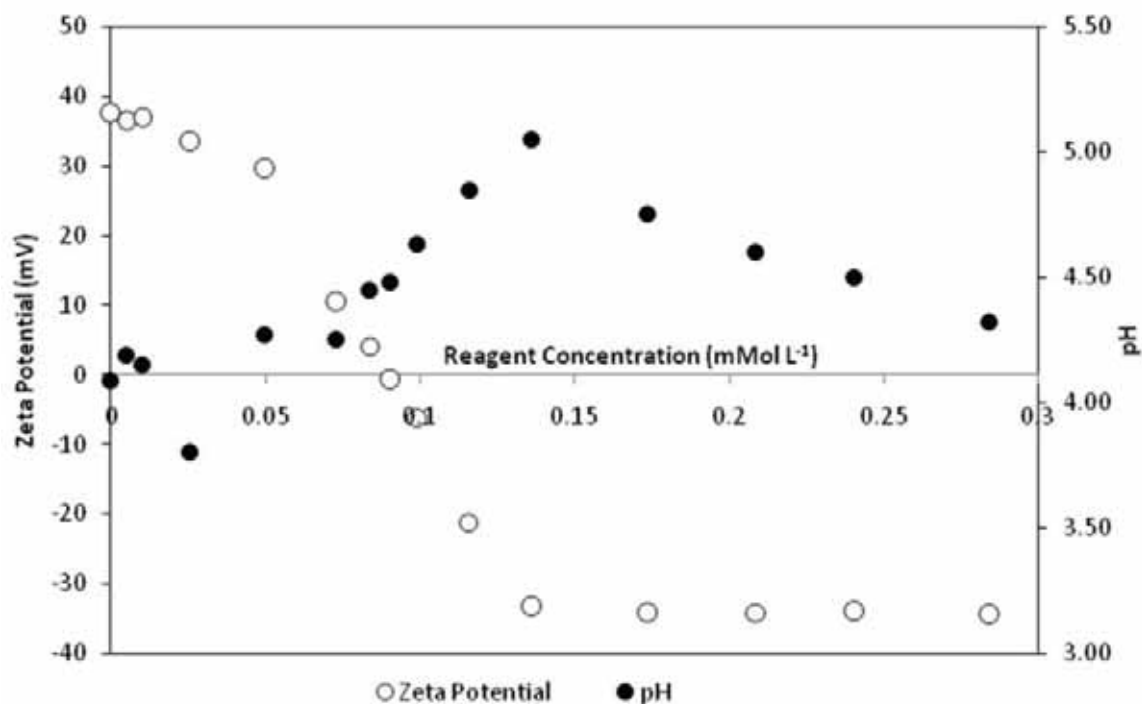


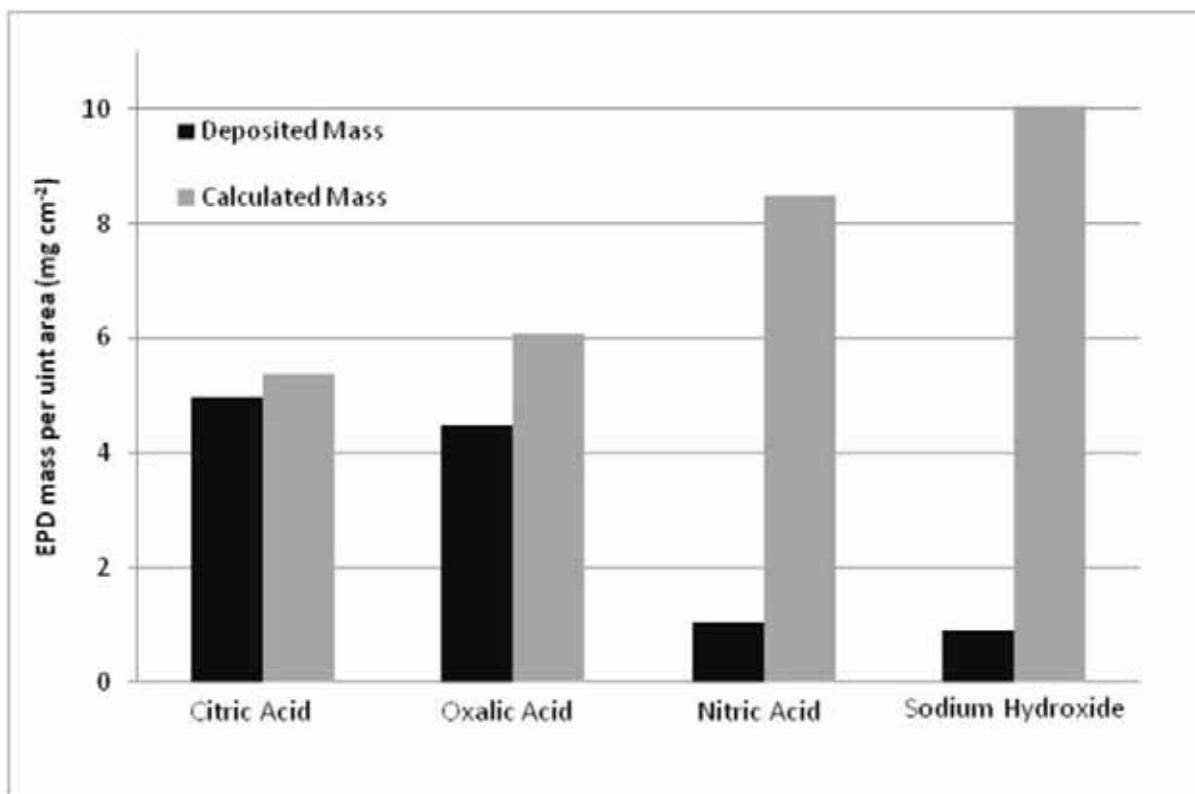
Fig. 7.6. Variation of zeta potential and pH of a ZrO_2 suspension (initial pH=4) with additions of citric acid also at pH=4.

7.3.4. Electrophoretic deposition

The effects of carboxylic acids on the EPD of ZrO_2 were examined by anodic and cathodic depositions and are outlined in Table 7.1. Citric and oxalic acids improved suspension stability and facilitated effective deposition of thick films on the graphite substrates. In contrast it was found that despite high absolute values of electrophoretic mobility (and zeta potential), using nitric acid and sodium hydroxide for pH adjustment in cathodic and anodic depositions respectively resulted in low deposit densities due to settling of ZrO_2 particles in the suspension. In addition to the sedimentation of ZrO_2 , EPD with nitric acid resulted a frothing of the suspension at the cathode which caused further deterioration to the integrity of the deposit. A comparison of calculated deposit mass per unit area predicted using the Hamaker equation (Eq. 7.1.) is illustrated in Fig. 7.7.

Table 7.1. Electrophoretic deposition data.

Reagent	pH	EPD Type	Mobility ($10^{-4}\text{cm}^2\text{V}^{-1}\text{S}^{-1}$)	Deposit Mass (mg cm^{-2})	Calculated Mass (mg cm^{-2})
Citric Acid	3.43	Anodic	-1.79	4.96	5.37
Oxalic Acid	3.57	Anodic	-2.02	4.48	6.06
Nitric Acid	2.98	Cathodic	2.83	1.03	8.49
Sodium Hydroxide	9.88	Anodic	-3.35	0.91	10.05

**Fig. 7.7. EPD of ZrO_2 : a comparison of deposited mass with calculated mass using the Haamaker equation.**

The quality of electrophoretically deposited thick films was significantly improved in the presence of citric or oxalic acids. This can be seen in Fig. 7.8. While in the presence of oxalic or citric acids continuous thick films were deposited, cathodic depositions with nitric acid for zeta potential adjustment yielded non-homogeneously deposited material and sodium hydroxide yielded very sparse anodic depositions exhibiting a low density of adhered particles.

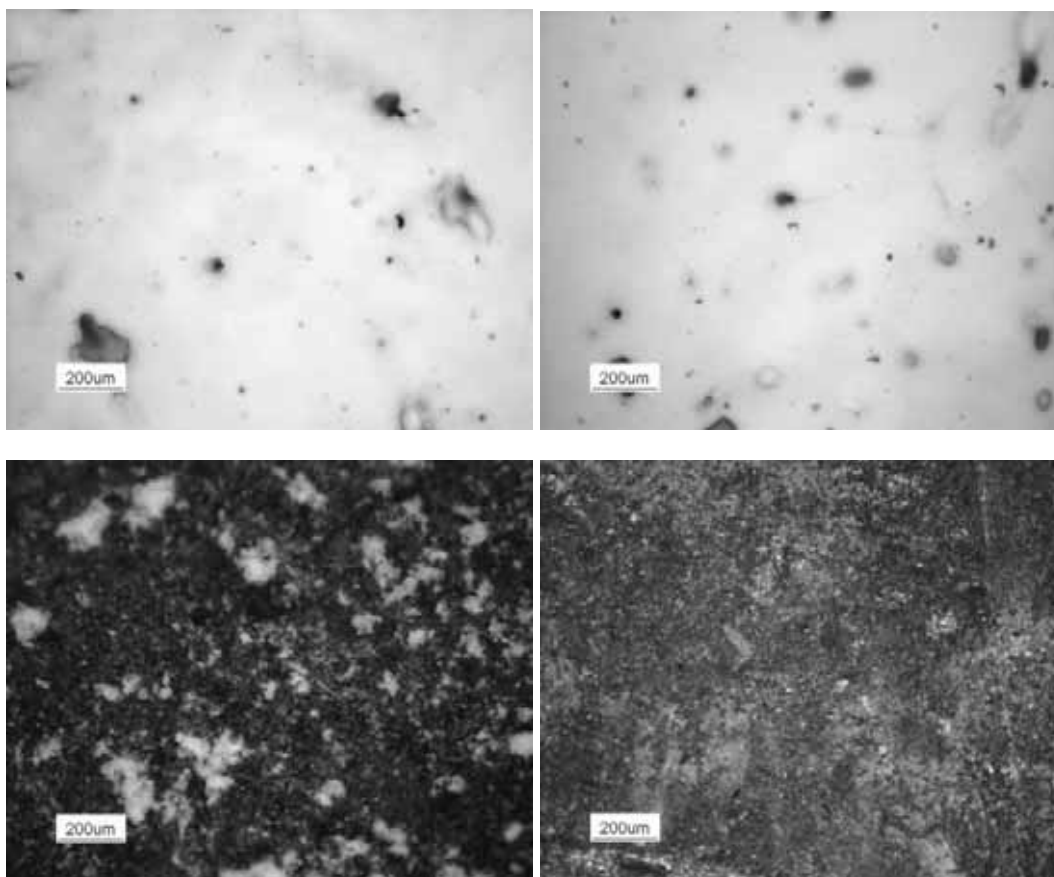


Fig. 7.8. Electrophoretically deposited ZrO_2 on graphite substrates from aqueous suspensions with (a) citric acid (b) oxalic acid (c) nitric acid and (d) sodium hydroxide additions.

7.4. Discussion

The data for conventional zeta potential variation with pH, as shown in Fig. 7.2, is similar to that of other systems and consistent with data in the literature. [15, 26] In contrast, as shown in Fig. 7.3, when citric acid was used for acidity adjustment, the zeta potential/pH curve shifted downwards by ~ 40 mV (relative to the values in Fig. 7.2), showing only negative values for the zeta potential at pH levels higher than 2, similar to that of polyelectrolyte dispersants. [26, 42] This effect is attributed to the ligation of negative carboxylate groups to particle surfaces, in similarity to the case for alumina particles in aqueous suspensions. [11, 22] Further, while the use of conventional pH variation results in the expected observation of electrostatic dispersion at zeta potential values greater than ~ 30 mV and agglomeration at lower zeta potential values, the

presence of citric acid maintained dispersion of ZrO_2 at all pH levels used in the present work. At low pH levels achieved with the use of citric acid, a zeta potential value of ~ 18 mV was observed without the occurrence of agglomeration. In the case of electrostatic dispersion such values of zeta potential are typically not sufficient to maintain particle dispersion, [37] and indeed suspensions of similar zeta potentials achieved with conventional pH adjustment (Fig. 7.2) were observed to show significant agglomeration. This is evidence that with the use of citric acid, in addition to the enhanced electrostatic repulsion imparted by a larger zeta-potential values, a steric barrier prevents particle approach and agglomeration, thus the mechanism of dispersion by citric acid is electrosteric rather than simply electrostatic. The stabilising effect of the steric barrier depends on the size of the adsorbed molecule, and thus smaller carboxylate groups, such as oxalate are likely to impart smaller steric barriers. [42, 43]

Since the adsorption of carboxylate groups on the particle surfaces is the mechanism by which particle dispersion was achieved, this effect was studied with the use of controlled concentrations of carboxylic acids of variable sizes, number of available carboxyl (anchor) groups, and speciation characteristics. Model structures of the three carboxylic acids, exhibiting symmetrical stereochemistry, are shown in Fig. 7.9.

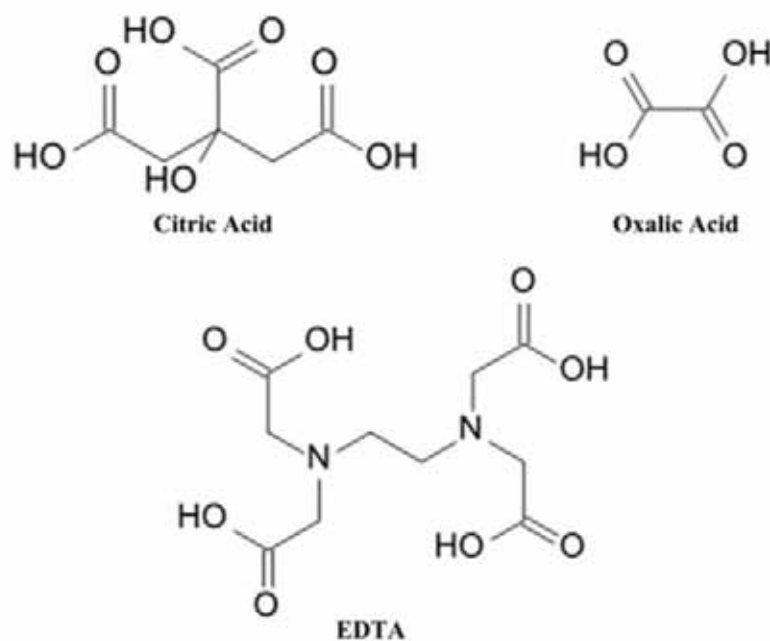


Fig. 7.9. Molecular structures of carboxylic acids used in the present work.

As shown in Table 7.2, reported pK_a values were used to determine the expected speciation behaviour at the pH levels used in the present work using Hyperquad Simulation and Speciation (HySS) software.[44] Speciation diagrams are shown in Fig. 7.10.

Table 7.2. Aqueous dissociation characteristics of carboxylic acids used in the present work [45–47].

Reagent	pK_{a1}	pK_{a2}	pK_{a3}	Expected Speciation at pH=4	Expected Speciation at pH=5.4
Citric Acid	3.14	4.77	6.40	76% AH_2^-	75% AH_2^-
				13% AH^{2-}	17% AH_2^-
				11% AH_3	8% A^{3-}
Oxalic Acid	1.25	4.14	N/A	57% AH^-	94% A^{2-}
				43% A^{2-}	6% AH^-
EDTA	2.00	2.67	6.16	95% AH_2^{2-}	85% AH_2^{2-}
				4% AH_3^-	15% AH^{3-}
				1% AH^{3-}	

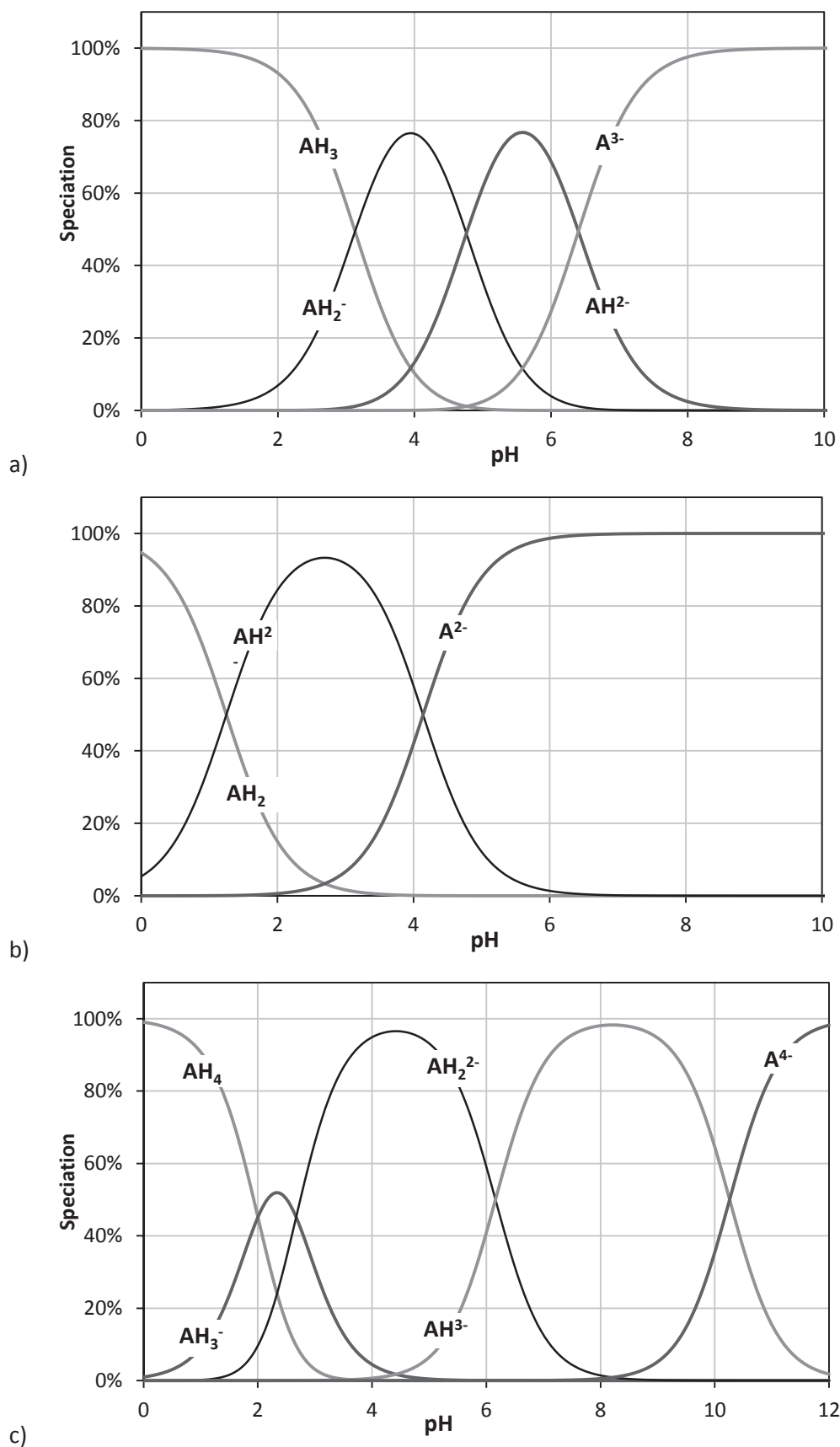


Fig. 7.10. Aqueous speciation diagrams of (a) Citric acid (b) Oxalic acid and (c) EDTA.

Fig. 7.4 shows the effect of carboxylic acid additions on the zeta potential of a suspension at pH ~ 4 and Fig. 7.5 shows the effect of the same reagents on a ZrO_2 suspension at pH ~ 5.4 , the native pH of the suspension. The decrease in zeta potential of 50–55 mV supports the conclusion of the ligation of the negative carboxylate groups and the levelling of the zeta potential drop corresponds to the surface saturation by these groups. The zeta potential and additive concentration at which the latter occurs depend principally on the surface charge imparted by the adsorbed species and their adsorption cross section on the particle surface. The effects of the carboxylic acids on zeta potential can thus be discussed in terms of size, surface coordination and speciation of the reagents used.

With the addition of citric acid and EDTA particle surface saturation is achieved at similar additive concentrations while with oxalic acid this occurs at higher addition levels. It is probable that a greater amount of oxalic acid was adsorbed owing to its smaller effective size and thus a smaller adsorption cross section relative to the other two reagents. Despite the larger molecular size of EDTA relative to citric acid, the adsorption cross section may be similar due to a similar surface complexation with ZrO_2 surfaces. Considering the surface area of the ZrO_2 powder, as determined from N_2 adsorption isotherms using BET methods, it is apparent that the surfaces monoclinic ZrO_2 reach saturation with citric acid / EDTA at $\sim 1.1 \mu\text{Mol m}^{-2}$ while oxalic acid saturates particle surfaces at $\sim 2.4 \mu\text{Mol m}^{-2}$. This corresponds to an adsorption cross section area of $\sim 1.5 \text{ nm}^2$ for citric and EDTA and $\sim 0.7 \text{ nm}^2$ for oxalic acid. This value is somewhat larger than the adsorption cross section reported for citric acid on alumina surfaces. [22]

The adsorption of citric acid to oxide particle surfaces is reported to take place through ligand exchange of surface-adsorbed hydroxyl groups with two carboxylate groups. [22, 36, 48] As evident from its adsorption cross section, similar surface complexation is likely to take place with EDTA. From consideration of the pK_a values and consequent speciation characteristics of EDTA

and citric acid as shown in Fig. 7.10, it would be expected that, contrary to observed behaviour, EDTA would impart a stronger negative charge to ZrO_2 particles. However, as reported elsewhere, [36] adsorbed organic acids exhibit lower acidity constants and greater deprotonation relative to species in solution and thus the negative charges imparted by ZrO_2 adsorbed carboxylate groups are greater in magnitude than those predicted by Fig. 7.10. Taking into account the presence of the hydroxyl group in citric acid, greater negative charge density on particle surfaces may be achievable with this reagent. From considerations of structure and speciation, it is likely that fully deprotonated oxalate groups coordinate to particle surfaces with one carboxylate group, giving rise to a lower adsorption cross section and similar surface charge density to citric acid.

An increase in pH occurs as citric acid adsorbs to particle surfaces reaching a maximum as particle surfaces reach saturation, as shown in Fig. 7.6. This is most likely due to the displacement of hydroxyl groups from ZrO_2 surfaces. Further, it is possible that due to increased negative surface charges, more positively charged species in solution become trapped in a thicker electrical double layer surrounding the particles thus leading to a higher pH reading.

Using conventional reagents (nitric acid and sodium hydroxide) to modify the zeta potential of particles in suspension resulted in poor electrophoretic deposition behaviour as shown in Figs 7.7 and 7.8. This occurred mainly as a result of significant settling of particles in suspension, which is an expected consequence of the large particle size of the powder used in this work shown in Fig. 7.1. The electrophoretic deposition of thick ZrO_2 films from the powder used in this work was made possible when citric acid and oxalic acids were used as dispersants. This is further evidence that in addition to the modification of the zeta potential, carboxylic acids facilitate enhanced dispersion through steric barriers.

7.5. Conclusions

Carboxylic acids have been shown to act as effective low molecular weight dispersants for aqueous suspensions of ZrO_2 . The use of a small quantity of a carboxylic acid reagent is sufficient to cover particle surfaces with negatively charged species, impart highly negative zeta potential values and maintain the oxide particles in suspension over a wide range of pH levels without the onset of agglomeration. The formation of a steric barrier is likely to also be a contributing factor in maintaining stabilization of particle suspensions. The use of carboxylic dispersing reagents has been shown to highly be beneficial in the electrophoretic deposition of ZrO_2 thick films, enabling the deposition of micron-range particles.

Acknowledgements

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8. Single- and mixed-phase TiO₂ powders prepared by excess-hydrolysis of a titanium alkoxide

This chapter presents a manuscript which has been accepted for publication in *Advances in Applied Ceramics: Structural Functional and Bioceramics*.

Using a wide variety of analytical techniques, in collaboration with the Australian Nuclear Science and Technology Organisation, the research project presented in this chapter investigated and discussed in depth the effects of precipitation routes and thermal treatment on the properties of titanium dioxide powders prepared by the hydrolysis of titanium tetra-isopropoxide, a common precursor chemical for the preparation of TiO₂ powders. Although the hydrolysis of titanium alkoxides is a common approach to the fabrication of titanium dioxide powders, few studies have discussed the fundamental mechanisms by which hydrolysis ratios influence the properties of precipitated TiO₂ powders. The parameters investigated in this chapter, which include surface area, crystallinity and phase assemblage of TiO₂ powders, are critical to the performance of these materials in photocatalytic applications.

In this chapter it is shown that mixed brookite-anatase-rutile TiO₂ powders can be fabricated through the use of appropriate precipitation conditions and thermal treatment. Such powders can be immobilised using methods explored and reported in chapters 5–7 of this thesis in order to achieve mixed phase immobilised TiO₂ photocatalysts for water purification applications. Alternatively such powders can be used as loose powder in suspensions, giving a higher available surface area at the expense of requiring a catalyst recovery procedure.

	Primary Author	Manuscript Preparation	Literature Research	Experimental Work	Data Analysis	Editing and Revision	Supervisory Role	Formatting and Layout	Advice and Support	Surface Area Analysis	Elemental Analysis
Dorian A. H. Hanaor	✓	✓	✓	✓	✓	✓		✓			
Charles C. Sorrell						✓	✓	✓	✓		
Ilkay Chironi										✓	
Inna Kharachevtseva											✓
Gerry Triani									✓		

Key Findings

- The ratio of water to Ti precursor was found to have significant consequences on the crystallinity, mineralogy and morphology of powders prepared through the hydrolysis of titanium alkoxides.
- Mixed anatase-rutile-brookite powders were obtained through excess hydrolysis of titanium isopropoxide and thermal treatment of powders
- Significant grain growth was observed during the anatase to rutile phase transformation
- A reduction in surface area and increase in pore diameter was observed in powders thermally treated above the anatase to rutile transformation temperature
- Morphological, mineralogical and crystallographic phenomena were interpreted in terms of precipitation and growth mechanisms

Single- and Mixed-Phase TiO₂ Powders Prepared by Excess-Hydrolysis of a Titanium Alkoxide

Dorian A.H. Hanaor^{[a]*}, Ilkay Chironi^[b], Inna Karatchevtseva^[b], Gerry Triani^[b], and Charles C. Sorrell^[a]

[a] University of New South Wales, School of Materials Science and Engineering, Sydney, NSW 2052, Australia

[b] Australian Nuclear Science and Technology Organisation, Institute of Materials and Engineering Sciences, Menai, NSW 2234, Australia

**Corresponding Author: Email: dorian@student.unsw.edu.au, Ph. (+61)-404-188810*

Abstract: To investigate excess-hydrolysis of titanium alkoxides, TiO₂ powders were fabricated from titanium-tetra-isopropoxide using 6:1 and 100:1 H₂O:Ti (r) ratios. Powders were dried and fired at a range of temperatures ($\leq 800^{\circ}\text{C}$). Hydroxylation and organic content in powders were characterised using ATR-FTIR, laser Raman microspectroscopy, and elemental microanalysis; surface area and pore size distribution were evaluated using N₂ gas adsorption; phase composition was analysed using XRD and laser Raman microspectroscopy; and crystallite size was evaluated by XRD, TEM and SEM. Results showed near-complete hydrolysis in a predominantly aqueous medium (r = 100), resulting in precipitated crystalline powders exhibiting brookite and anatase, which begin to transform to rutile below 500°C. Powders precipitated in a predominantly organic medium (r = 6) underwent partial hydrolysis, were highly porous and exhibited an amorphous structure, with crystallisation of anatase occurring at $\sim 300^{\circ}\text{C}$ and transformation to rutile beginning at 500°-600°C.

Keywords: TiO₂, Hydrolysis, Photocatalyst, Phase Transformation

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8.1. Introduction

Titanium dioxide is attracting increasing interest owing to its ability to function as a semiconductor photocatalyst. In photocatalysis, irradiation exceeding the semiconductor band gap is absorbed to generate electron-hole pairs, which can facilitate reactions of significant environmental importance, including water purification [1–4] and hydrogen production through water splitting [5–7].

The use of TiO₂ photocatalysts as dispersed powders provides the potential for a catalyst of higher available surface area in comparison with supported materials in the form of films or coatings. As photocatalysed reactions take place at close proximity to catalyst surfaces, TiO₂ powders have been used in aqueous suspensions for water purification applications [8–10] and hydrogen production [7, 11].

Titanium dioxide powders of high surface area are produced frequently by the hydrolysis of Ti alkoxides, as this approach gives rise to higher surface areas in comparison with industrially produced pigmentary TiO₂ [12, 13].

If no gelation-inducing reagents (hydrolysis catalysts) are used, the initial hydrolysis of titanium alkoxides results in the formation of titanium hydroxide monomers according to equation 8.1 [14–18], where R represents an organic chain of the formula (C_xH_{2x+1}):



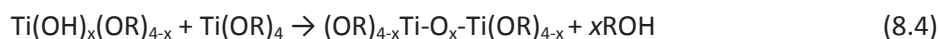
Titanium dioxide with OH-terminated surfaces forms and precipitates through the condensation of hydroxide monomers to form a network of Ti-O bonds. This reaction, described in equation 8.2 [15–19], takes place through a nucleation and growth process:



Equation 1 generally does not proceed stoichiometrically and, in the absence of peptising agents, the rapid formation of partially hydrolysed species occurs [17, 18, 20–22]:



This is accompanied by the condensation reaction and resultant precipitation described by equation 8.4. [23, 24]:



In the fabrication of titanium dioxide powders, the H₂O:Ti ratio, known as the hydrolysis ratio r , is a key factor in governing the size, morphology, and crystallinity of the precipitates that form. Using low hydrolysis ratios tends to result in partial hydrolysis, with retained organic groups present in the precipitate. Higher hydrolysis ratios are necessary for complete or near-complete hydrolysis to take place [17].

The precipitation of amorphous material from solution occurs when the incipiently formed nuclei are smaller than one unit cell, while larger nuclei give rise to growth of crystalline precipitates [25]. As a larger degree of supersaturation leads to the formation of larger nuclei, excess hydrolysis above a certain ratio, reported between 6 and 30, is necessary for the precipitation of crystalline TiO₂ from titanium alkoxide solutions, while the use of lower hydrolysis ratios generally results in the precipitation of amorphous materials, which transform to the anatase phase through heat treatment [17, 24, 26].

pH levels and temperatures are critical in determining the crystalline phases of TiO₂ that result from precipitation [27]. As with the surface area, the phase content of TiO₂ has a significant effect on the resultant photocatalytic performance of the material, with anatase and brookite reported to exhibit superior activity to that of the equilibrium rutile phase [28–30]. Furthermore, it is reported frequently that a mixed anatase/rutile or anatase/brookite/rutile phase composition is

advantageous for photocatalytic applications owing to improved charge carrier separation [31–33].

The present work investigates the use of excess hydrolysis at near-neutral pH and its effects on the resultant surface area, organic group retention, phase composition, and morphological properties in TiO₂ powders formed by precipitation from a titanium alkoxide.

8.2. Experimental procedure

8.2.1. Powder synthesis

Powders were synthesised from solutions of titanium tetra-isopropoxide (TTIP, 97%, Sigma Aldrich, USA) precipitated by hydrolysis at room temperature using moderate and high levels of excess water. For the former, a 150 mL solution of 0.5 M TTIP in isopropanol was hydrolysed by the dropwise addition of a solution of distilled water in 20 mL isopropanol under rapid magnetic stirring to give a 6:1 hydrolysis ratio. This resulted in visible precipitation occurring after 1–2 min of continued stirring at a pH level of 5.6. For precipitation with a high excess of water, a 50 mL of a 50 vol% solution of TTIP was added dropwise to 150 mL of distilled water with stirring to yield a H₂O:Ti ratio of 100:1, resulting in rapid precipitation of dispersed agglomerates and a pH level of ~5.4. Powders were denoted $r = 6$, representing those synthesised in a predominantly organic medium with 6:1 hydrolysis ratio, while $r = 100$ denoted powders precipitated in a predominantly aqueous medium.

8.2.2. Heat treatment

Precipitated powders were dried at 110°C for 48h to remove physically adsorbed water and residual isopropanol. The dried powders were placed in dense alumina crucibles and fired in air in

a muffle furnace at temperatures in the range 200°-800°C for 4h, with heating and initial cooling rates of 2°C/min.

8.2.3. Compositional analysis

The presence of hydroxyl groups and organic species in the powders was assessed using attenuated total reflection Fourier transform infrared spectroscopy (ATR FTIR) and elemental microanalysis. These analyses were done using a Spotlight 400 FTIR and Carlo Erba 1106 Microanalyser, respectively.

8.2.4. Morphological characterisation

The morphology of powders was assessed by scanning electron microscopy (SEM) using an FEI NanoSEM-230 microscope and by transmission electron microscopy (TEM) using an FEI Tecnai G2 microscope. The grain size was assessed using high-magnification SEM images ($\geq 40,000\times$) using the linear intercept method while crystallite sizes were similarly assessed from TEM images.

X-ray diffraction (XRD) patterns were collected using a Philips MPD unit with CuK α radiation. XRD spectra were used to calculate the lower crystallite size limit using the Scherrer equation [34, 35]. The phase contents of the powders were determined using a slightly modified version of the method of Spurr and Myers, as shown in equation 8.5 [36].

$$X_{A+B} = 1 - X_R = (1 + 1.26 \frac{I_{27.5}}{I_{25.3}})^{-1} \quad (8.5)$$

Where the subscripts A, B, and R represent anatase, brookite, and rutile, respectively.

Whereas the original version of this equation evaluates only X_A/X_R ratios, the present modified version incorporates the X_{A+B}/X_R ratio, where the former is the combined anatase + brookite fraction. $I_{27.5}$ and $I_{25.3}$ are the relative intensities of the rutile (110) peak at $\sim 27.5^\circ 2\theta$ and the

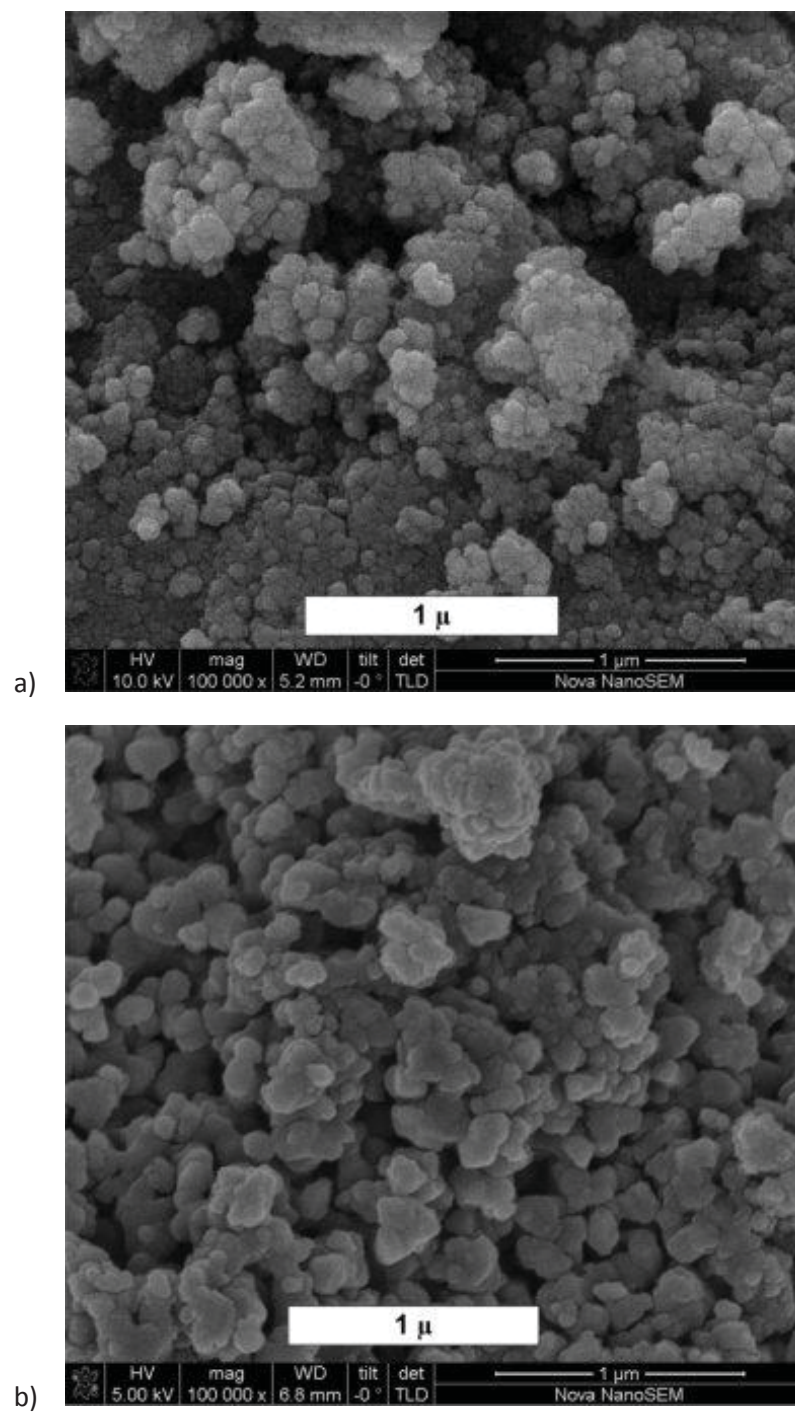
anatase (101) at $\sim 25.3^\circ 2\theta$. Since latter is a single broad and symmetric peak, with no shoulder, it coincides with the brookite (111) peak at $\sim 25.3^\circ 2\theta$ [28, 37].

Surface areas were assessed by N₂ adsorption at 77 K using a Micrometrics ASAP 2020 Physisorption Analyser (Brunauer Emmett Teller, BET method). These data were correlated with those determined using the Langmuir calculation method. The average pore diameters were assessed by N₂ adsorption at 77 K using the same instrument by the Barrett Joyner Halenda (BJH) analysis method.

8.3. Results

8.3.1. SEM micrographs

Representative SEM images, shown in Fig. 8.1 and Fig. 8.2, show isotropic grains of increasing size with firing temperature. The increase in grain size and density is particularly significant between 600°C and 800°C. Agglomeration was evident in all samples, with larger, more consolidated agglomerates, present in the $r = 100$ powders. A significant amount of porosity was prevalent in all samples, with larger pores visible in the well-consolidated agglomerates in the $r = 100$ powders fired at 700°-800°C. Samples precipitated at $r = 6$ exhibited less agglomeration, with a loosely packed porous structure retained after firing at 800°C, as evident from comparison of Fig. 8.2c with Fig. 8.1c



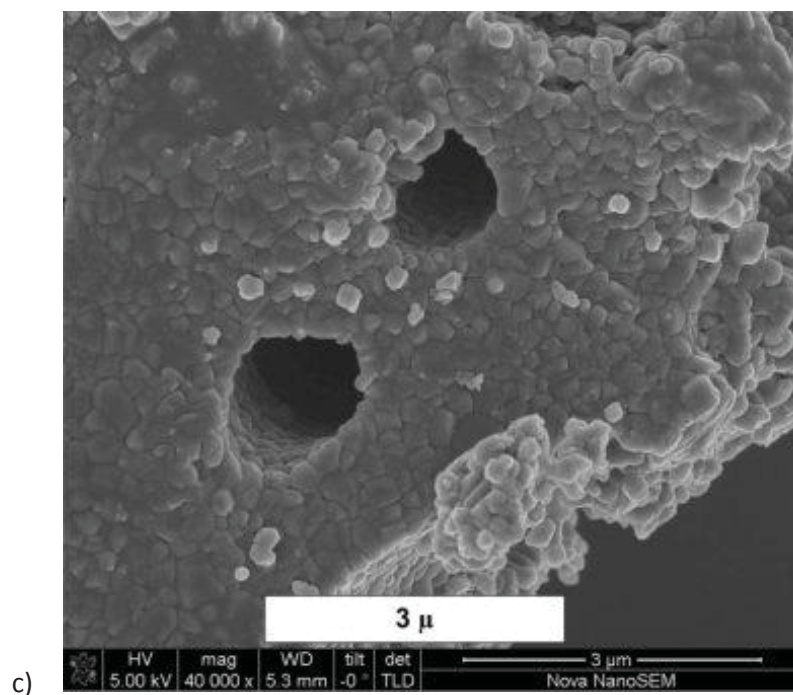
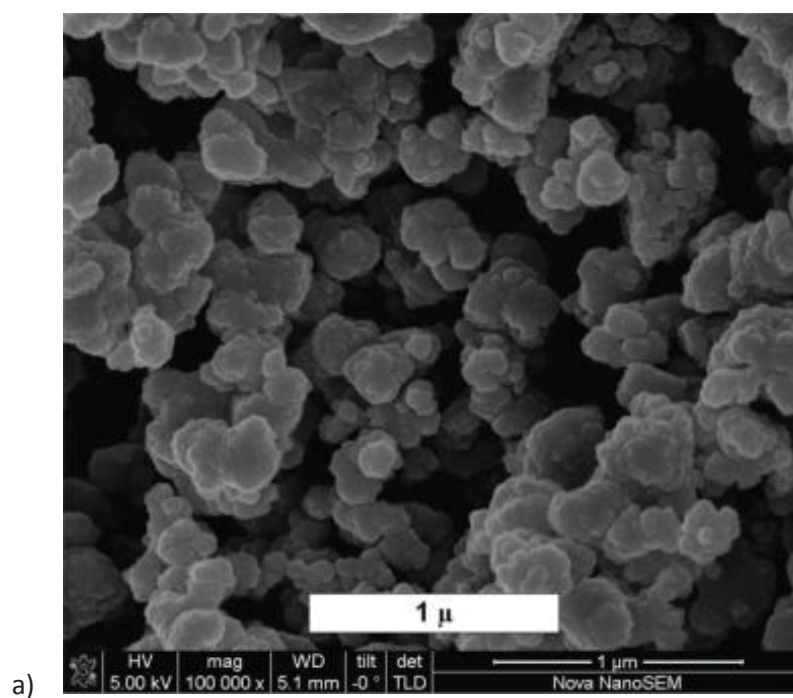


Fig. 8.1. Powders from precipitation at $r = 100$ fired at (a) 200°C, (b) 600°C, and (c) 800°C.



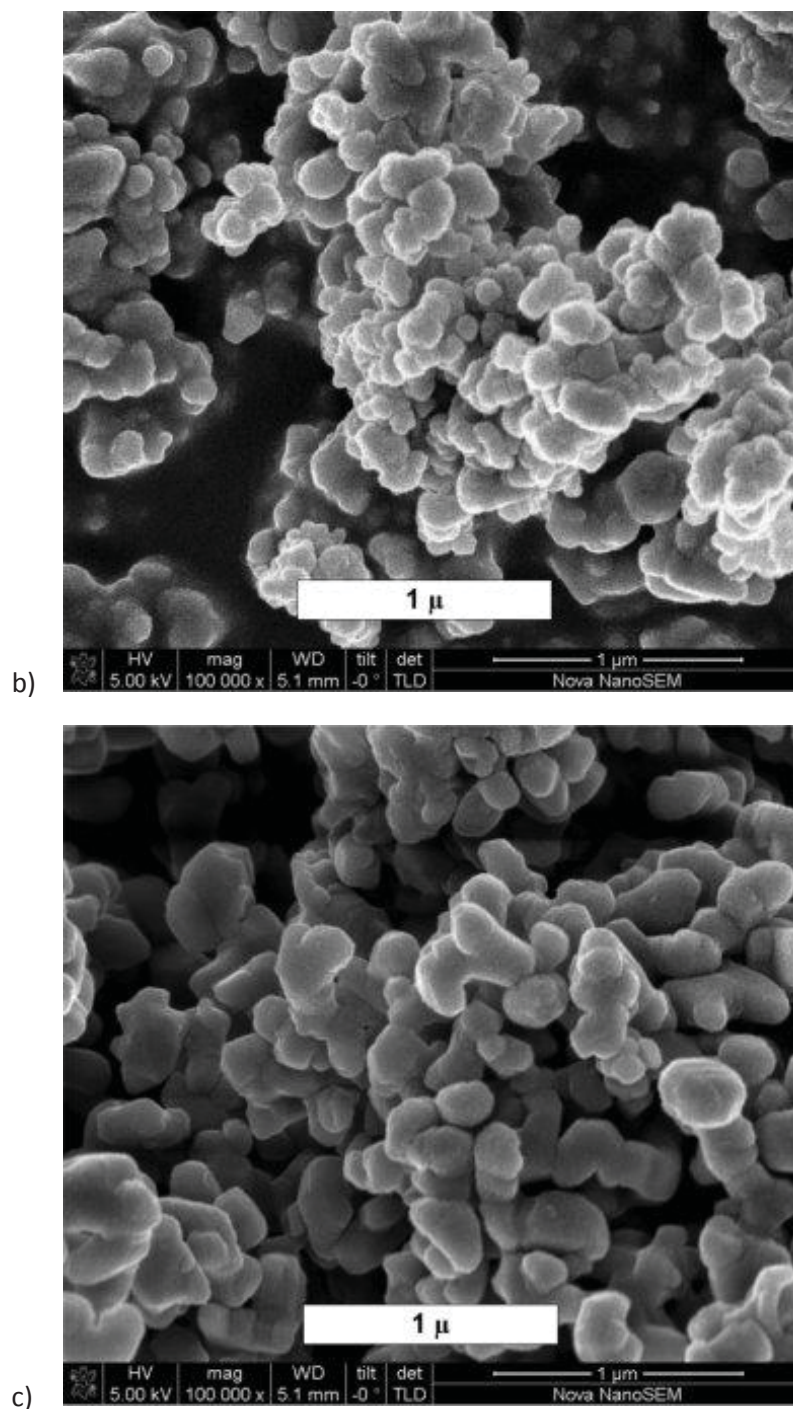
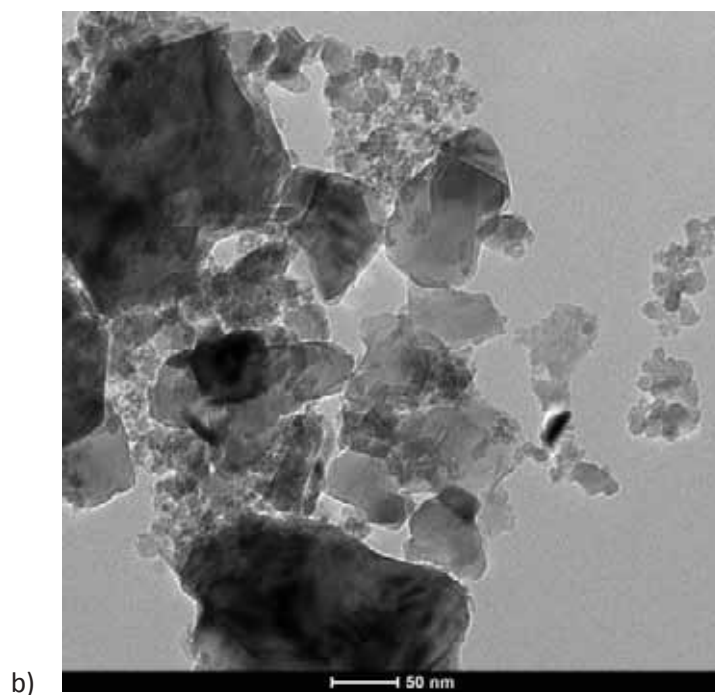
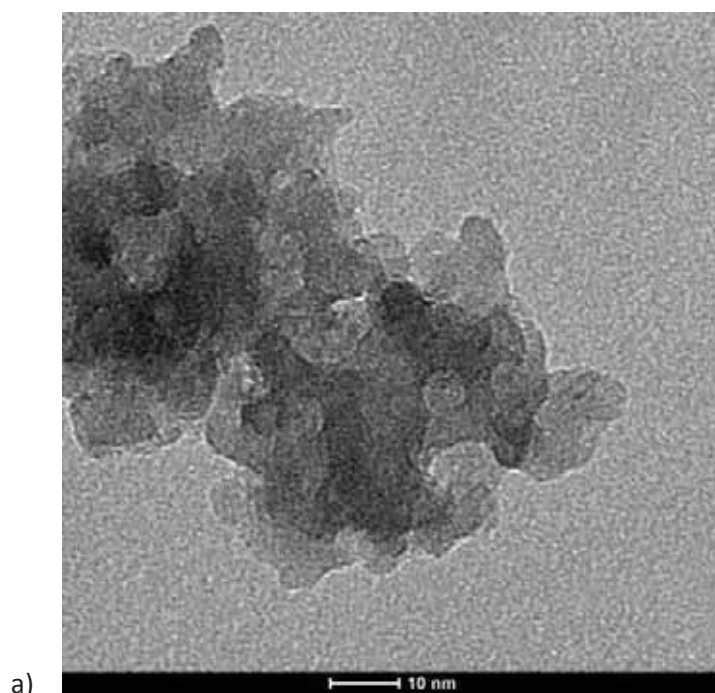


Fig. 8.2. Powders from precipitation at $r = 6$ fired at (a) 200°C, (b) 600°C, and (c) 800°C.

8.3.2. TEM analysis

Fig. 8.3 and Fig. 8.4 show TEM images. TEM analysis revealed that the grains visible in SEM micrographs from low temperature fired samples ($\leq 600^\circ\text{C}$) are comprised of finer crystallites.

These crystallites exhibit significant growth in the transformation to rutile. After firing at 600°C crystallite size shows significant divergence with smaller crystallites, possibly residual anatase, coexisting alongside larger crystallites of rutile. TEM imagery is inappropriate for agglomerate size analysis as a result of sample preparation methods and the electron-opacity of larger particles.



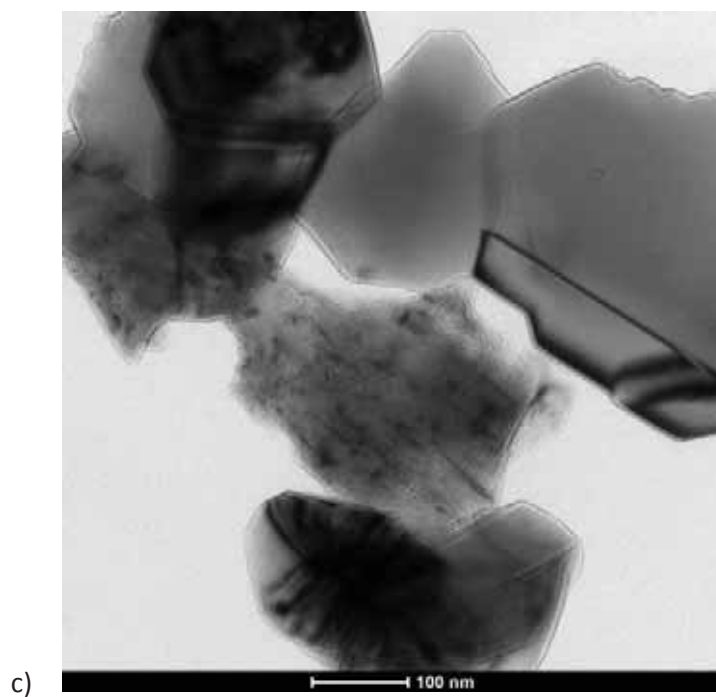
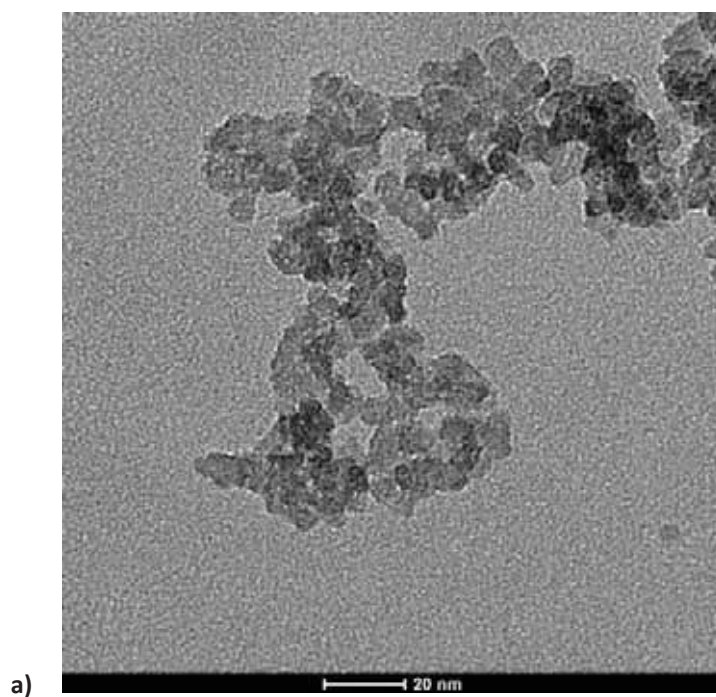


Fig. 8.3. TEM micrographs of $r = 100$ powders fired at (a) 200°C, (b) 600°C and (c) 800°C.



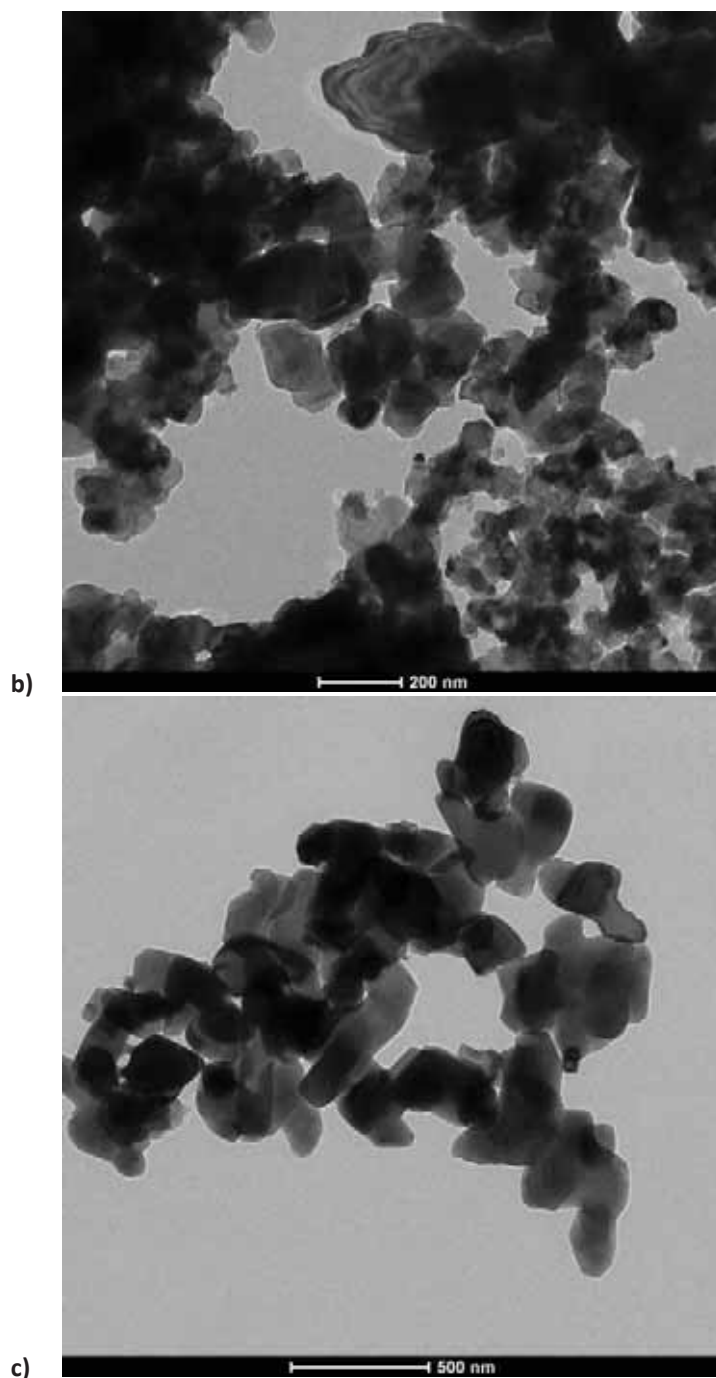


Fig. 8.4. TEM images of $r = 6$ powders fired at (a) 200°C, (b) 600°C and (c) 800°C.

8.3.3. Elemental analysis

The results for elemental analysis, shown in Fig. 8.5, show the reduction in residual carbon content in powders with increasing firing temperature. In comparison with powders precipitated in a predominantly aqueous medium, powders precipitated in a predominantly organic medium

show higher levels of carbon owing to the presence of retained organic groups in the hydrolysis product. After firing at temperatures $\geq 400^\circ\text{C}$, the carbon contents approach the same baseline value.

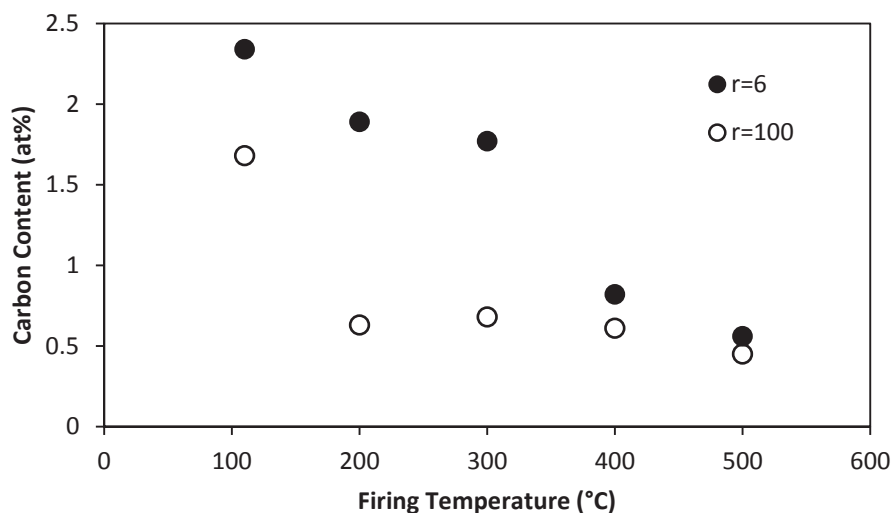


Fig. 8.5. Residual carbon content in TiO₂ powders as a function of firing temperature

8.3.4. Spectroscopy

ATR-FTIR spectra, shown in Fig. 8.6, show the presence of a broad band at $3000\text{--}3600\text{ cm}^{-1}$ corresponding to the stretching vibration of terminating hydroxyl groups in samples fired up to 500°C . The peak at 1630 cm^{-1} corresponds to the bending vibration of residual surface-adsorbed H₂O, with the decrease in intensity with increasing temperature corresponding to the increase in bulk density (and hence decrease in surface area). Powders precipitated at $r = 6$ show the presence of residual organic groups after low-temperature firing, evident from the C-H stretching at 2976 cm^{-1} and $900\text{--}1300\text{ cm}^{-1}$ [23, 38].

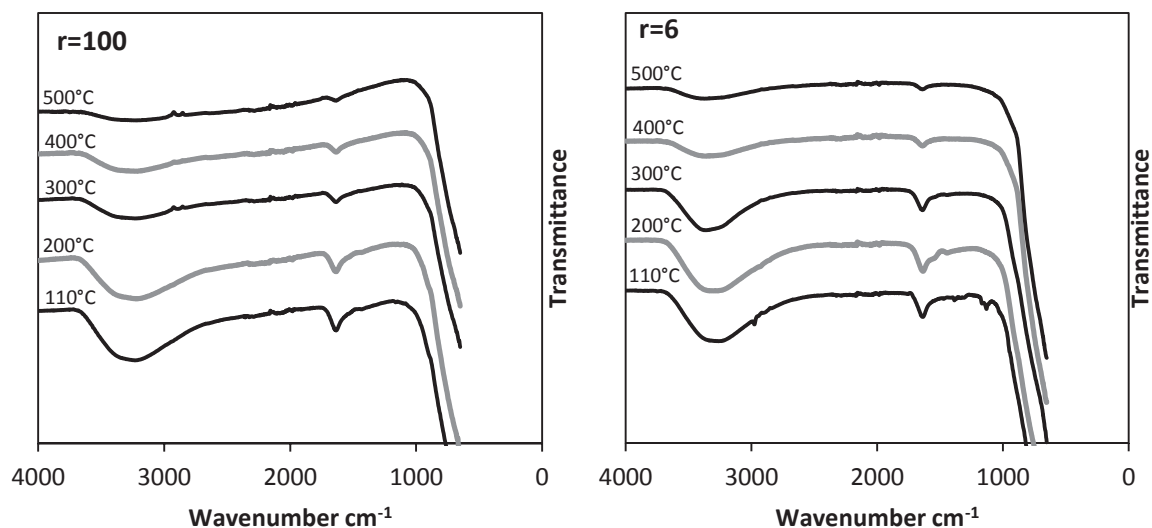


Fig. 8.6. ATR-FTIR spectra at (a) $r = 100$ powders and (b) $r = 6$ powders fired at different temperatures.

Laser Raman microspectra for the low-temperature-fired samples are shown in Fig. 8.7. Similar to the ATR-FTIR spectra, peaks at $2900\text{--}3000\text{ cm}^{-1}$ are present in $r = 6$ powders heated at 110°C (dried powder) and 200°C , resulting from the stretching of CH_2 and CH_3 groups. These data confirm partial hydrolysis of the alkoxide at $r = 6$ with the retention of organic groups in the precipitate. The broad peaks at 410 and 630 cm^{-1} result from TiO_6 octahedral units. The high peak at 144 cm^{-1} is characteristic of the anatase phase. However, short-range anatase-like order in amorphous TiO_2 may give rise to this peak owing to similar Ti-O bond lengths [39].

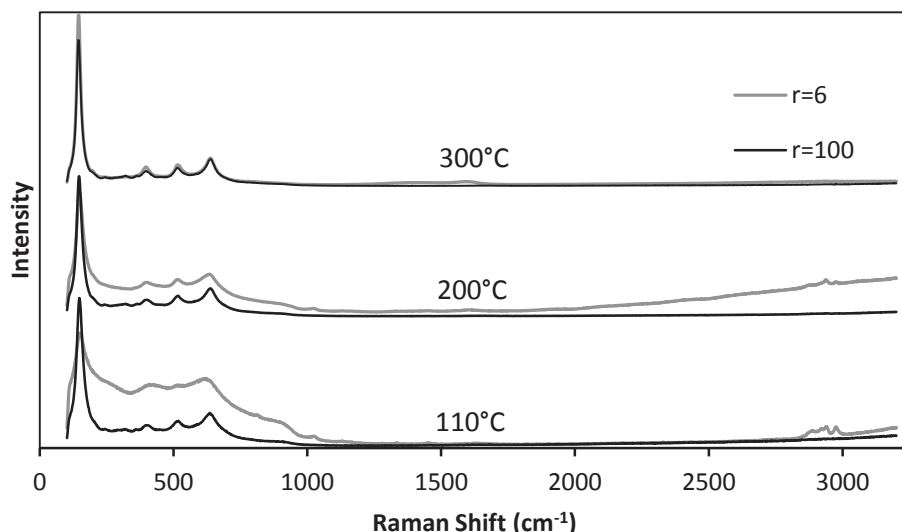


Fig. 8.7. Raman spectra of powders heated at different temperatures showing anatase peaks.

8.3.5. X-ray diffraction

XRD spectra from powders precipitated at $r = 100$, shown in Fig. 8.8, show broad diffuse anatase peaks after firing at low temperatures owing to the presence of crystalline phases from precipitation. At samples fired at $\leq 500^\circ\text{C}$, the brookite (121) peak at $\sim 30.5^\circ 2\theta$ is visible. The brookite (210) and (111) peaks at ~ 25.3 and $\sim 25.7^\circ 2\theta$ coincide with the anatase (101) peak, giving rise to further peak heightening as well as broadening. As shown in Fig. 8.9, powders precipitated at $r = 6$ exhibit only amorphous content below 300°C , the temperature at which the anatase phase becomes observable; there is no evidence of brookite at any temperature. A small rutile (110) peak at $\sim 27.3^\circ 2\theta$ is apparent at 500°C in $r = 100$ powders; this peak is not present at this temperature in $r = 6$ powders.

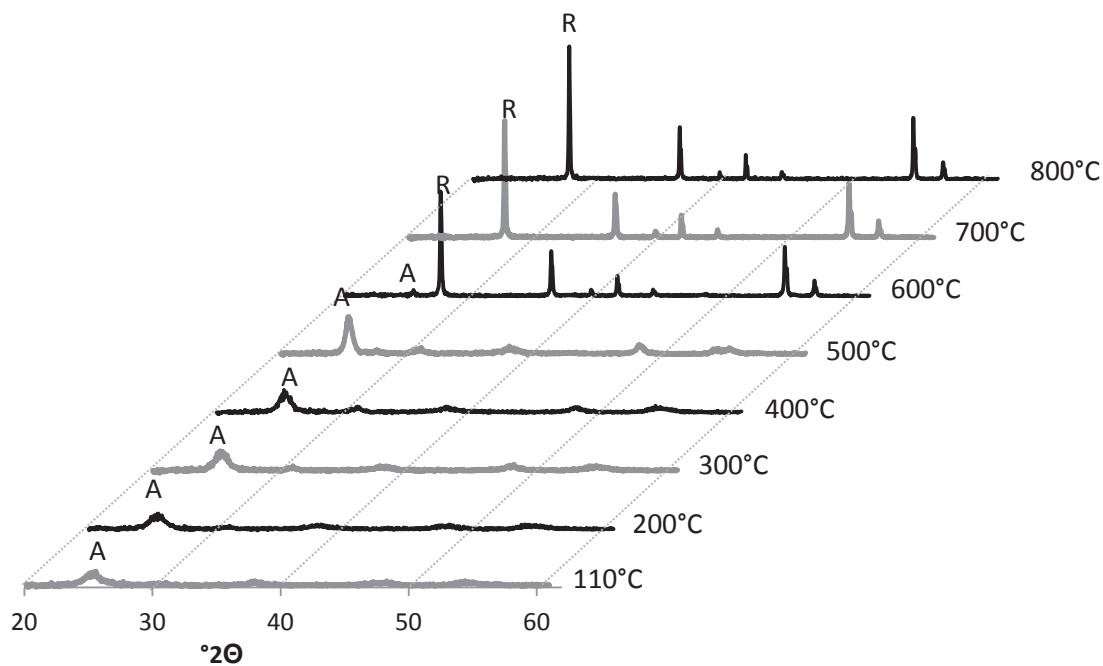


Fig. 8.8. XRD patterns of $r = 100$ powders fired at different temperatures.

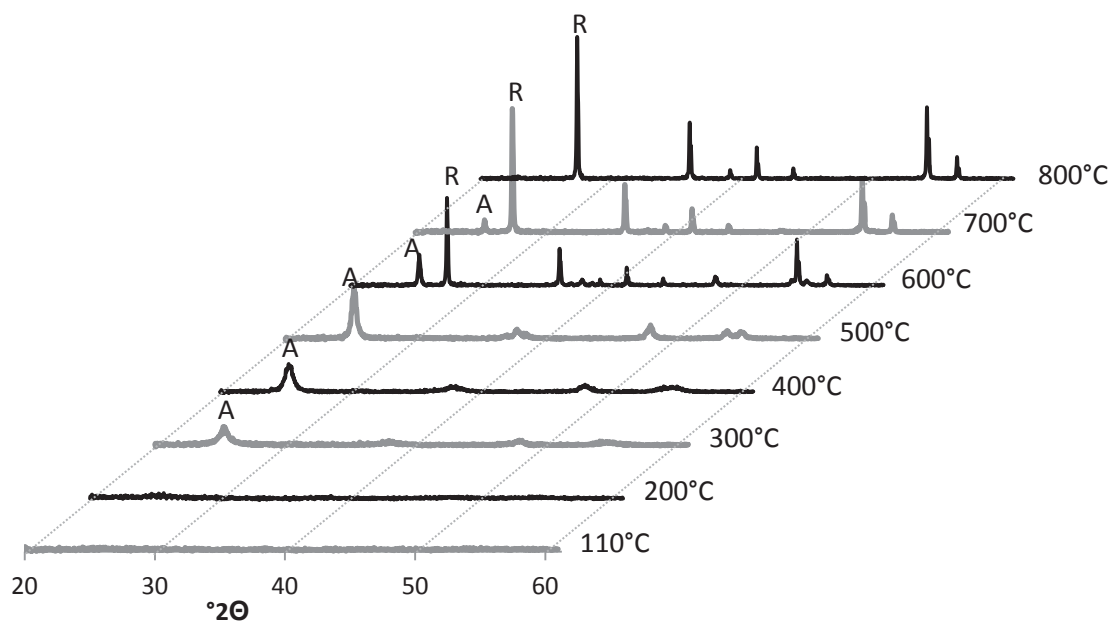


Fig. 8.9. XRD patterns of $r = 6$ powders fired at different temperatures.

8.3.6. Analysis of morphology and phase composition

TEM micrographs and XRD spectra were analysed to ascertain the variation in crystallite sizes with firing temperature, while the analysis of SEM micrographs shows the variation in grain size. A summary of these data is shown in Fig. 8.10. A significant increase in both grain and crystallite size accompanies the anatase to rutile transformation at ~600°C. As revealed by TEM analysis, grains visible in SEM analysis consist of nano-crystallites after firing at lower temperatures ($\leq 500^\circ\text{C}$). After firing at higher temperatures the grain size observed by SEM is approximately consistent with the crystallite size observed by TEM. The interpretation of XRD data using the Scherrer equation [34, 35] for morphological analysis is applicable only for crystalline materials with crystallites smaller than ~100 nm and provides an estimate of the lower limit for the crystallite size [40]. Crystallite sizes estimated by the Scherrer equation are consistent with TEM results at lower temperatures ($\leq 500^\circ\text{C}$), while at higher temperatures XRD analyses yield smaller crystallite size values. This is a result of the divergence in crystallite sizes shown also in Fig 8.3b and Fig. 8.4b along with the aforementioned ineffectiveness of XRD methods for the morphological analysis of coarse-grained material. It should be noted that after treatment at 110° and 200°C, r = 6 powders are amorphous and thus cannot be analysed for crystallite size by XRD methods. Grains of these amorphous powders are still comprised of nanoscale subgrains as evident in Fig. 8.2a and Fig. 8.4a. Grains observed by SEM as well as crystallites observed by TEM were larger in r = 100 powders fired under 500°C in comparison with r=6 powders.

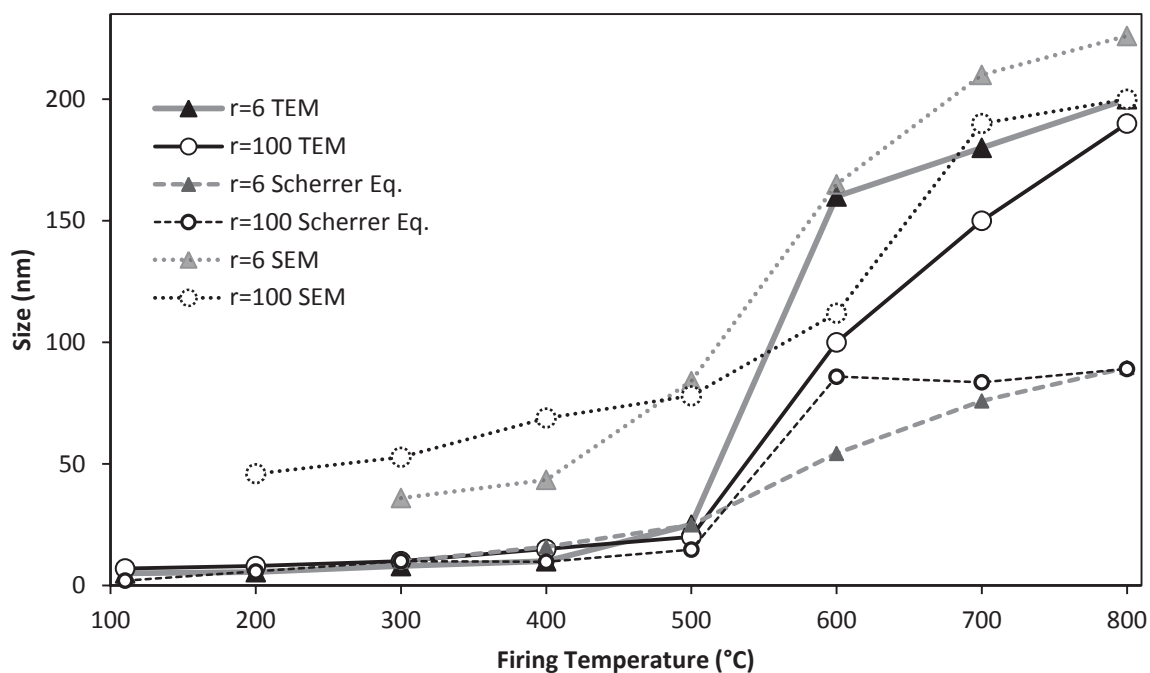


Fig. 8.10. Crystallite and grain size analyses by TEM, XRD and SEM.

As shown in Fig. 8.11, the phase composition, determined from the XRD patterns using the modified method of Spurr and Myers [36] shows a more rapid transformation to rutile in samples formed from aqueous precipitation. The initial appearance of rutile appears to be at ~500°C in $r = 100$ powders and at ~600°C in $r = 6$ powders. A more accurate approximation of the phase transformation onset temperature would require extended firing durations at narrower temperature intervals [41].

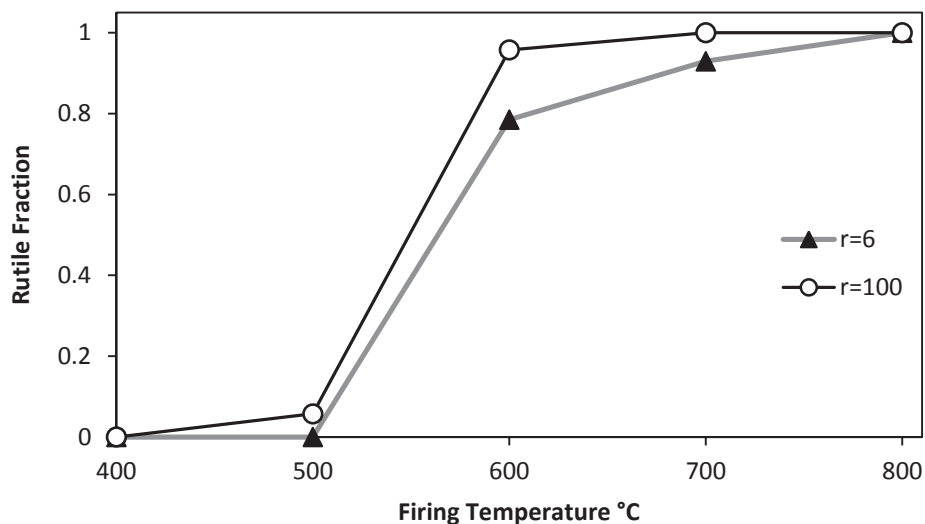


Fig. 8.11. Rutile fraction calculated from XRD peaks using the method of Spurr and Myers [36].

8.3.7. Surface area analysis

Plots of N₂ gas adsorption at 77 K used to determine the surface areas according to the BET method [42, 43] are shown in Fig. 8.12. In these figures, Q is the quantity of gas adsorbed in mmol·g⁻¹ and P/P₀ is the ratio of adsorptive pressure to saturation pressure. The slope and intercept of these plots were used to determine the surface area of powders, where a high value of intercept and slope translate to a low surface area. A large shift in slope and intercept of these plots is evident at a firing temperature of 600°C in r = 100 powders. This shift is present to a significantly lesser extent in powders precipitated at r = 6.

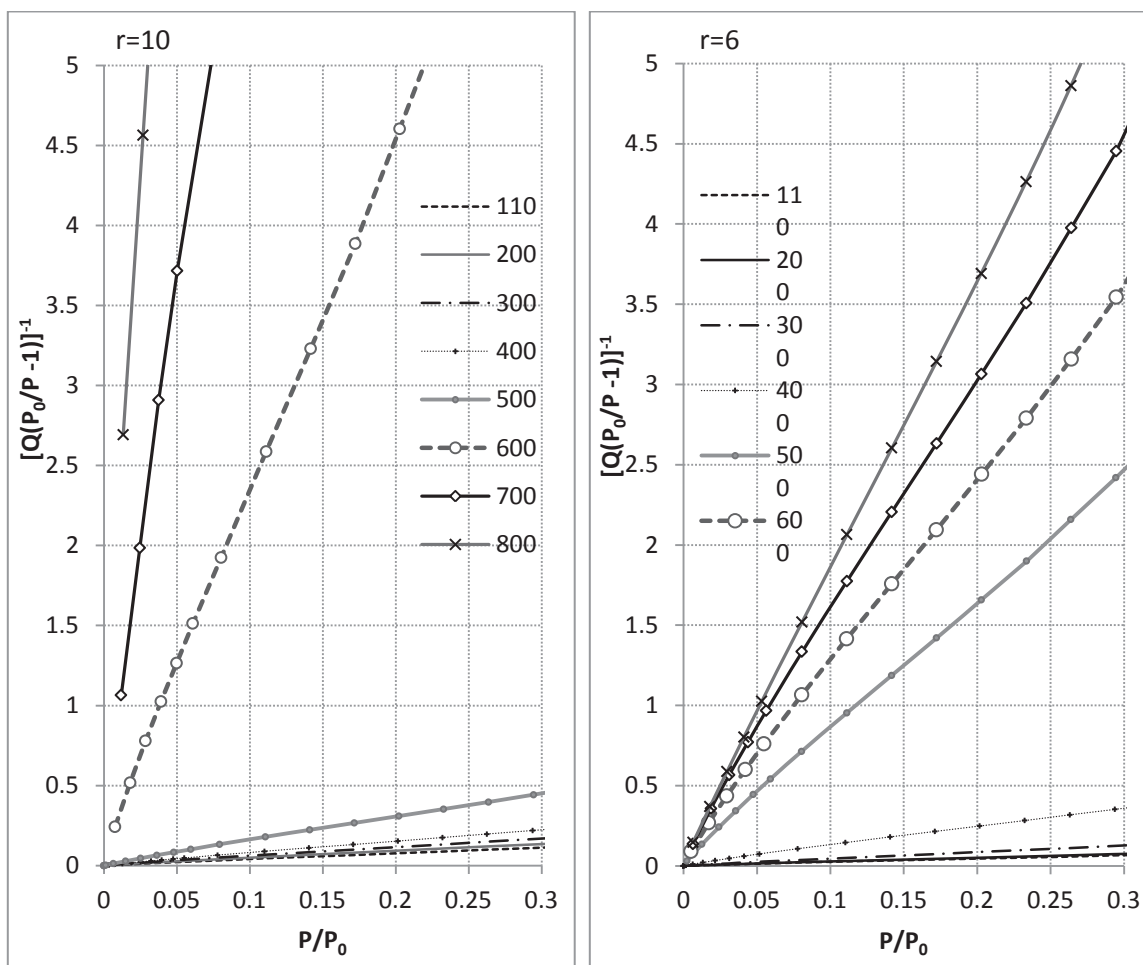


Fig. 8.12. N₂ adsorption at 77 K for (a) $r = 100$ powders and (b) $r = 6$ powders.

The surface areas determined by these data are shown in Fig. 8.13. This figure shows an initial higher surface area in $r = 6$ powder in comparison with $r = 100$ powders, with a sharp decrease in surface area occurring with increasing firing temperature. As evident from the slopes of the N₂ adsorption curves in Fig. 8.12, the drop in surface area at 600 °C is more significant in $r = 100$. The expanded view of the surface area after firing at 600°-800 °C shows the surface area of the $r = 100$ powders following the anatase to rutile transformation is significantly lower in comparison with powders precipitated in an organic medium.

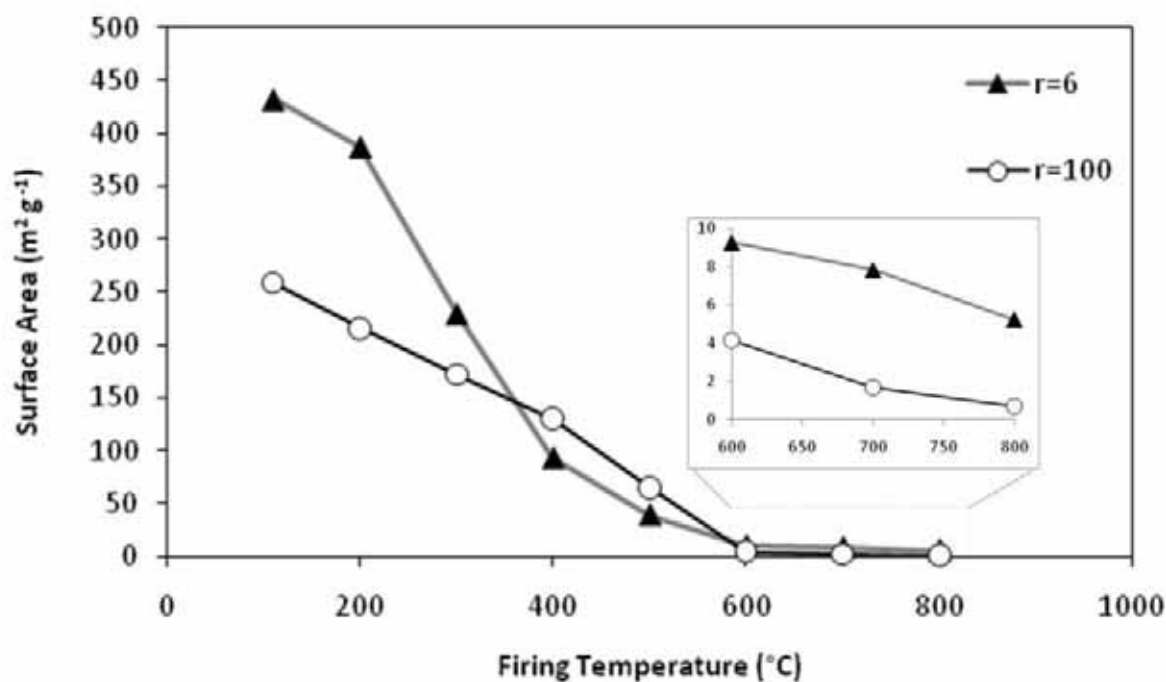


Fig. 8.13. Surface areas determined by BET analysis.

The average pore diameter, determined from BJH analysis of the adsorption isotherms, exhibits an increase with firing temperature, as shown in Fig. 8.14. This is more evident in powders from aqueous precipitation, where the average pore diameter continued to increase at higher temperatures. In contrast, powders precipitated at $r = 6$ did not exhibit as significant an increase in pore size at high temperatures. These results are consistent with the densification behaviour of the agglomerates, which results in expansion of the inter-agglomerate pore size [44]. Hence, this effect is enhanced in the more agglomerated $r = 100$ powders, as indicated in SEM images shown in Figs. 8.1 and 8.2.

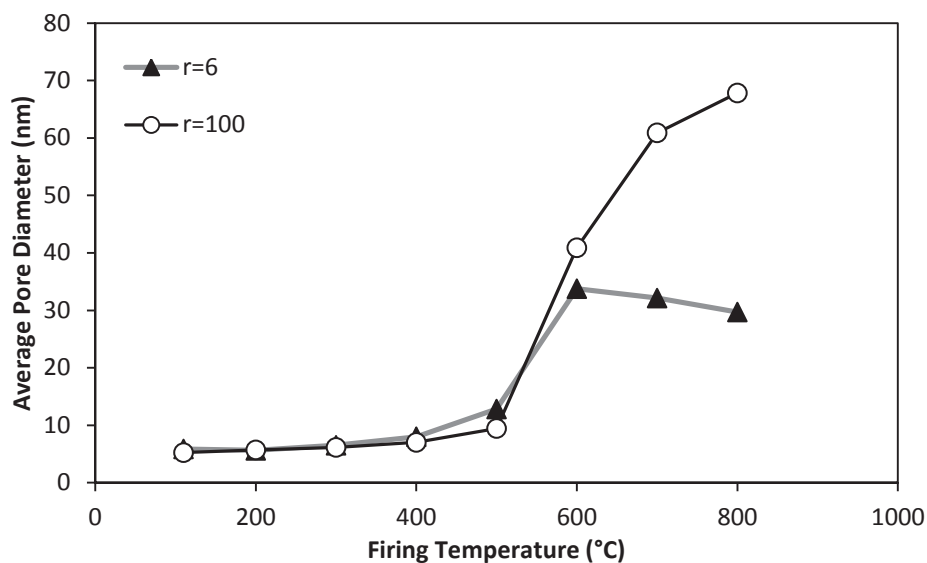


Fig. 8.14. Average pore diameters determined by BJH analysis.

8.4. Discussion

8.4.1. Organic content

In the present work, commonly employed hydrolysis catalysts were not used. Hence, the hydrolysis at $r = 6$ was incomplete at room temperature. The carbon retained in the precipitates was still present after drying at 110°C and the associated removal of residual volatile compounds. This is evident from the presence of the C-H vibrations in ATR-FTIR and laser Raman microspectroscopy and from the elemental microanalysis results. The absence of C-H vibrations in the ATR-FTIR and Raman spectra from powders fabricated through aqueous precipitation suggests that in these samples hydrolysis was complete, although carbon may have been present as an adsorbate on TiO₂ surfaces resulting from the combustion of ROH species during drying.

The requirement of a significant excess of water for complete hydrolysis of titanium alkoxides has been reported previously [17, 45]. However, it is likely that the hydrolysis level adequate for complete hydrolysis is dependent on the peptisation and pH levels. The presence of retained

organic groups in the precipitates is likely to impact on the morphology, phase composition, and performance of TiO₂ powders prepared by the hydrolysis of alkoxides.

8.4.2. Precipitate Phase Formation

As shown by XRD analysis, hydrolysis at $r = 100$ caused crystalline precipitation of anatase and brookite, which is likely to be a result of a higher level of supersaturation of the solution by water and the consequent incipient formation of larger nuclei [25]. In contrast, $r = 6$ results in precipitation of an amorphous phase, most likely due to lower supersaturation and consequent incipient formation of nuclei smaller than one unit cell, the minimal nucleus size required for crystalline precipitation. It also is possible that the retention of organic groups contributes to prevention of the formation of the ordered anatase lattice. This phase formation behaviour is consistent with other reports of precipitate formation in titanium alkoxides [27, 46].

8.4.3. Morphology

From the analysis of the SEM and TEM images, $r = 100$ powders fired below 500°C exhibited larger grains in comparison with $r = 6$ powders. These grains were shown by TEM to be comprised of nano-scale crystallites which too were larger in $r = 100$ powders. This difference in crystallite size was less evident from XRD analysis as the coincidence of the anatase and brookite peaks in the $r = 100$ samples may have led to peak broadening and a lower resultant crystallite size determined by the Scherrer equation [40]. Since the growth of precipitates typically is controlled by processes at the particle/solution interface, the formation of larger grains in the $r = 100$ powders probably results from the lower free energy of crystalline solids in comparison to amorphous ones [44].

That is, the interface-controlled growth of crystalline precipitates would be expected to occur at more rapid growth kinetics compared with those in amorphous precipitates.

Powders prepared by precipitation in a predominantly aqueous medium exhibited a greater extent of agglomeration and lower extent of porosity. This is a result of a more rapid precipitation at $r = 100$ coupled with the denser particle packing that crystalline particles exhibit during drying in comparison with amorphous particles [47]. As shown in Fig. 14 and Fig. 8.1, pores in $r = 100$ powders were larger than those in $r = 6$ powders following the transformation to rutile. This is attributed to the aforementioned densification of agglomerates.

8.4.4. Phase transformation

The powders precipitated at $r = 100$ show a mixture of anatase and brookite. The ratio of anatase to brookite these powders has not been determined as the method of Spurr and Myers [36] is applicable only to anatase + rutile mixtures. Using the modified version of this method, substituting $X_A + X_B$ for X_A , the analysis shows that the transformation of anatase to rutile in $r = 6$ appeared to be slower than that of anatase + brookite to rutile in $r = 100$ powders. The presence of brookite in $r=100$ powders is likely to have enhanced the formation of rutile in these powders through a higher density of phase interfaces and consequently higher interfacial energy. This is supported by numerous publications in which brookite has been reported to act as a nucleation site for rutile formation in anatase [47–50]. This also may explain the phase transformation onset temperature of $\leq 500^\circ\text{C}$ observed in $r = 100$ powders, a temperature lower than what is generally reported as the onset temperature of the anatase to rutile phase transformation [41].

The faster rutilation of $r = 100$ powders could also be the result of larger metastable crystallites transforming more readily to the equilibrium rutile phase due to enhanced growth kinetics. Conversely, the higher level of retained carbon in samples prepared by precipitation in organic

media may have enhanced the anatase to rutile phase transformation in $r = 6$ through increased levels of oxygen vacancies as the carbon may act as a reducing agent. Increased levels of oxygen vacancies also would facilitate the structural rearrangement involved in the anatase to rutile phase transformation [41], and offset the slower transformation kinetics in the absence of brookite.

8.4.5. Surface area

The surface area of powders prepared in this work compare favourably to alkoxide-derived powders synthesised in other work [13, 18], although powders prepared by hydrolysis of TiCl₄ generally show higher surface areas [51]. As shown in Fig. 8.12 and Fig. 8.13, a sharp reduction in surface area accompanied the anatase to rutile phase transformation at $\sim 600^\circ\text{C}$. This effect has been reported elsewhere [52–54] and results from the previously described grain growth associated with the anatase to rutile and the brookite to rutile phase transformations. The reduction in surface area is further evident from the decreased levels of terminating hydroxyl groups observed in ATR-FTIR analysis, shown in Fig. 8.6. As shown in the insert in Fig. 8.13, the reduction in surface area accompanying the anatase + brookite to rutile phase transformation is more significant in powders precipitated at $r = 100$ and the surface area of rutile powders fabricated this way exhibit low surface areas around $0.5\text{--}2\text{ m}^2\text{g}^{-1}$. Such low surface areas are undesirable from the photocatalysis perspective.

At lower temperatures, the variation in surface areas is consistent with that of the grain sizes while, at higher temperatures, the decrease in surface area is larger in $r = 100$ powders despite a more moderate increase in grain size. Again, this resulted from the densification of agglomerates, as emphasised in Fig. 8.1c. The lower surface areas of samples precipitated at $r = 100$ and heated at $110^\circ\text{--}400^\circ\text{C}$ is a result of the aforementioned faster nucleation and growth of crystalline

precipitates and denser packing of these particles. The denser grain packing in $r = 100$ powders also explains the increase in the average pore diameter shown in Fig. 8.14 as small pores become closed during densification.

As crystallinity is required for photocatalytic activity in TiO₂, the high surface area of amorphous powders is not likely to enhance photocatalytic performance in such powders. The highest photocatalytic activity would be expected in powders synthesised at $r = 100$ heated at 110°C. Under these conditions, a comparatively high surface area in conjunction with the presence of a mixed anatase-brookite phase composition are expected to yield enhanced photocatalytic performance.

8.5. Conclusions

- The formation of crystalline phases by precipitation from of titanium isopropoxide solutions requires a significant excess hydrolysis ratio.
- Mixed anatase/brookite/rutile TiO₂ powders can be formed by appropriate thermal treatment of powder precipitated with a significant excess of water.
- The anatase to rutile phase transformation is enhanced in the presence of a secondary brookite phase.
- Surface area is enhanced through reduced agglomeration in powders precipitated at lower hydrolysis ratios.
- The use of higher hydrolysis ratio may be advantageous for the fabrication of photocatalysts due the formation of high surface area crystalline precipitates at low temperatures

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9. Fabrication and characterisation of sand-supported mixed phase TiO₂ photocatalysts

As described extensively in this thesis, the immobilisation of TiO₂ photocatalysts on support materials is of great importance for water purification applications as the use of titanium dioxide powders entails a catalyst/water separation step, which makes such materials inappropriate for large scale applications.

In the present Chapter, which presents a manuscript submitted to the Journal of Applied Catalysis, the fabrication of titanium dioxide supported on grains of sand is described. These materials were fabricated using similar precursor materials to those reported in chapter four. In this case however, titanium dioxide films are obtained on the surfaces of grains of sand rather than single crystal substrates.

The support materials used in the present chapter are advantageous owing to their low-costs and ready availability. Economic factors are critical in applying TiO₂ photocatalysts for water purification, as the large scale of such applications prohibits the use of costly raw materials. For this reason the novel approach taken in using sands as support materials is of great value.

A breakdown of the contributions of the authors to the preparation of the manuscript presented in this chapter is shown below:

	Primary Author	Manuscript Preparation	Literature Research	Experimental Work	Data Analysis	Editing and Revision	Supervisory Role	Formatting and Layout		
Dorian A. H. Hanaor	✓	✓	✓	✓	✓	✓		✓		
Charles C. Sorrell						✓	✓	✓		

Key Findings:

- Uniform well adhered coatings of TiO₂ were applied to grains of different types of sand for surface area enhanced immobilisation.
- The suspension of sand particles in a Ti bearing sol-gel matrix was found to result in uneven spalling coatings of TiO₂ on the grains of sand.
- The anatase to rutile phase transformation in TiO₂ coatings on sand grains occurred at higher temperatures relative to unsupported powders, in similarity to films on quartz substrates.
- The use of TiO₂ coated sands in the form of a packed bed impedes the full realisation of the advantages of utilising high surface area support materials.

Sand Supported Mixed-Phase TiO₂ Photocatalysts for Water Purification

Dorian A.H. Hanaor^{*} and Charles C. Sorrell

University of New South Wales, School of Materials Science and Engineering, Sydney, NSW 2052, Australia

^{*}Corresponding Author: Email: dorian@student.unsw.edu.au, Ph: +61-404-188810

Abstract: Using a titanium isopropoxide precursor, photocatalytic TiO₂ coatings were fabricated on quartz, zircon and rutile sands and fired in air. Raman spectroscopy and Scanning electron microscopy were employed to characterise the phase composition and morphology of the coatings. A packed bed reactor was used to study the inactivation of *Escherichia coli* in recirculating water. It was found that the sand grains were well coated with a homogenous layer of TiO₂ and coatings were well adhered, exhibited a mixed anatase-rutile composition after firing at 850°C. Photocatalytic activity was highest in coatings applied to quartz sand, although sterilisation of the recirculating water was not achieved with any of the supported photocatalysts. The advantages of quartz as a catalyst support are likely a result of this material's higher purity and optical transmittance.

Keywords: Coating; Sol-gel; Phase transformations; Raman spectroscopy; Catalysis

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9.1. Introduction

Titanium dioxide photocatalysts are attracting increasing attention for their potential applications in environmental remediation. TiO₂ has been shown to facilitate the destruction of organic pollutants and pesticides and the inactivation of bacteria in water through the formation of adsorbed radicals by photogenerated electron-hole pairs at the photocatalyst surface [1–3].

The two main phases of TiO₂ are anatase and rutile, with the anatase phase generally being the first phase formed through most synthesis routes and transforming to rutile through thermal treatment [4]. Rutile, which exhibits a lower band gap relative to anatase, generally exhibits lower surface area and consequently lower photocatalytic activity than anatase owing to significant grain growth which takes place in the process of the anatase to rutile transformation [4–9]. It is widely reported that anatase-rutile mixtures exhibit enhanced photocatalytic activity, relative to single phase TiO₂, through enhanced electron-hole separation (improved exciton lifetime), allowing higher levels of radicals to be generated [10–12].

Water purification by TiO₂ photocatalysis is commonly studied using suspensions of powders in treated water [13–15]; however this approach entails a catalyst recovery step in order to remove the dispersed powder from the treated water. The use of immobilised TiO₂ on catalyst supports of high surface area is an attractive approach for applying photocatalysis in water purification applications without the requirement of a liquid/powder separation processes, this is particularly important for upscaling such processes to large capacity applications.

Various catalyst support materials of increased surface area have been utilised to enhance the available surface area of immobilised TiO₂ photocatalysts for water purification applications. These support materials include glass fibres [16, 17], porous silica [18], silica gel [19], amorphous

silica nano-particles [20], carbon particles [21, 22], and molecular sieves, such as zeolites [23]. These materials have been used, with varying degrees of success, to facilitate the photocatalytic degradation of contaminants in water.

Sands are attractive as enhanced-surface-area catalyst support materials for large scale water purification as a result of their low costs and the ease with which they can be separated from water. Owing to differing compositions and crystal structures, different types of sand as catalyst supports may enhance or impair photocatalytic activity of TiO₂ immobilised on the sand grain surfaces.

The present work investigates the fabrication of nano-crystalline mixed-phase TiO₂ coatings on quartz, zircon and rutile sand for use in water purification.

TiO₂ immobilised on quartz sand (SiO₂) may exhibit enhanced photoactivity caused by the diffusion of Si atoms from the underlying sand into the TiO₂ coating. Doping by Si has been reported to improve the performance of TiO₂ photocatalysts in water purification applications [24–26]. This has been reported to be a result of improved charge carrier separation at TiO₂-SiO₂ interfaces.

Immobilised TiO₂ on zircon sand (ZrSiO₄) too has the potential to impart enhanced photocatalytic performance as a result of the nucleation of elongated prismatic rutile crystallites on zircon surfaces alongside residual anatase as observed previously [27]. Further, diffusion of Zr from the underlying sand may enhance performance as suggested by reports that Zr doping enhances surface area and photoactivity of TiO₂ [28, 29].

The use of rutile sand for the immobilisation of TiO₂ may improve charge carrier separation through the previously reported synergism between large rutile grains and fine anatase particles in the coating [30, 31]

9.2. Experimental procedure

9.2.1. Support materials

Glassmaking quartz sand and naturally occurring rutile sand and zircon sands (Wallarah Minerals, Doyalson North, Australia) were used as support materials. 50 gram samples of sand were ultrasonically cleaned in acetone (Univar, 99.5% purity, 0.001% evaporation residue, Univar, Australia), to remove organic contamination and subsequently dried in air. The crystallography of the sands was examined by X-ray diffraction (XRD) carried out using a Phillips X'pert MPD XRD system. Surface area of the sands was evaluated using N₂ gas adsorption in conjunction with BET analysis methods using a Micromeritics ASAP 2020 Physisorption Analyzer. Impurity levels in the sands were analysed by wavelength dispersive X-ray fluorescence (XRF) using a Philips PW2400 XRF spectrometer.

9.2.2. Sol-gel matrix coating method

Initial experiments utilised a gel-matrix method to deposit a coating of TiO₂ on the support material. This was expected to yield homogenous coatings as the sand particles were immobilised in the gel-matrix and thus not in mutual contact.

In this method, ultrasonically cleaned sand samples of 50 grams were added gradually to 50 mL of 0.5 M solution of titanium tetra-isopropoxide, TTIP (97%, Sigma Aldrich, USA) in isopropyl alcohol (100% Univar) during rapid stirring by a magnetic stirrer, thereby forming a slurry. Gelation was achieved by the addition of 2 mL of 2 M HCl added dropwise to the slurry. The concentration of 0.5 M was found to enable the formation of a firm gel capable of supporting the sand particles in suspension. Lower concentrations did not form gels capable of holding sand particles in

suspension. Once immobilised in a Ti bearing sol-gel matrix, the sand was dried in air at 110°C for 12h.

9.2.3. Colloidal suspension coating method

Owing to the poor quality of coatings achieved using the sol-gel matrix method, the use of this method was discontinued and an alternative coating method using a colloidal suspension was employed. In this method, subsequent to cleaning, the sands were added gradually to a solution of 0.5M titanium tetra-isopropoxide, TTIP (97%, Sigma Aldrich, USA) in 50 ml of isopropyl alcohol (100%, Univar) under rapid stirring by a magnetic stirrer. The rapidly stirring slurry of sand in TTIP solution was hydrolysed at a hydrolysis ratio of $r=4$ by the addition of a mixture of water diluted to 10 mL with isopropanol added dropwise to the stirring slurry. The additional isopropanol and dropwise addition were used for the purpose of moderating the hydrolysis reaction rate. After ~5 minutes of continued stirring the slurry visibly exhibited precipitation of amorphous TiO₂.

9.2.4. Thermal treatment

Coatings on the different sands were crystallised and adhered by firing in air using a muffle furnace at 850°C with heating /cooling rates of 2° min⁻¹. These firing parameters were chosen, subsequent to experimentation with various firing regimens, as they were found to yield a mixed phase composition of TiO₂ coatings. The slow rates of heating / cooling were chosen in order to reduce spalling through thermal shock.

9.2.5. Coating characterisation

Laser Raman microspectroscopy was carried out in conjunction with optical microscopy to ascertain the phase composition of the coatings using an InVia Raman Microspectrometer with laser excitation at 514 nm. Scanning electron microscopy (SEM) was carried out using Hitachi s900

and s3400 microscopes in order to examine the quality of TiO₂ coatings on the sand particles and the morphologies of TiO₂ grains within these coatings.

9.2.6. Photocatalytic performance

Photocatalytic efficiency of the supported TiO₂ prepared in this work was evaluated by studying the inactivation *Escherichia coli* (*E. coli*) AN180 (School of Biotechnology and Biomolecular Sciences, UNSW, Australia), using the bactericidal reactor shown in Fig. 9.1. Experimental apparatus was sterilised by recirculating 80 vol% ethanol and subsequently the system was flushed with distilled water which had been sterilised by autoclaving. A reservoir of 1L of sterilised distilled water was used for recirculation. Recirculating water was inoculated with 1 ml of overnight-incubated *E. coli* culture in Tryptone Soy Broth (Oxoid, Basingstoke, UK). Recirculating water flowed through a packed bed of 40g of coated sand which was irradiated over a length of 350mm and width of 20mm placed 50mm below a 15 W UV light source with an emission peak at 350 nm (Sylvania) giving an irradiance level of $\sim 3.7 \text{ Wm}^{-2}$ at the catalyst surface as determined using a Digitech QM 1587 light-meter.

Inactivation of the bacteria in the recirculating water was examined by determining the concentration of colony forming units (CFUs) in the recirculating water according to ASTM D5465 [32]. 1 ml aliquots of water were taken at fixed time intervals and serially diluted at 1:9 ratios in sterile 0.1% peptone water (Oxoid). Subsequently, 0.1 ml aliquots of the appropriate dilutions were spread-plated on Tryptone Soy Agar (Oxoid) and the plates were incubated for 24 hours at 37°C. After incubation, colonies were enumerated and the concentration of CFUs in the reactor water was determined.

To evaluate the penetration of UV irradiation through the different types of sand in the packed bed reactor. UV-vis transmission, through 1 mm layers of sand, was measured using a Perkin Elmer Lambda-35 UV-visible spectrometer.

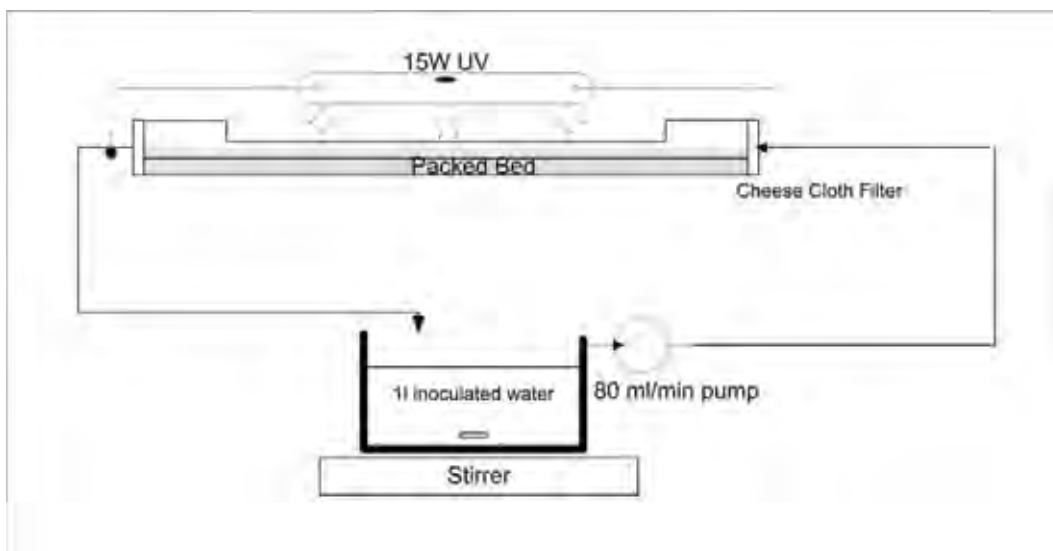


Fig. 9.1. Diagram of bactericidal reactor.

9.3. Results

9.3.1. Characterisation of support materials

XRD patterns of sands are shown in Fig. 9.2. Quartz sand is of the α -quartz structure, space group $P3_121$ Zircon sand exhibits a tetragonal structure, space group $I4_1/amd$ and Rutile sand exhibits a tetragonal structure, space group $P4/mnm$ [33]. No secondary crystalline phases were identified in the sands by XRD.

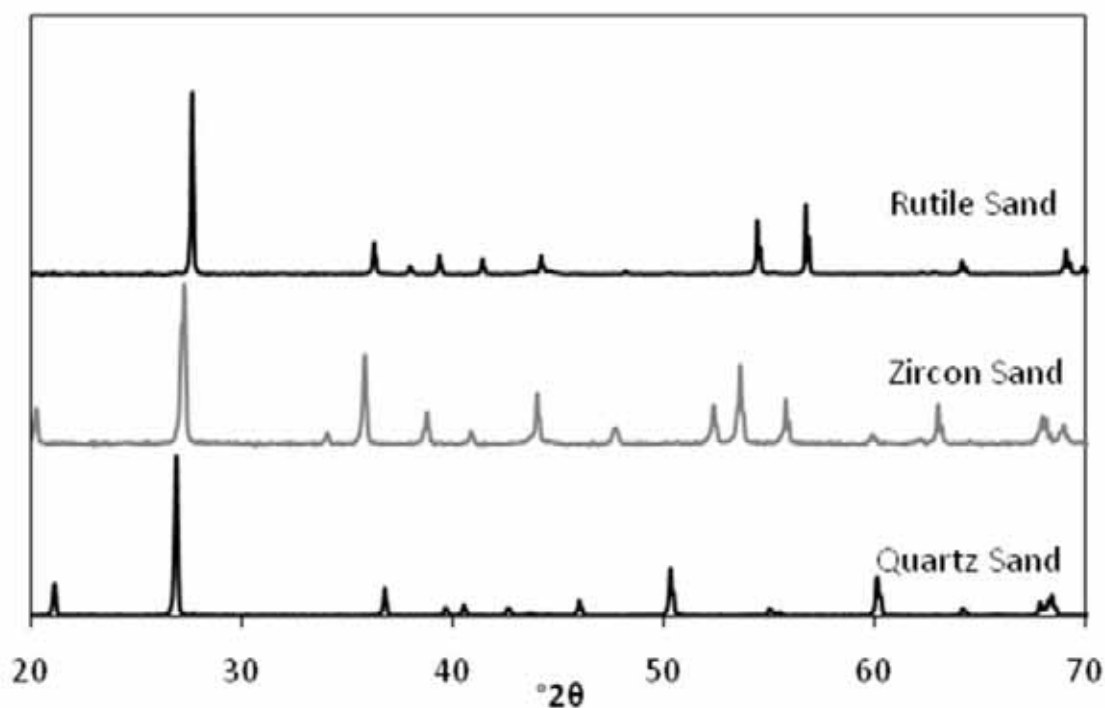


Fig. 9.2. XRD patterns of sands used as catalyst support materials.

The properties of the sands used as catalyst support materials are summarised in Table 9.1. It can be seen that quartz sand exhibits a lower surface area in comparison with zircon and rutile sands. This is a natural consequence of the larger sizes, smoother surfaces and more spherical morphologies of grains of this type of sand. While no secondary crystalline structures were apparent through XRD analysis, XRF shows significant levels of impurities in zircon and rutile sands. The levels of impurities as determined by XRF show rutile sand has the highest levels of impurities while quartz sand exhibits low levels of impurities. This was expected as the quartz sand used in this work is of glassmaking specification.

Table 9.1. Summary of support materials used in the present work.

Sand	Formula	Average Grain size (μm)	Surface area (BET) m ² g ⁻¹	Crystal structure	Impurities (wt%)
Quartz	SiO ₂	~250	0.019	Trigonal	Al ₂ O ₃ : 0.03% ZrO ₂ 0.05%

					TiO ₂ : 0.04%
					Fe ₂ O ₃ : 0.01%
Zircon	ZrSiO ₄	~120	0.248	Tetragonal	HfO ₂ : 1.54%
					Al ₂ O ₃ : 0.56%
					TiO ₂ : 0.24%
					Fe ₂ O ₃ : 0.13%
Rutile	TiO ₂	~100	0.105	Tetragonal	SiO ₂ : 1.76%
					ZrO ₂ : 0.73%
					Fe ₂ O ₃ : 0.42%
					Al ₂ O ₃ : 0.24%
					Na ₂ O: 0.20%

UV-vis transmission spectroscopy of the sands used as photocatalyst support materials, was carried out to ascertain the penetration of light through the packed bed of sand used in the bactericidal reactor. The UV-vis transmission through 1 mm of quartz sand was significantly higher than the transmission through a similar profile of the darker zircon and rutile sands.

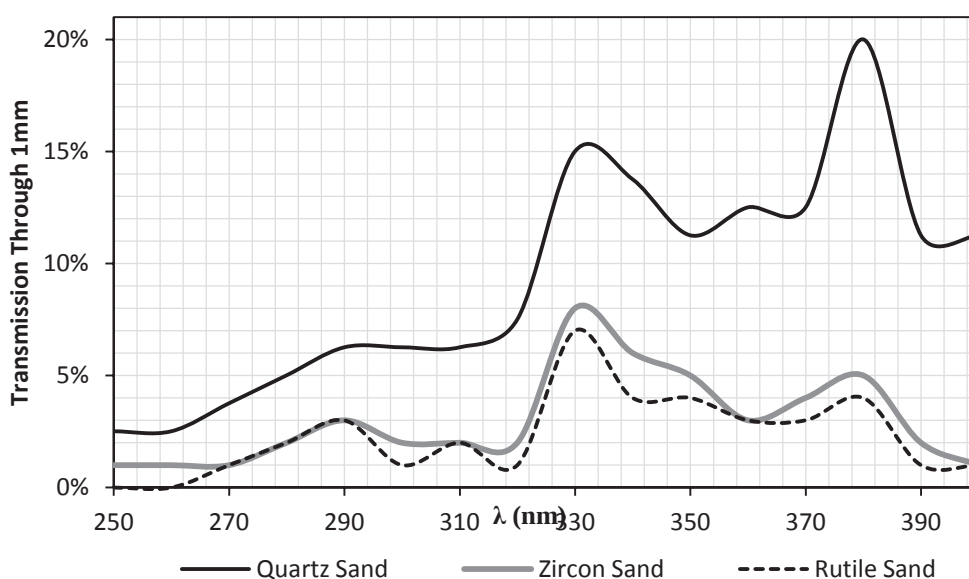


Fig. 9.3. UV-vis transmission through 1 mm of the sands used in this work.

9.3.2. Sol-gel matrix coating method

Initial samples fabricated using the sol-gel matrix method exhibiting inconsistent coatings. Many grains were observed to be devoid of coating while others exhibited thick cracked coatings, exhibiting thicknesses of 5–50 μm with extensive spalling. Poor adhesion of coatings formed using the sol-gel matrix method was particularly evident in coatings on rutile sand.

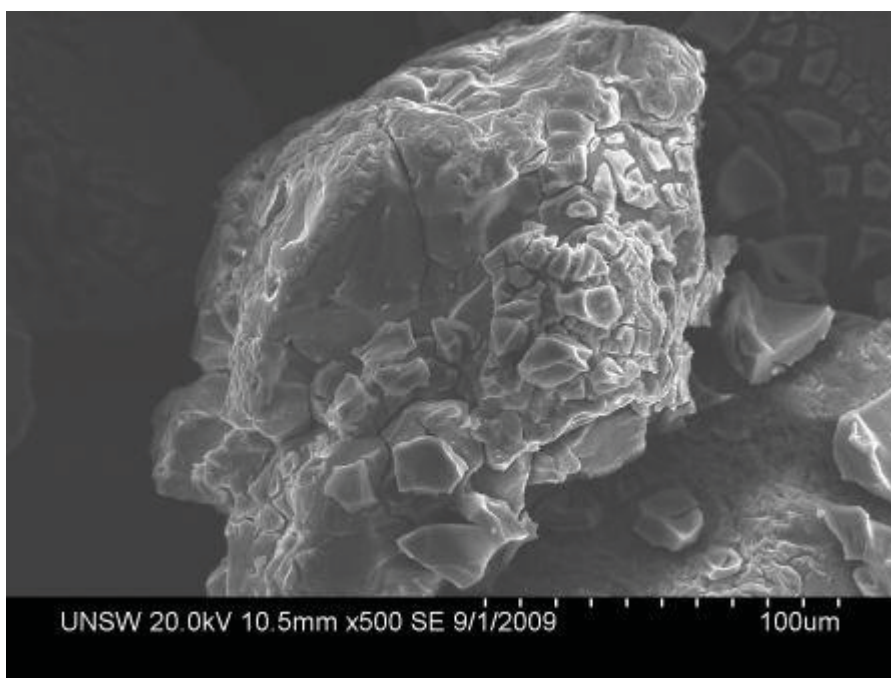


Fig. 9.4. Thick broken Sol-gel Matrix coating on quartz sand.

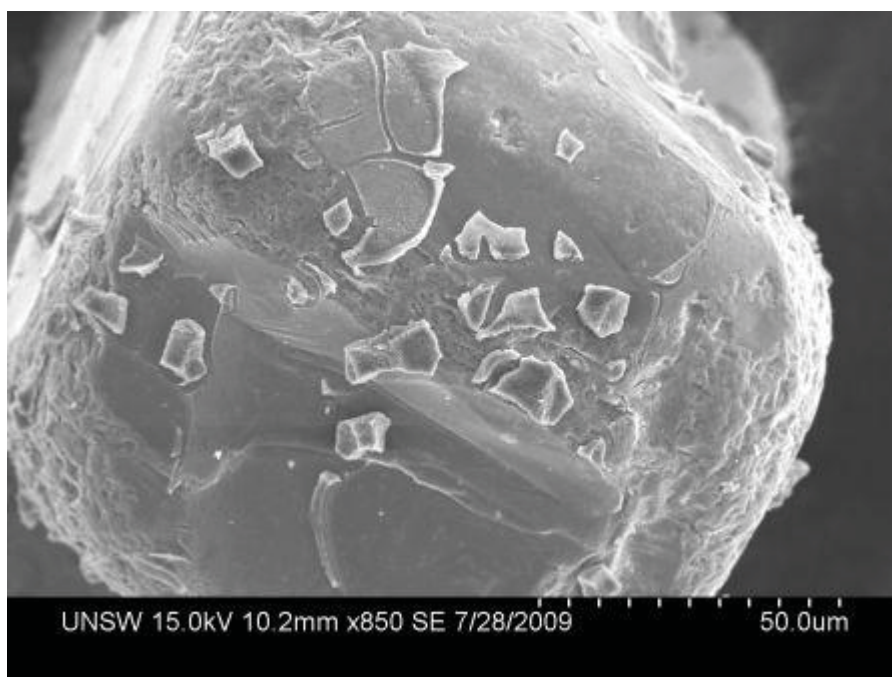


Fig. 9.5. Coating on zircon sand fabricated using a sol-gel matrix.

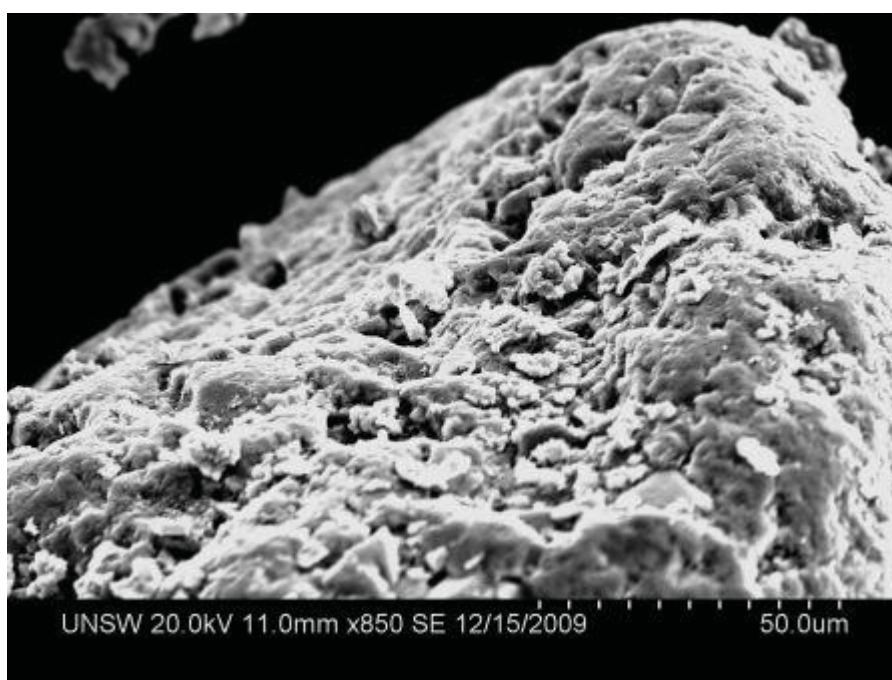


Fig. 9.6. Sparse coating on rutile sand resulting from the sol-gel matrix fabrication method.

9.3.3. Coating morphology

Once the sol-gel method was discarded, coatings were fabricated without gelation. The coatings on all types of sand (formed without a gelled matrix) were consistent in appearance and coating thicknesses varied in the region of $\sim 30\text{--}300\text{ nm}$, with an average coating thickness of $\sim 150\text{ nm}$. The typical appearance of coatings is shown in Fig. 9.7. Localised regions exhibiting the absence of TiO_2 coating as a result of spalling were observed in rutile sand, as shown in Fig. 9.8, however this was an infrequent observation and overall coatings were well-adhered. The microstructure of the coatings consisted of TiO_2 grains of $30\text{--}50\text{ nm}$ as shown in Fig. 9.9. Cracking was prevalent to a similar extent in all coatings. As shown in Fig. 9.10, SEM images of unfired coated sand showed that cracking was present subsequent to drying rather than formed in the process of firing. The coatings were resistant to prolonged use in the recirculating bactericidal reactor and no significant deterioration in coatings was evident subsequent to use in the reactor shown in Fig. 9.1.

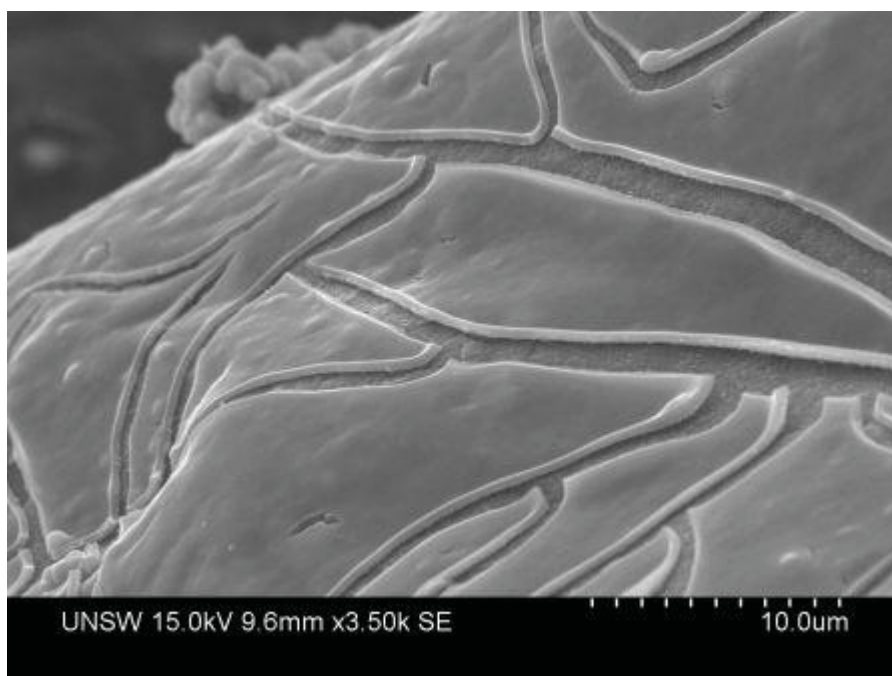
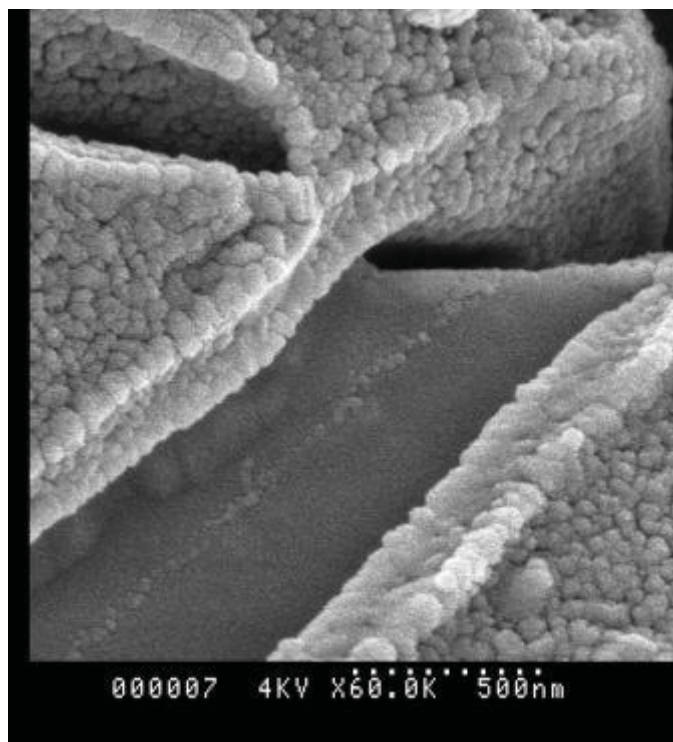


Fig. 9.7. Typical coating of TiO_2 on all types of sand (rutile sand shown).



Fig. 9.8. Region of spalling TiO_2 coating on sand (rutile).



a)

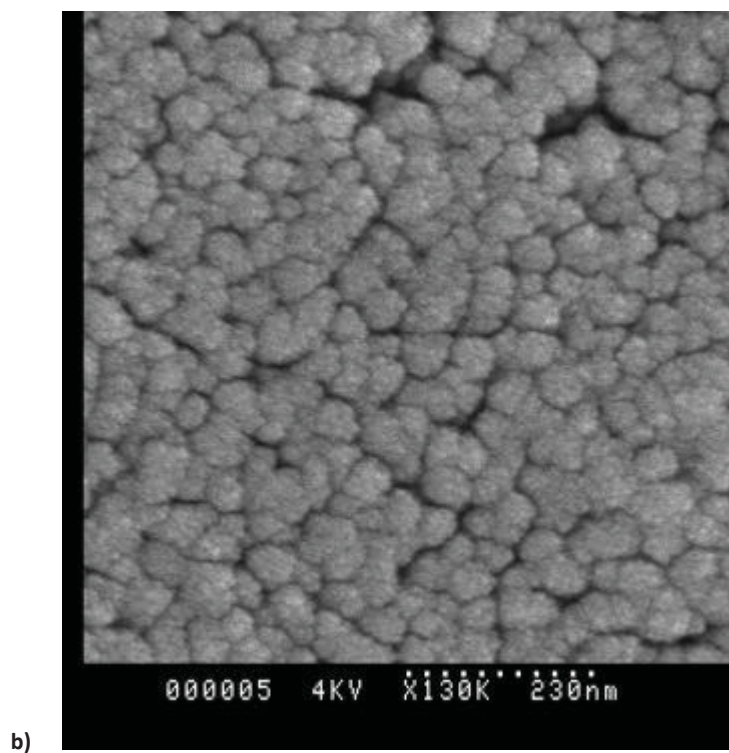


Fig.9.9. Microstructure of TiO_2 coatings on sand (quartz) (a) Cracked coating interface (b) Coating micrograph.

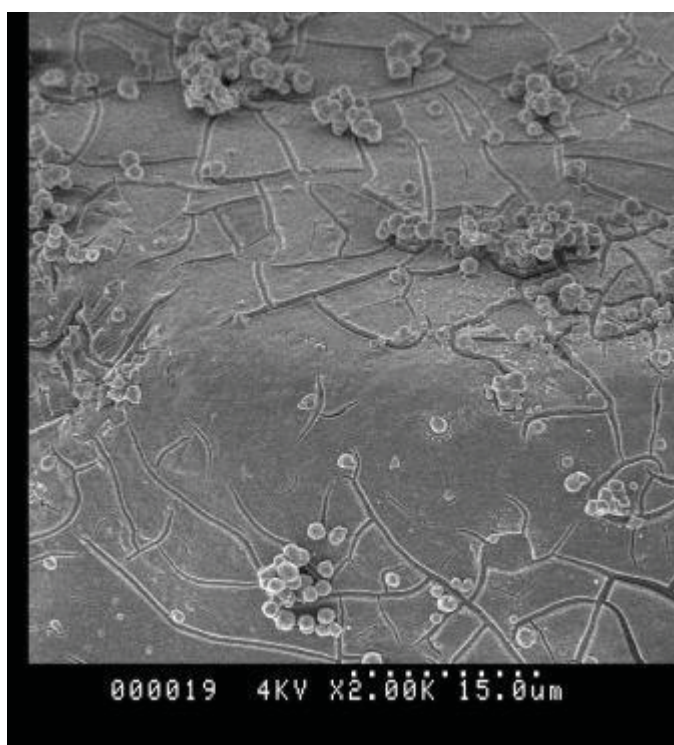


Fig 9.10. Unfired TiO_2 coated sand (Zircon).

9.3.4. Phase composition of coatings

XRD analysis was deemed to be unsuitable for phase analysis of coatings as the peaks from the grains of sand are significantly more dominant in such analyses relative to peaks from the nanocrystalline coatings. For this reason laser Raman microspectroscopy was used to differentiate the phases present in coatings. Alongside varying significant levels of peaks from the underlying and partly exposed sands, Raman spectra of coated sands fired in air at 850°C , shown in fig. 9.11, show biphasic anatase + rutile compositions in the coatings with anatase peaks being dominant (in part, a result of the stronger Raman shift by this phase). The rutile Raman shifts present in coatings on zircon and quartz sands are evident in the shoulders of the anatase peaks 395 and at 640 cm^{-1} . The rutile Raman shift in coatings on rutile sands is strong as a result of the combined effects from a rutile phase in the coating and from the underlying support material. The Raman spectra shown here are not appropriate for quantitative analysis, however it is likely that anatase is present in a larger quantity than rutile, owing to the weak Raman shift exhibited by rutile in these spectra.

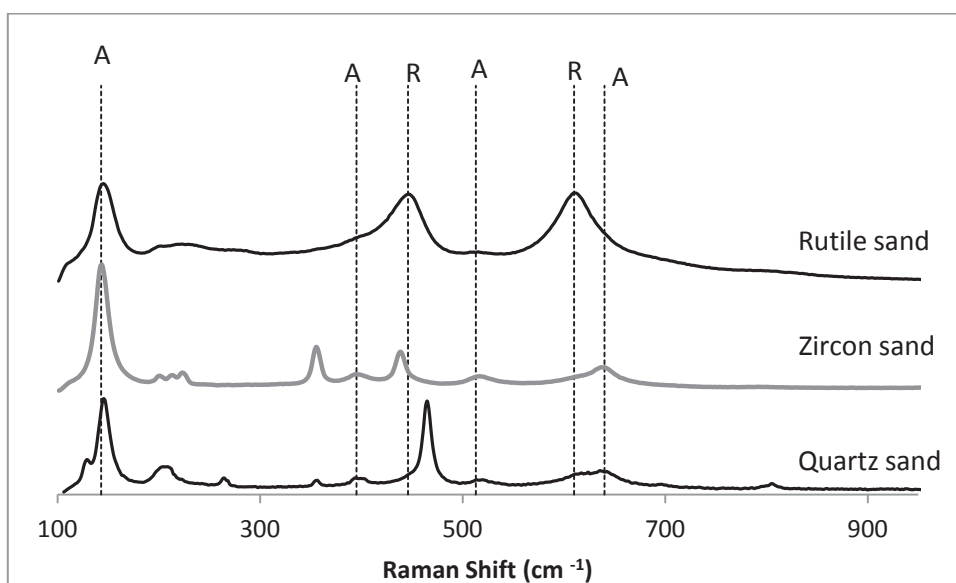


Fig. 9.11. Raman spectra of TiO_2 coatings on grains of sand.

9.3.5. Bactericidal activity

The photocatalyzed inactivation of bacteria is shown in Fig. 9.12. In order to determine the background bactericidal activity in the absence of a photocatalyst, uncoated quartz sand was used in the reactor with and without UV irradiation. It can be seen that the inactivation of *E. coli* in the absence of TiO₂ coatings is negligible even in the presence of UV irradiation. This is a result of the longer wavelength of the UV source used in comparison with UV irradiation typically used in antimicrobial lamps [34]. In the presence of TiO₂ coated sand, inactivation of bacteria under UV irradiation is evident, being significantly more pronounced in the coated quartz sand. No complete sterilisation of the recirculating water was achieved within the timeframe of the experiments, rather the concentration of *E. coli*, as determined by counting CFUs, reached a level at which the bactericidal activity of the photocatalyst was in offset by the natural multiplication of the bacteria in the water.

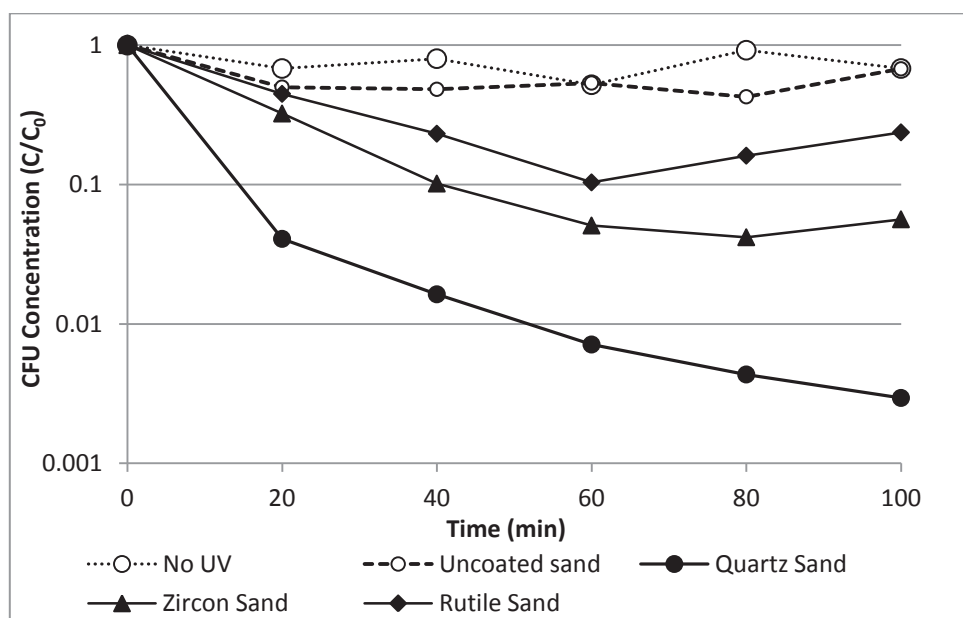


Fig. 9.12. Bactericidal activity of coated sands as determined by CFU counts.

9.4. Discussion

9.4.1. Sol-gel matrix method

The use of the sol-gel matrix method resulted in thick, fragmented coatings of poor quality as evident from Figs. 9.4–6. Adhesion was poor and spalling was prevalent. Many sand grains exhibited partial or effectively complete absence of visibly identifiable coatings of TiO₂. The inconsistent and irregular coating that resulted from the sol-gel matrix method could be due to several causes:

- Shrinkage of the gel during drying
- Shrinkage of the dried coating during firing
- Poor wetting of the sand grains by the gel
- Excessive coating thickness, leading to poor mechanical strength
- Excessive Ti : sand ratio, resulting in the formation of xerogel particles upon drying

Owing the poor quality of coatings obtained using the sol-gel matrix method, this fabrication technique was discarded and subsequent experimentation focused entirely on material fabricated without gelation.

9.4.2. Coating morphology

Without the use of a gel matrix, grains of all types of sand exhibited homogenous coverage by TiO₂ coatings as shown in Fig. 9.7. The superior quality of coatings achieved when the Ti sol was hydrolysed without gelation (using water rather than HCl) is likely the result of thinner TiO₂ layers,

lower volumetric shrinkage and lower Ti : sand ratios. Cracking was prevalent in all coatings and SEM micrographs of unfired material, such as that shown in Fig. 9.10, demonstrate that this cracking occurred during drying. Although most grains were well coated, infrequently occurring areas devoid of TiO₂ were observed, particularly in coatings on rutile sands. Spalling of TiO₂ coatings may have occurred as a result of differential shrinkage in combination with localised poor adhesion. As rutile sand was of the lowest purity, poor coating adhesion on this material may have been the result of the combustion of residual organic material and/or other impurities on the sand surfaces. The nanocrystalline microstructure of TiO₂ grains resembles photocatalytic films synthesised on quartz substrates and subjected to a similar thermal treatment [6]. Overall coating adhesion was good on all three support materials with a little deterioration of the coating evident after use in the bactericidal reactor.

9.4.3. Phase composition

As indicated by Raman spectra, TiO₂ coatings exhibited a mixed phase composition after firing at 850°C. The phase transformation behaviour of these coatings is similar to what has been observed in coatings fabricated on single crystal quartz substrates [6]. The anatase to rutile phase transformation is inhibited in coatings on the sands used in this work in comparison with unsupported anatase which is generally reported to transform to rutile at temperatures around 600°C [4, 35]. The stabilisation of the anatase phase in coatings on sand is likely a result of the diffusion of Si, Zr and Al into the TiO₂ coatings. These elements are reported to inhibit the formation of rutile through the restriction of the atomic rearrangement involved in the phase transformation [26, 36–39].

9.4.4. Photocatalytic performance

Experimental results from the inactivation of *E. coli* in recirculating water it is apparent that quartz sand is a superior support material despite exhibiting a lower surface area as determined by BET analysis. This is most likely the result of higher purity and thus lower levels of contamination of the photocatalyst by transition and alkaline metals which could act as charge carrier recombination centres. Rutile sand, and to a lesser extent zircon sand, exhibited significant levels of iron impurities as shown by XRF analysis. Fe, and other transition metals [40–43] and alkali impurities [44–46], have been reported to impair photocatalytic activity and it is likely the presence of such impurities in rutile and zircon sands contributed to the poor bactericidal performance of TiO₂ coatings supported on these materials. It should be noted that the presence of very low levels of transition metal dopants/impurities, such as the levels observed in quartz sand by XRF, has been reported as being beneficial for photoactivity [47].

Diffusion of Si from the quartz sand into the TiO₂ lattice may enhance photoactivity in similarity to observations reported elsewhere [24–26]. While this effect is likely also in zircon sand and in rutile sand (owing to the SiO₂ impurities in this material), it is possible that the levels of diffusion from quartz are greater, and/or the beneficial effects of Si doping are outweighed by detrimental levels of transition and alkali metal impurities.

Further impairing the performance of rutile and zircon sands in the bactericidal reactor is the poor UV-vis transmittance of these materials, as shown in Fig. 9.3. This leads to low penetration of the UV irradiation into the packed bed and thus lower levels of irradiated TiO₂ coated surfaces.

A packed bed reactor such as the one used in this work suffers the drawback of poor catalyst exposure as only the top layer of grains is exposed directly to the UV source. This reactor was chosen due to its simplicity and the ease with which experiments could be repeated. However a more effective reactor would involve greater levels coated surfaces subjected to impinging UV irradiation. The low cost of the raw materials used in the present work mean that large scale fabrication can be undertaken inexpensively.

9.5. Conclusions

Thin well-adhered coatings of nanocrystalline TiO₂ can be fabricated on various types of sand enabling the cheap production of a enhanced-surface area supported photocatalyst.

The anatase to rutile phase transformation is inhibited in TiO₂ supported on sand grains as a result of the diffusion of structure-stuffing cations, which restrict the atomic rearrangement involved in the formation of rutile from anatase.

The use of glass-making quartz sand as a photocatalyst support material appears to bring about superior photoactivity in comparison with naturally occurring zircon and rutile sands, likely as a result of higher purity and optical transmittance.

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10. Abnormal grain growth in TiO_2 induced by zircon dopants

In the course of fabricating titanium dioxide photocatalysts in various forms, the phenomenon of abnormally growing rutile crystallites was observed in the presence of solid state zircon dopants. The phenomenon of such grain growth has been observed in other ceramic systems however the findings made in the present work are novel and open the door to further work into abnormal grain growth in TiO_2 .

Although it remains undetermined, the abnormal growth of prismatic rutile alongside residual untransformed anatase is likely to have significant consequences on the photocatalytic performance of such mixed phase materials. The growth of rutile as observed and reported in this chapter may give rise to faceted grain boundaries and improved charge carrier transfer between the anatase and rutile phases. Alternatively the growth of long rutile grains may impart improved mechanical properties to sintered TiO_2 materials, potentially improving fracture toughness.

Significant work remains to be carried out in the investigation of AGG in TiO_2 however the present chapter as presented is an important initial investigation and presentation of this phenomenon.

	Primary Author	Manuscript Preparation	Literature Research	Experimental Work	Data Analysis	Editing and Revision	Supervisory Role	Formatting and Layout	Advice and Support	Calculation of orientation relationship
Dorian Hanaor	✓	✓	✓	✓	✓	✓		✓		
Martin Xu									✓	✓
Charles C. Sorrell						✓	✓	✓	✓	
Michael Ferry							✓			

Key Findings

- In the presence of solid state zircon, ZrSiO_4 , TiO_2 subjected to thermal treatment above the anatase to rutile phase transformation temperature exhibits abnormal grain growth of the rutile phase
- A distinct crystallographic orientation relationship was found with close atomic position matching between ZrSiO_4 and rutile TiO_2
- Zircon induced abnormal grain growth of rutile was observed in thin films, powder compacts and coatings applied to grains of zircon sand
- Abnormal grain growth phenomena were discussed in terms of crystallographic orientation relationships, fluxing effects, grain boundary pinning and phase equilibrium

Abnormal Grain Growth of Rutile TiO_2 Induced by ZrSiO_4

Dorian Hanaor^{*}, Martin Xu, Michael Ferry and Charles C. Sorrell

*School of Materials Science and Engineering, University of New South Wales / Kensington,
NSW 2052, Australia*

*Corresponding Author: Email dorian@student.unsw.edu.au Ph: +61404188810

Abstract : Abnormal grain growth was observed in rutile TiO_2 in the presence of zircon ZrSiO_4 . This morphological behaviour was seen to occur in sintered powder compacts and thin films with solid state zircon dopants and in TiO_2 coatings on grains of zircon sand. In order to clarify the mechanism by which this grain growth is caused, various methods were investigated. It was found that doping by Zr and/or Si does not give rise to abnormal grain growth. The observed phenomena were discussed in terms of morphological and energetic considerations. It is likely that a distinct orientation relationship between TiO_2 and ZrSiO_4 and possible grain boundary liquid formation play a role in giving rise to the rapid growth of faceted prismatic rutile.

Keywords: Abnormal Grain Growth; TiO_2 ; Rutile; Morphology

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10.1. Introduction

The phenomenon of abnormal grain growth (AGG), also known as exaggerated grain growth, involves the rapid growth of certain grains in a matrix of finer grains exhibiting much slower growth rates [1, 2]. This phenomenon has been widely reported in alumina (Al_2O_3) [3–6] and barium titanate (0.1 mol% excess BaTiO_3) [7–9]. In single phase and two-phase systems the phenomenon of AGG is generally considered to result from high anisotropy in surface energy along with a high level of chemical inequilibrium and local rates of atomic migration [1, 2].

Titanium dioxide, which is primarily used as a pigment, has been attracting increasing attention for its potential in photocatalysis, utilising solar irradiation to facilitate environmental remediation through the destruction of contaminants in water. The anatase-rutile phase assemblage and grain morphology in TiO_2 has significant consequences on the photocatalytic performance of this material [10–12], and for this reason TiO_2 exhibiting AGG of the rutile phase is of interest. To date AGG has not been reported in TiO_2 . Further potential benefits of AGG in TiO_2 may include improved fracture toughness in sintered material.

The current work reports the abnormal grain growth of rutile TiO_2 which takes place when anatase TiO_2 is treated at high temperatures in the presence of Zircon, ZrSiO_4 , crystal surfaces. The phenomena reported in the present work present a new approach to controlling the morphology of mixed and single phase TiO_2 .

10.2. Experimental procedures

10.2.1. Powder compacts

Undoped powder compacts were prepared from anatase powder (>99.5%, Merck Chemicals, Australia) ground in an agate mortar and pestle and subsequently pressed in a uniaxial press at 30 kN (23.9 MPa) to form 20 mm diameter powder compacts. Zircon doped samples were made following the same procedure with the addition of 1–15 wt% zircon flour (300 Mesh, Wallarah Minerals, Doyalson, NSW). These powder compacts were fired in air for 4h at 1025°C with a heating rate of 2°/min. Firing durations were extended to 12h to examine microstructure development.

For comparison purposes powder compacts were prepared from anatase powder blended with 10.6 wt% monoclinic zirconia ZrO_2 (Z-Tech, USA) to give the same Zr content as the 15 wt% zircon flour doped sample (7.14 at%). This was done to determine whether the observed growth habit was a result of Zr diffusion into the TiO_2 lattice.

To further examine Zr and Si doping on the grain growth morphology of TiO_2 , powders were prepared with dopants introduced using a wet impregnation method. In this method TiO_2 powders were suspended in 0.2 M suspensions of zirconium isopropoxide and tetra-ethyl-orthosilicate (both Sigma Aldrich, USA) and subsequently dried in air. Using this method TiO_2 powders doped with 10 at% Si, 10 at% Zr and co-doped with 5 at% Si/Zr were prepared.

Powders were fired at 1025°C in an electric muffle furnace with a heating rate of 2°/minute. Undoped samples and Zircon doped powder compacts were fired for 4h while zirconia doped samples were fired for 2h as it was found that this resulted in an anatase : rutile phase ratio similar to that of the zircon doped material.

10.2.2. Thin films

Undoped and zircon flour doped TiO_2 thin films on quartz substrates were prepared by spin coating using a sol-gel precursor. A solution of 0.5 M titanium tetra-isopropoxide (TTIP) (Sigma Aldrich, USA) in isopropanol (100%) was hydrolysed under stirring with the dropwise addition of 2M HCl giving a molar ratio of 2:1 $\text{H}_2\text{O}:\text{Ti}$. Thin films containing zircon flour were prepared using a 0.03 g/ml suspension of zircon flour in the sol-gel described above. Films were cast on 20 mm x 20 mm x 1 mm quartz substrates using a Laurell WS-650Sz spin coater at 1000 RPM. Films were fired in a muffle furnace at 900°C for 12 hours with a heating rate of 2°/minute in order to achieve complete transformation to the rutile phase.

10.2.3. Coated sand

High surface area supported photocatalysts were prepared through the application of sol-gel coatings of TiO_2 on zircon sand and quartz sand (both Wallarah minerals, Doyalson, NSW, Australia). These materials were made by suspending 50 g of sand in a 50 ml rapidly stirring 0.5 M TTIP solution in isopropanol. Distilled water was added to give a 6:1 hydrolysis ratio which resulted in the precipitation of colloidal amorphous TiO_2 particles. This was followed by the sedimentation of the sand in the suspension and the removal of excess precipitates from the supernatant subsequent to solvent evaporation. Coated sands were fired in air at 1000°C for 4h with a heating rate of 2°/minute to give rutile coatings on the sands.

10.2.4. Coatings on facets of single crystals of zircon

To determine the effects of different ZrSiO_4 crystallographic planes on the grain growth of rutile, TiO_2 coatings were applied to polished surfaces of a sectioned single crystal of zircon (Peixes, Brazil). Single crystal X-ray Diffraction (XRD) was carried out using a Bruker Kappa Apex Single Crystal Diffractometer to determine the crystallographic planes present in the sections. A single

crystal White ZrSiO_4 gemstone (Aurora, USA) was further used without sectioning. Coatings were applied to crystal surfaces by the dropwise addition of 0.5M TTIP solution in isopropanol and allowed to dry in ambient air. Coated single crystal surfaces were then fired at 1000°C for 4h in air with a heating rate of $2^\circ/\text{minute}$.

10.2.5. Analysis

The contaminants present in raw materials used were analysed using X-Ray Fluorescence (XRF) using a Philips PW2400 XRF spectrometer.

Phase analysis of powders was carried out by X-ray diffraction (XRD) using a Phillips multi-purpose diffractometer (MPD) system. Phase content was calculated using the method of Spurr and Myers [13].

Microstructural analysis was performed by Scanning electron microscopy (SEM) using Hitachi S3400, S4500 and S900 microscopes. Samples were sputter-coated with chromium to facilitate electrical conductivity. Uncoated specimens of coated single crystal facets were analysed using a Hitachi TM3000 table-top SEM.

Phase analysis with reference to microstructural features in sintered powder compacts was facilitated by laser Raman microspectroscopy in conjunction with optical microscopy using an Invia Raman unit with excitation by a 514 nm wavelength laser. This system allows the interpretation of phase assemblage with reference to microscopically visible features. Laser Raman microspectroscopy was used also for the mineralogical analysis of TiO_2 coatings on sand as XRD analysis was inappropriate for such materials due to the dominance of peaks resulting from the sand support material.

10.3. Crystallographic relationships between ZrSiO_4 and TiO_2

Rutile is known to exhibit preferential growth along the c-axis owing to the lower surface energies of planes exposed in this growth habit. This has been demonstrated through the use of Wulff constructions [14]. The phenomenon of c-axis oriented AGG in rutile TiO_2 induced by zircon particles may be the result of an orientation relationship existing between the product rutile phase formed from the thermal treatment of anatase and planes of zircon and the consequent reduction in activation energy for rutile formation. This relationship may be predicted according to various models, such as edge-edge matching model, based on the principle of lattice structure and parameter matches of these two phases [15]. The possible orientation relationship between rutile and zircon particle is predicted based on the matching principle, and the lattice structures and parameters of rutile and zircon (Table 10.1).

$$[001]_{\text{Zr}} // [001]_{\text{Ti}}, (020)_{\text{Zr}} // (110)_{\text{Ti}} \text{ or } (200)_{\text{Zr}} // (110)_{\text{Ti}}$$

The interplanar spacings (d-value) for the two close-packed matching planes of these two phases are 0.3302 nm for $(020)_{\text{Zr}}$ and 0.3248 nm for $(110)_{\text{Ti}}$, and the interatomic spacing along the close-packed atomic rows are 0.299 nm for $[001]_{\text{Zr}}$ and 0.296 nm for $[001]_{\text{Ti}}$ (Zr denoted as zircon and Ti as rutile). The interplanar spacing (d-value) mismatch between the matching planes, and the interatomic spacing misfit along the matching directions, of these two phases, is 1.6% and 1.0% respectively; these are well below the critical values 6% for interplanar spacing mismatch and 10% for the interatomic spacing misfit of the two matching phases in the edge-edge matching model of Kelly and Zhang [15]. Fig. 10.1, calculated based on this orientation relationship, clearly shows a near perfect match of Ti, Zr and Si atoms in the two matching $(020)_{\text{Zr}}$ and $(110)_{\text{Ti}}$ planes along the matching directions of $[001]_{\text{Zr}}$ and $[001]_{\text{Ti}}$.

Table 10.1: Crystallographic properties of zircon rutile and anatase

Phase	Stability		Crystal Structure	Space Group	Lattice Parameters Å	Atoms per unit cell
Zircon	Equilibrium Phase up to 1676°C [16, 17] (decomposition)	up	Tetragonal	$I4_1/amd$	$a=6.6; c=5.98$	4
Rutile	Equilibrium Phase up to 1870°C [18–20] (congruent melting)	up	Tetragonal	$P 4/mnm$	$a=4.6; c=2.96$	2
Anatase	Metastable Transformation to rutile ~650°C [21, 22]	Phase to	Tetragonal	$I4_1/amd$	$a=3.8; c=9.51$	4

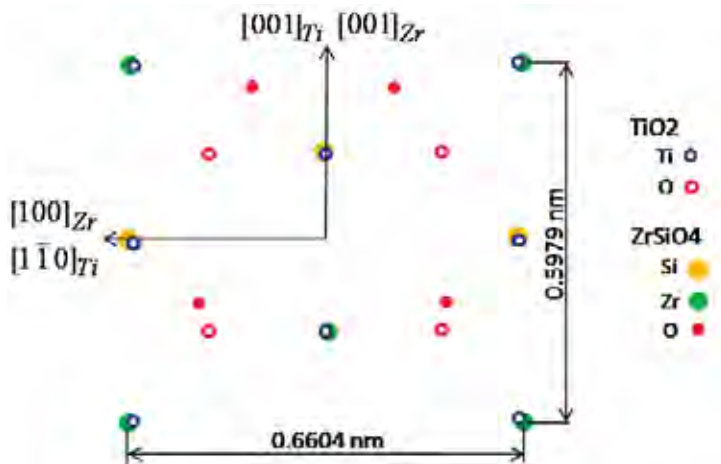


Fig. 10.1. Match of Zr, Si and Ti atoms in the close-packed matching planes of $(020)_{Zr}$ and $(110)_{Ti}$ along the close-packed matching directions of $[001]_{Zr}$ and $[001]_{Ti}$, according to the predicted orientation relationship between zircon and rutile.

10.4. Experimental results

10.4.1. Powder compacts

XRD patterns gathered from crushed sintered powder compacts were interpreted using the method of Spurr and Myers [13] to determine the fraction of the retained anatase phase. This is shown in Fig. 10.2. Undoped anatase shows complete transformation to rutile after 4h of firing at 1025°C. Under the same conditions, zircon doped samples show significant anatase retention. The inhibition of the anatase to rutile phase transformation in the presence of zircon a dopant is likely the result of the diffusion of Si and Zr into the TiO_2 lattice and the consequent restriction of the atomic rearrangement and grain growth involved in the phase transformation as reported elsewhere [23–26].

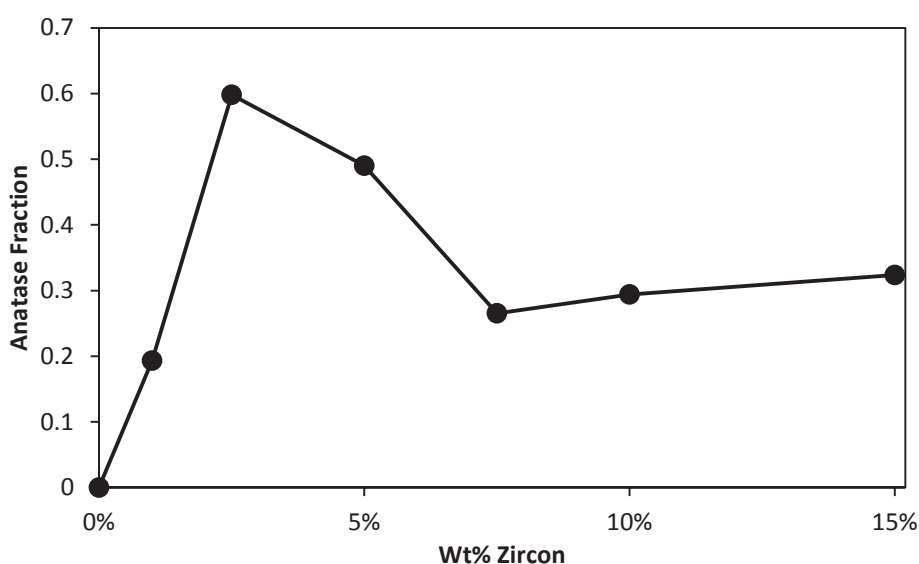


Fig. 10.2. Retained anatase fraction in powder compacts doped with zircon flour fired at 1025°C for 4h.

Undoped TiO_2 samples exhibit rounded isotropic grains of rutile, exhibiting sizes in the region 200–500 nm. This is shown in Fig. 10.3. The morphology of rutile formed from the thermal treatment of anatase in the absence of dopants is consistent with reported results from the thermal treatment of similar precursor material [27, 28]. In contrast, SEM analyses of all zircon flour doped sintered powder compacts showed large elongated prismatic grains growing in close proximity to zircon particles as shown in Fig. 10.4. These grains exhibited significantly larger sizes approximately 1–5 μm in width and 5–30 μm in length. As illustrated by Fig. 10.5, these large prismatic grains formed around zircon particles and subsequent to extended firing (12h) such grains had grown throughout the entire sample. Growth of elongated prismatic grains progressed until the point when such grains impinged on each other. As the anatase particles were not present in a preferred orientation, the formation of abnormally large elongated rutile grains would involve the crystal rotation during the coarsening process as reported elsewhere [28].

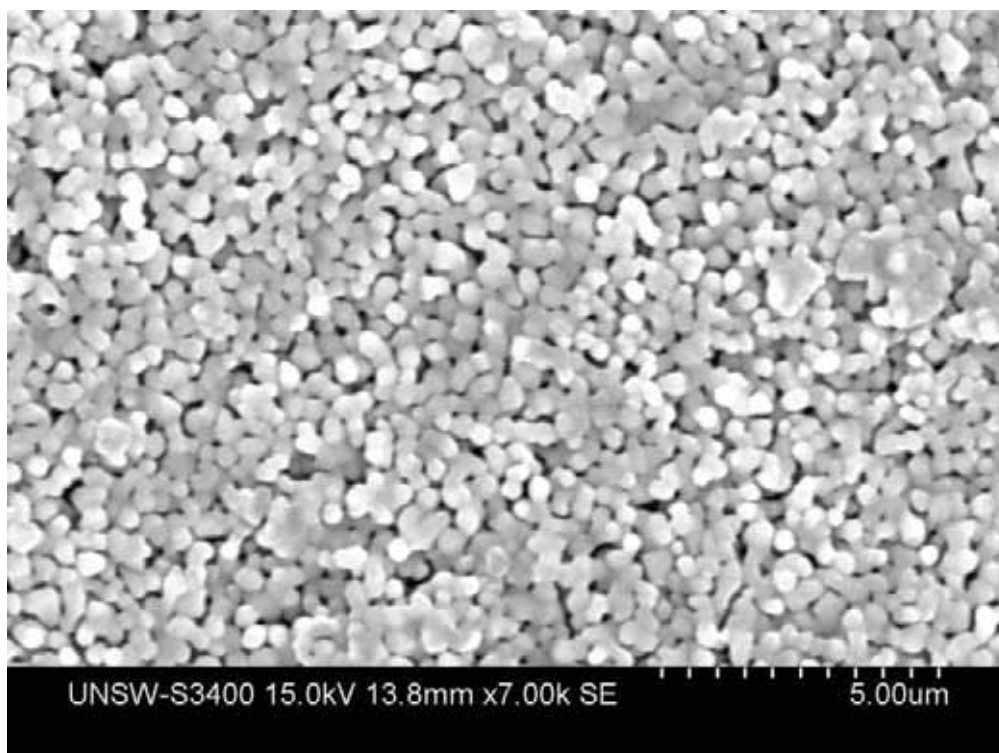


Fig. 10.3. Sintered TiO_2 fully transformed to rutile exhibiting normal grain growth typical of undoped samples.

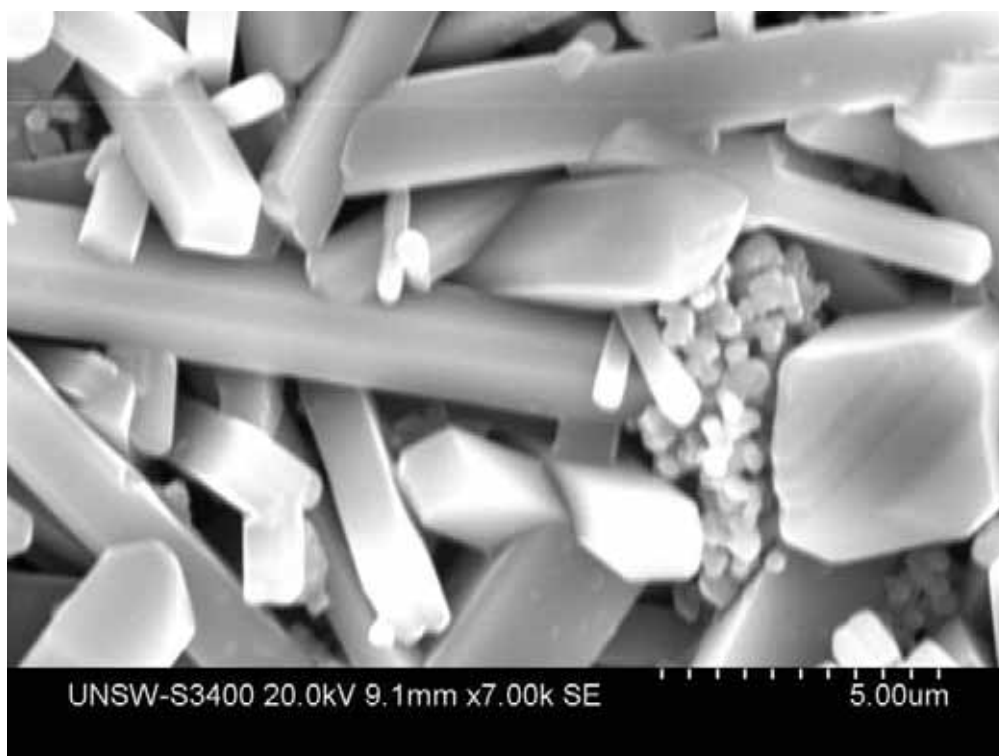


Fig. 10.4. Rutile exhibiting abnormal grain growth in a zircon doped samples (15 wt%).

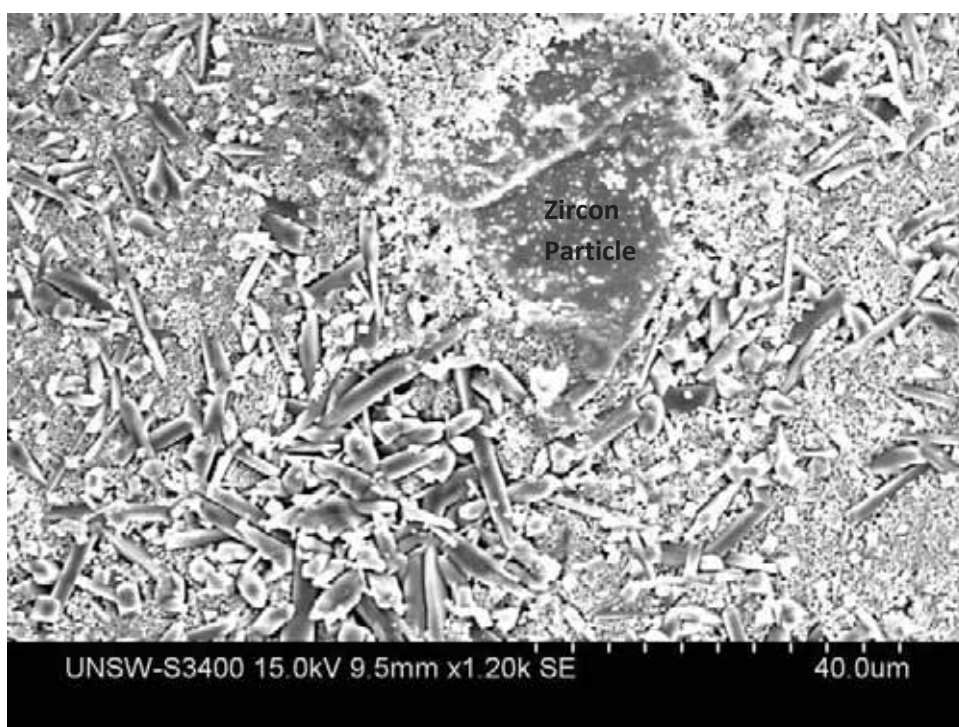
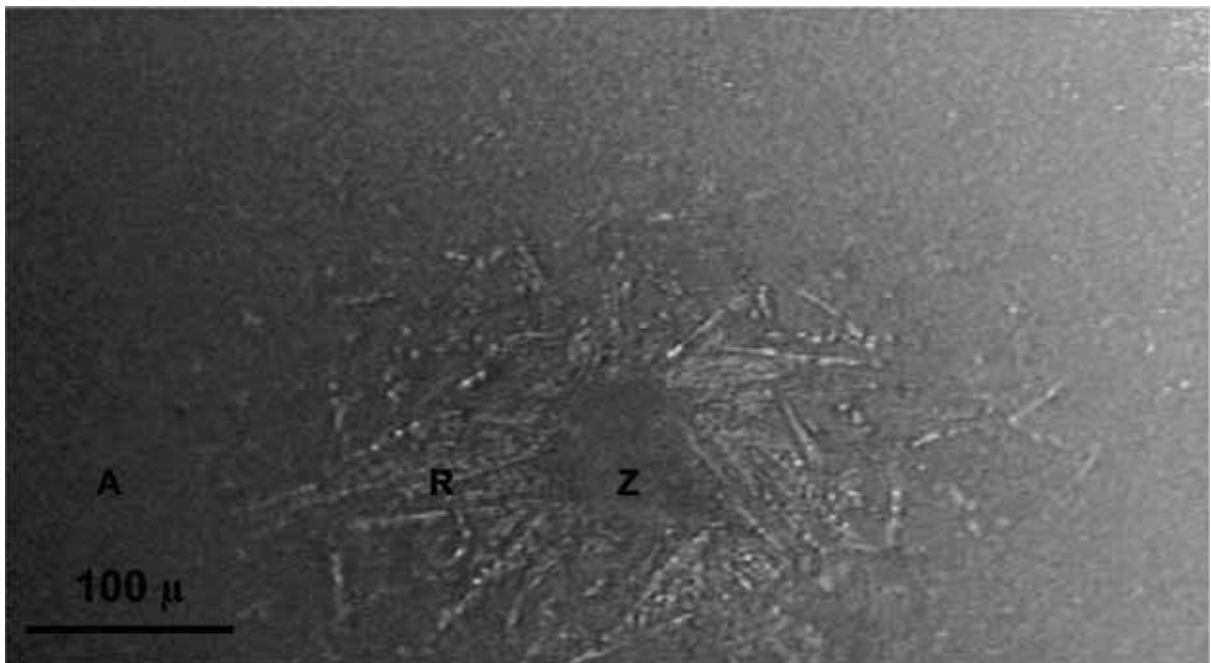


Fig. 10.5. Abnormal grain growth of rutile in the vicinity of a zircon particle (identified by EDS).

Abnormally large grains were visible in optical micrographs. Raman spectra gathered from the regions of abnormal grain growth showed that these grains are of the rutile phase, while anatase is the dominant phase in the regions devoid of these grains. Fig. 10.6 Shows an optical micrograph showing needles of rutile growing in the region surrounding a zircon particle the labels A, R and Z mark respectively anatase, rutile and zircon as identified by laser Raman microspectroscopy. It should be noted that Raman spectra are inappropriate for quantitative analysis and the anatase phase tends to exhibit stronger Raman shifts relative to rutile, as reported elsewhere [21, 29].



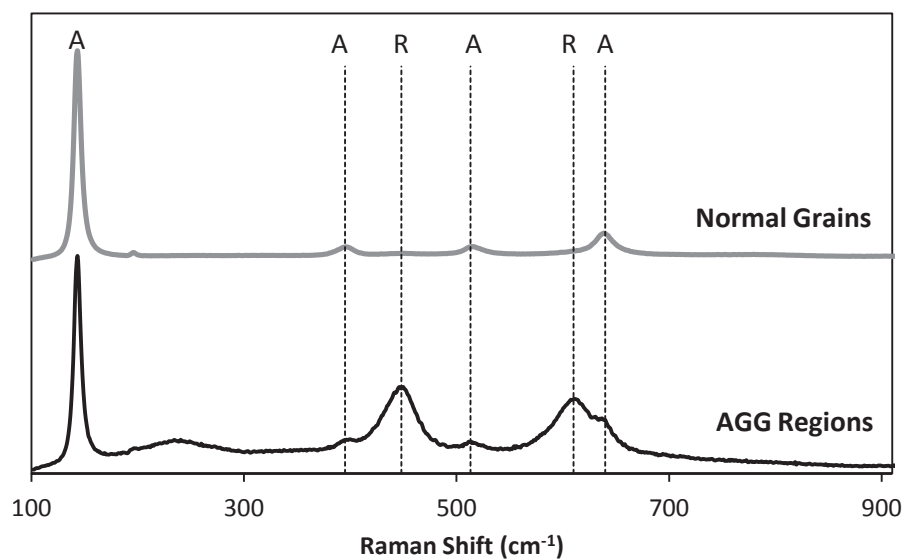


Fig. 10.6. (a) Optical microscope image of zircon particle surrounded by AGG rutile in a 10 wt% ZrSiO_4 doped sample (b) Raman patterns from regions of normal grain growth and AGG. A, R and Z represent anatase rutile and zircon.

Table 10.2 outlines the impurity oxides which were present in the raw materials as determined by X-Ray fluorescence (XRF).

Table 10.2. Impurities in raw materials as determined by XRF.

Raw Material	Impurity	Level (at%)
Anatase	Na_2O	0.22
	MgO	0.11
	SiO_2	0.11
	P_2O_5	0.32
	K_2O	0.21
Zircon Flour	HfO_2	1.19
	Fe_2O_3	0.18
	Al_2O_3	0.62
	TiO_2	0.30
	MgO	0.08

In contrast to doping with ZrSiO_4 , doping with ZrO_2 and SiO_2 does not lead to abnormal grain growth. This is demonstrated in Fig. 10.7, which depicts the morphology of TiO_2 in the region of a

ZrO_2 particle. The presence of ZrO_2 particle was confirmed using EDS. Additions of SiO_2 powders and quartz sand to powder compacts also did not produce AGG.

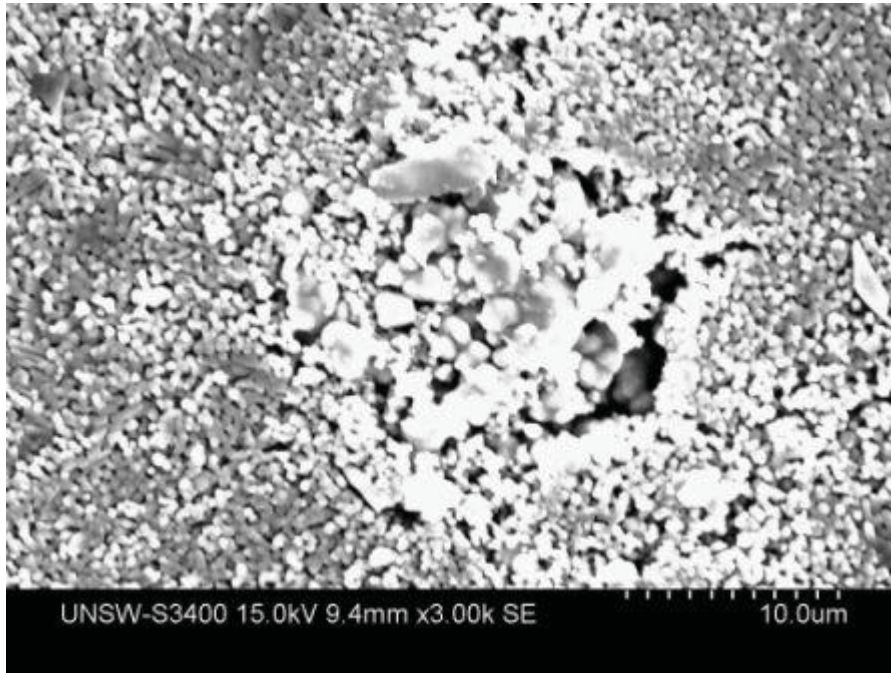


Fig. 10.7. Morphology of TiO_2 surrounding an agglomerated particle of monoclinic ZrO_2 (identified by EDS)

Further ruling out the influence dopant effects on the growth habit, the introduction of Si and Zr dopants using the wet impregnation method did not bring about abnormal grain growth as shown in the micrographs in Fig. 10.8.

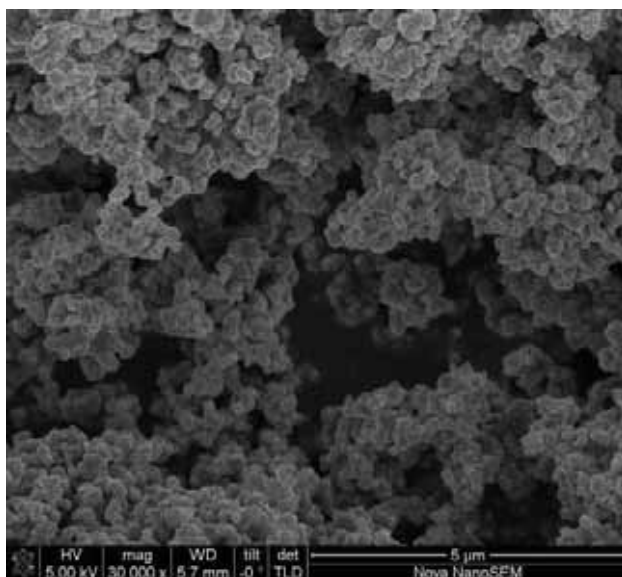


Fig. 10.8. TiO_2 powder doped by wet impregnation with 5 at% Si and 5 at% Zr fired at 1025°C.

10.4.2. Thin films

Thin films were fabricated on quartz substrates using a spin coating method similar to that reported elsewhere [30]. Owing to the use of a single deposition, deposited TiO_2 layers were too thin to form fully dense films, which are easily obtained by the spin coating of more viscous sol or by the use of multiple depositions [30]. The use of Raman spectroscopy and glancing angle XRD confirmed films were fully transformed to the rutile phase after firing at 900°C. Here too the presence of zircon particles induced abnormal grain growth in the TiO_2 film. As shown in Fig. 10.9a, needle like grains of rutile were observed emanating from regions at or close to interfaces with particles of zircon. Zircon particles appear bright in SEM micrographs owing to their greater density. Owing to the finer crystallite size of the precursor anatase, the acicular rutile grains in thin films were smaller than those observed in powders and varied in size from 0.1–3 μm in width and up to 20 μm in length. Such AGG was absent in undoped films as shown in Fig. 10.9b. It should be noted that abnormal grain growth was not observed in the vicinity of all zircon particles which

is likely the result of varying levels of contact between the TiO_2 film and the zircon particulate inclusions.

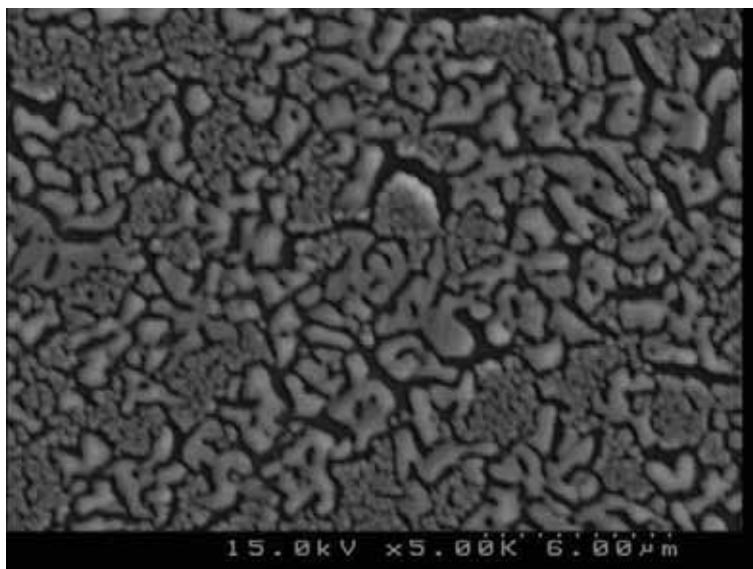
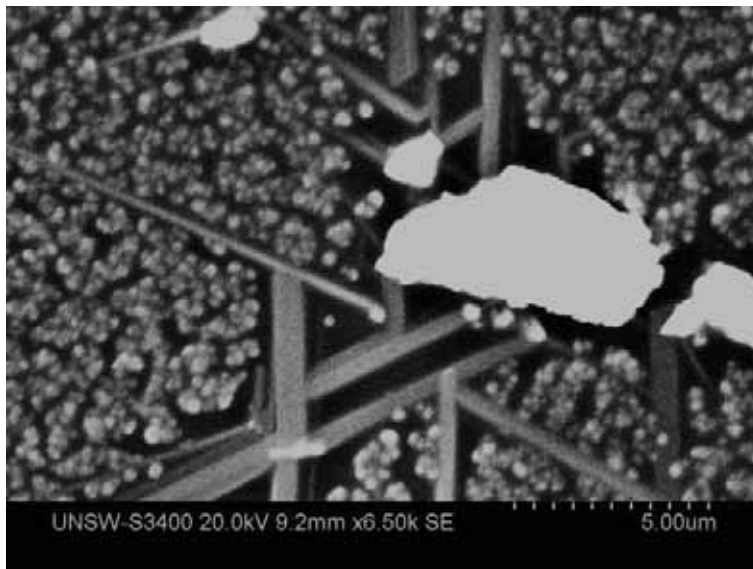
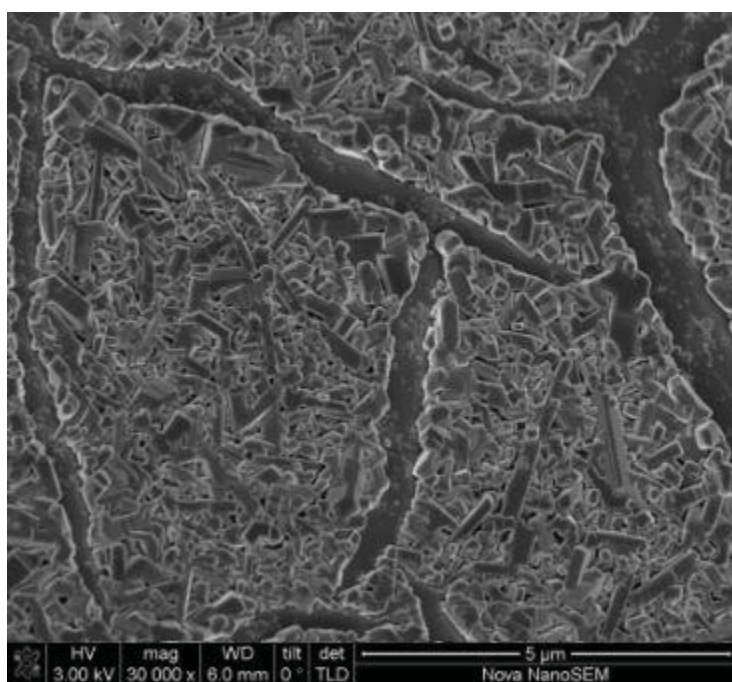


Fig. 10.9. Morphology of thin films of TiO_2 on quartz (a) with ZrSiO_4 particles (b) undoped.

10.4.3. Coated sands

Titanium dioxide coatings were fabricated on grains of sand as part of an effort to produce high surface area supported photocatalysts for water purification applications. It was observed that when zircon sand was used as a catalyst support material, coatings which had been fired at sufficiently high temperatures to form the rutile phase of TiO_2 exhibited elongated grains in a prismatic growth habit on certain facets of sand grains. This can be seen in Fig. 10.10a. In contrast, coatings of TiO_2 supported on quartz sand did not exhibit abnormal grain growth rather exhibited finer rounded rutile crystallites in the region of 50–500nm which varied in size with the thickness of the coating as shown in Fig 10.10b. It should be noted that the morphology of coatings on zircon sand varied across different regions, with acicular grains such as those visible in fig 10.10a observed only on certain facets of some grains. This suggests the crystallographic orientation of zircon plays an important role in giving rise to AGG TiO_2 .



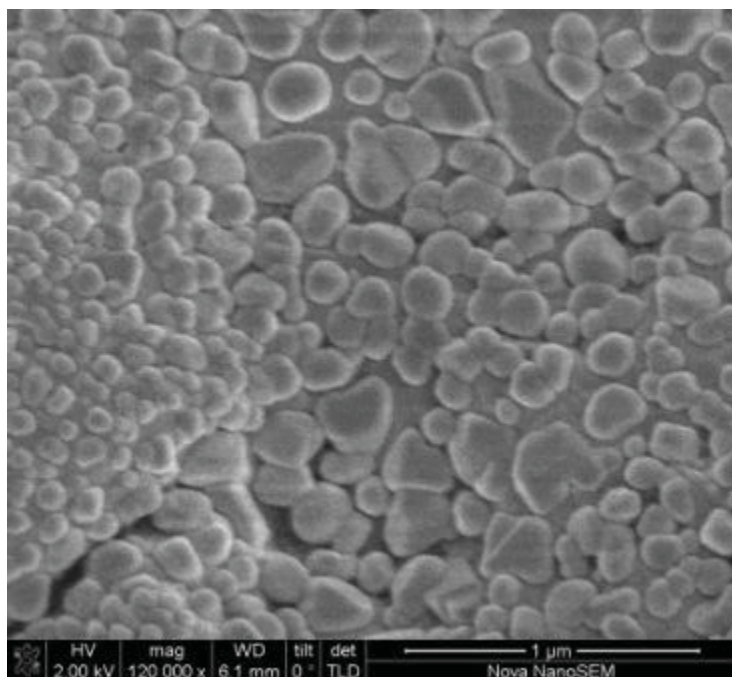


Fig. 10.10. Morphologies of rutile TiO_2 coatings on (a) Zircon sand and (b) quartz sand.

10.4.4. Growth habit of TiO_2 on crystal planes of zircon

A single crystal of zircon was used to examine the growth habit of TiO_2 on different crystallographic planes of ZrSiO_4 . XRD of small crushed and ground piece of the single crystal used confirmed the specimen to be of a zircon structure, although colour inducing contaminants were present. After cutting the single crystal into several pieces and polishing the revealed faces, single crystal XRD was employed to determine the planes present in each section. These are outlined in table 3.

Table 3. Rutile TiO_2 coatings on facets of a sectioned ZrSiO_4 single crystal.

Piece	Plane(s) identified	Growth habit
A	(111) (010)	AGG
B	(122)	Normal
C	(403)	AGG/Normal
D	(011)	AGG
E	(001)	AGG
F	(012) (011)	Mostly normal
G	(011)	Mostly normal
H	(112)	AGG
I	(001)	AGG

J	(011) (101)	AGG
Artificial Gemstone	(010)	AGG

On single crystal ZrSiO_4 surfaces exhibiting AGG of TiO_2 , large prismatic grains were frequently observed growing in preferred orientations, although smaller needle like grains were observed growing in random orientations. Abnormal grain growth of TiO_2 on the majority of surfaces suggests a particular orientation of ZrSiO_4 is not a prerequisite for this type of grain growth in TiO_2 .

10.5. Discussion

While the formation of elongated rutile crystallites has been reported previously, this has typically involved the formation of nano-sized rutile crystallites from precursor solutions using hydrothermal synthesis routes [31–33]. Or through the intermediate formation of sodium titanate compounds [34, 35]. The abnormal grain growth of rutile TiO_2 from a polycrystalline anatase precursor as shown in this work has not been previously reported.

Abnormal grain growth resemblant of that observed in this work has been reported in various ceramic systems including Al_2O_3 [3, 6], 0.1 mol% TiO_2 excess BaTiO_3 [7, 8], Si_3N_4 [36], and $(\text{Na,K})\text{NbO}_3$ piezoelectric ceramics [37].

Abnormal grain growth involves the rapid anisotropic growth of certain grains in comparison with surrounding material. The conditions which have been reported to give rise to such growth include high anisotropy in interfacial energy, high chemical inequilibrium and/or an non-uniform distribution of second phase particles [38]. Within single phase systems faceted grain boundaries are frequently reported as a prerequisite for the onset of AGG. We can consider these conditions in reference to the systems studied in the present work.

10.5.1. Epitaxial nucleation

The elemental diffusion of Si or Zr has been shown not to cause AGG in TiO₂. Thus the initiation of AGG at zircon surfaces suggests a crystallographic nucleation effect. This is supported also by the discovery of a particularly high level of matching between atom positions in rutile and zircon in certain planes. Furthermore, in coatings fabricated on grains of zircon sand, large prismatic rutile grains were only observed on particular facets of sand, suggesting a particular orientation may be necessary for this phenomenon to occur.

In contrast, it should be noted that the random orientation of AGG grains in proximity to zircon particles does not suggest an orientation relationship between zircon surfaces and abnormally large prismatic grains of rutile exists. Rather the formation of AGG TiO₂ in proximity to zircon particles appears visually consistent with diffusion effects.

10.5.2. Distribution and size of second phase particles

In a publication on the theory of normal and abnormal grain growth, Hillert [38] considered 2 and 3 dimensional systems containing pinning second phase particles, here it was suggested that abnormal grain growth occurs when the average grain size in a material lies within a particular interval relative to the volume fraction and size of the second phase particles.

From the mathematical analysis of hexagonally shaped densely packed grains with uniformly distributed pinning second phase particles of constant size, abnormal grain growth was predicted to arise when the average grain size R lies in the range:

$$\frac{4r}{9f} < \bar{R} < \frac{2r}{3f} \quad (1)$$

In this equation r and f are respectively the radius and volume fraction of the second phase particles in the system.

The applicability of this analysis to the systems investigated as part of this work is unclear. Grains in this work are not of hexagonal shape and are not fully dense as the grains used in Hillert's analysis. Furthermore owing to the large sizes of the zircon secondary particles in comparison with the TiO₂ grains in the powder compacts the condition of Eq. 1. Is not met. Moreover the occurrence of AGG in TiO₂ coatings on the surfaces grains of zircon sand single crystals cannot be explained by such a mechanism. Furthermore, if a simple grain-edge pinning mechanism was sufficient to cause AGG in TiO₂ powders, this phenomenon would occur with the use of other stable solid state dopants rather than just zircon.

10.5.3. Chemical inequilibrium and pinning forces

A high degree of inequilibrium is reported to facilitate AGG in single phase systems. It has been reported that in metallic systems where grain growth is pinned, abnormal grain growth may occur if the pinning force is rapidly lessened [2]. The applicability of these observations to a ceramic systems such as that studied in the present work is unclear. It is possible that the formation of the denser equilibrium rutile phase from the metastable anatase precursor brings about a rapid decrease in grain boundary pinning, however if this were the case, AGG would be expected in undoped samples which has been shown not to be the case.

10.5.4. Surface energy anisotropy

The anisotropy of surface energy in TiO₂ is well documented. It is reported that in rutile (110) planes consistently exhibit lower surface energy relative to other rutile planes [14]. This explains why rutile frequently forms in a prismatic or acicular growth habit extended along the c-axis [39]. The divergence of surface energies of the different planes varies with the type of surface terminating groups and it has been reported that under strongly basic conditions of surface

acidity (oxygenated surfaces) the elongation of rutile grains is most pronounced as a result of larger disparity in surface energies under such conditions [14, 40].

Surface energy anisotropy in rutile has not been reported to give rise to abnormal grain growth in polycrystalline TiO_2 such as that observed in this work. Furthermore, in the absence of zircon dopants, isotropic grains of anatase, in the various forms studied in the present work, were observed to transform into larger isotropic grains of rutile rather than elongated prismatic grains.

One could consider the hypothesis that the presence of zircon particles alters the surface chemistry of surrounding TiO_2 grains thus increasing the driving force for the formation of prismatic grains. This theory is unlikely as ZrSiO_4 surfaces do not exhibit strong surface basicity.

10.5.5. Fluxing impurities

The presence of a liquid phase at grain boundaries can be a contributing factor to the anisotropy in surface energy and thus give rise to the rapid growth along a particular crystallographic direction, giving rise to AGG [1, 3]. From consideration of phase equilibrium diagrams, the formation of liquid in the TiO_2 - ZrSiO_4 system is not expected to occur at the temperatures employed in the present work [41, 42]. However, the presence of fluxing impurities should be considered, particularly as the zircon flour used in this work exhibits ~ 0.3 at% Fe impurity according to the supplier's specifications. Studies which have investigated the FeO - ZrO_2 - SiO_2 system have shown liquid formation at temperatures lower than the ZrSiO_4 decomposition temperature at compositions with $> 5\%$ Fe levels [43, 44], however solidus temperatures reported are still significantly higher than those used in the present work. Furthermore, AGG was observed in TiO_2 coatings on the (010) surface of an artificial ZrSiO_4 gemstone, which did not exhibit any coloration, suggesting no significant levels of transition metal impurities. In spite of this, based on the appearance of the propagation of AGG in the vicinity of zircon particles, grain boundary liquid

formation appears a likely mechanistic candidate. The presence of low levels of alkali contaminants may be a contributing factor to this grain boundary liquid formation.

10.5.6. Faceted grain boundaries

The morphology of the precursor anatase material is crucial in determining whether rutile exhibiting abnormal grain growth will result from heat treatment. Although in reference to systems other than that studied in the present work, faceted grain boundaries have been reported to be a prerequisite for the occurrence of AGG [8, 45]. Thus rounded grains or grains exhibiting atomically rough or defaceted grain boundaries are not expected to exhibit AGG.

The random orientation of abnormally large prismatic rutile in the vicinity of zircon particles is inconsistent with the theory that epitaxial nucleation is the driving force for this grain growth as nucleation effects would involve a particular orientation relationship and one would expect to see preferred orientations of AGG rutile relative to the zircon particles. An alternative explanation may be the TiO_2 - ZrSiO_4 interface acts as a faceted grain boundary.

10.5.7. Combined effects

Whilst determining a distinct mechanism by which ZrSiO_4 imparts AGG in TiO_2 is difficult, it is likely that the observed phenomena are the result of the cumulative effects of different parameters.

- Grain size of precursor anatase TiO_2
- Crystallographic orientation relationship between TiO_2 and certain planes of zircon ZrSiO_4
- The presence of fluxing impurities
- Surface acidity

These factors are cumulatively involved in inducing AGG in rutile TiO_2 . Abnormally large faceted grains may then propagate throughout the bulk of the material through nucleation of prismatic grains at faceted boundaries.

10.6. Conclusions

The rutile phase of TiO_2 has been shown to exhibit abnormal grain growth in the presence of zircon ZrSiO_4 . Along with other factors, a distinct relationship between the crystallographies of the two materials, involving an unusually high degree of lattice matching, may play an important role in inducing this type of grain growth. It is likely that this type of grain growth can be achieved with the use of other dopants. Further studies are required to elucidate the mechanisms which can give rise to AGG in TiO_2 and examine the properties of materials exhibiting this type of grain growth in order to find beneficial applications for materials exhibiting the observed phenomena.

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11. Conclusions and recommendations

11.2. Key findings and achievements

11.2.1. The anatase to rutile phase transformation

- The effects of dopants on the promotion or inhibition of the anatase to rutile phase transformation were comprehensively presented for the first time and interpreted in terms of the parameters of valence and ionic radius.
- Predictive analysis of the effects of untested dopants on the kinetics of the anatase to rutile phase transformation was carried out.
- Mechanistic aspects of the formation of rutile from anatase and the inhibition or promotion of this phase transformation were explored and discussed.
- Methods of phase differentiation were critically discussed and the potential problems associated with XRD analysis of phase composition were presented.
- An understanding of the phase formation and transformation behaviour observed in the subsequent chapters of this thesis was facilitated.
- The use of nitrogen firing atmosphere was experimentally shown to enhance rutile formation relative to firing in air owing to the generation of defects in the form of oxygen vacancies.
- Confirming predictive analysis, carbon in graphite substrates was found to enhance the formation of rutile in electrophoretically deposited anatase relative to unsupported powders for the preceding reason.

11.2.2. Thin films

- Immobilisation on quartz substrates brings about an inhibition of the anatase to rutile phase transformation relative to unsupported materials.

- Films synthesised on single crystal quartz substrates exhibit a high degree of orientation as a result of TiO_2 - SiO_2 interface effects.
- In undoped films, rutile was observed to form as parallel bands in the parent anatase, a previously unreported phase-segregated morphology.
- It was experimentally shown that Cu doping enhances the anatase to rutile transformation kinetics through an increase in oxygen vacancy levels.
- Dopant segregation occurs in transition-metal-doped films despite homogeneous molecular level mixing of the precursor sol.
- A small quantity of rutile is sufficient to alter significantly the optical absorption edge of thin transparent films.

11.2.3. Powders

- The use of high levels of excess hydrolysis ratios is necessary for the precipitation of crystalline phases of TiO_2 .
- As a result of grain consolidation and growth, a significant reduction in surface area and an increase in pore diameter take place as anatase transforms to rutile.
- Precipitation by hydrolysis of titanium tetra-isopropoxide in a predominantly aqueous medium results in the formation of a mixed anatase-brookite material, which can form a tri-phasic anatase-brookite-rutile composition through thermal treatment.
- Grain growth and phase transformation take place more rapidly in powders prepared through aqueous precipitation relative to powders fabricated through precipitation in a predominantly organic medium.
- Supporting observations reported in the literature, the presence of a secondary brookite phase enhances the formation of rutile in nano-crystalline TiO_2 powders through interfacial nucleation.

11.2.4. Dispersion of oxide suspensions and EPD of thick films

- Carboxylic acids impart negative surface charge to oxide particles in suspension and form steric barriers that inhibit agglomeration and settling and thus improve dispersion.

- The use of carboxylic acids as dispersants significantly improves the quality of electrophoretically deposited coatings from aqueous suspensions.
- Anodic aqueous electrophoretic deposition from acidic suspensions can be achieved with reduced levels of gas bubble damage derived from water-electrolysis when carboxylic acids are used for pH adjustment.
- The adsorption cross-sections of carboxylic acids on a representative oxide (ZrO_2) were determined and discussed in terms of size, speciation and functional groups of these reagents.
- The mechanistic aspects of the dispersion of oxides by carboxylic acids were explored and discussed.
- Small additions of carboxylic reagents are sufficient to impart highly negative zeta potential values to oxide suspensions.

11.2.5. Sand-supported TiO_2

- Consistent well adhered coatings of TiO_2 can be applied to grains of different types of sand for surface-area-enhanced immobilisation.
- The use of sand grains as photocatalyst support materials offers a low-cost approach to the large-scale fabrication of immobilised TiO_2 photocatalytic materials for water purification applications.
- The suspension of sand particles in a Ti bearing sol-gel matrix was found to result in uneven spalling of coatings of TiO_2 on the grains of sand.
- The anatase to rutile phase transformation in TiO_2 coatings on sand grains occurred at higher temperatures relative to unsupported powders, similar to films on quartz substrates.

11.2.6. Supported TiO_2 in simulated water purification applications

- Water purification performance can be quantitatively analysed by the decomposition of organic dyes and through the inactivation of micro-organisms.

- Photocatalytic performance was observed to be higher in undoped quartz supported thin films relative to doped films as determined by the photo-oxidation of methylene blue.
- Nitrogen firing atmospheres were observed to enhance photocatalysed inactivation of *E. coli* bacteria and this was explained as the result of inter-band-gap states.
- Photocatalytic performances of thin films, thick films and coated sands were found to be poor, partially as a result of low irradiant flux of the UV lamps used relative to the flux of sunlight.
- TiO₂-coated sands in the form of a packed bed impede the full realisation of the advantages of utilising high-surface-area support materials.

11.2.7. Morphology and microstructural findings

- Significant grain growth occurs in the process of the anatase to rutile phase transformation, accompanied by a significant reduction in surface area. This was observed in all materials fabricated as part of this thesis.
- Low-valence cationic dopants promote rutile formation in thin TiO₂ films with a lessened degree of grain coarsening.
- In the presence of solid particles of ZrSiO₄, a previously unreported occurrence of abnormal grain growth in rutile TiO₂ was seen to take place.
- An exceptionally high degree of atomic position matching was found between certain planes of ZrSiO₄ and rutile TiO₂.

11.3. Discussion of fabrication methods

The work presented in this thesis involved the investigation of various approaches to the fabrication of titanium dioxide photocatalysts exhibiting a diversity of morphologies, mineralogies and bulk properties. Broadly speaking, the approaches utilised precursor chemicals or prefabricated TiO₂ powders to fabricate single- and mixed-phase materials in immobilised and powder form. The work presented in this thesis and the large number of cited studies from the literature show that a large variety of fabrication methods can be employed in the fabrication of TiO₂ materials for photocatalytic applications. Also, the parameters of chemical synthesis routes, support materials, surface area, thermal treatment can be controlled to give materials with divergent properties.

11.3.1. Thin films

The fabrication of titanium dioxide in thin-film form was investigated in the course of the work presented in this thesis and this investigation is presented chiefly in Chapter 4. Using flat single-crystal substrates and organometallic precursor chemicals, the formation of thin films of TiO₂ with a high degree of crystallite orientation was shown. Furthermore, a previously unreported type of phase segregation was observed in which parallel bands of rutile formed in the parent anatase through thermal treatment. This phenomenon was discussed in light of information presented in the review of the anatase to rutile phase transformation. Consistencies with the interpretive review of the phase transformation were found in the observed effects of dopants on the rutilation of thin TiO₂ films as well as the effects of quartz support material on the stabilisation of the anatase phase relative to unsupported materials such as those reported in Chapter 8. Precursor materials and quartz substrates used in the fabrication of thin films resemble the materials used in the fabrication of TiO₂ coatings on quartz sand, as reported in Chapter 9. Indeed, the phase transformation behaviour was observed to be similar, with biphasic anatase-rutile TiO₂ obtained in the range 800°-900°C.

11.3.2. Powders

The fabrication of TiO_2 powders for use in suspension or alternatively for immobilisation on support materials is of great importance and is widely reported in the literature. In Chapter 8 of the present thesis, an investigation into the effects of hydrolysis ratios on the morphology and crystallinity of unsupported powders prepared from a titanium alkoxide was presented. It was shown that it is possible to obtain materials of mixed anatase-brookite-rutile phase composition if the appropriate thermal treatments and hydrolysis methods are employed. Such mixed-phase powders may exhibit superior performance in photocatalytic applications and are suitable candidates for future work involving immobilisation by electrophoretic deposition through novel techniques explored in chapters 5–7 of this thesis.

11.3.3. Thick films

The manuscripts presented in this thesis form a nexus of ideas involving novel fabrication methods and investigations into the synthesis of mixed-phase TiO_2 photocatalysts. New methods of dispersing oxide particles in aqueous suspensions were investigated using the surface adsorption of carboxylic acids to facilitate improved electrokinetic properties in suspensions of ZrO_2 and TiO_2 . The investigation of carboxylic dispersion of oxides resulted in the development of effective electrophoretic deposition methods for the fabrication of thick films. Through the use of such methods in conjunction with appropriate firing regimens, novel biphasic supported titanium dioxide photocatalysts were produced as reported in Chapter 6. The positive economic attributes associated with the development of such material fabrication methods is warranted owing to their ability to utilise aqueous TiO_2 suspensions of low solids loadings for the fabrication of supported photocatalysts on a variety of substrates in processes that can be carried out at low

costs. The utilisation of sand-support materials, as reported in Chapter 9 of this thesis, also is motivated by the prospect of fabricating supported photocatalysts at low costs.

11.3.4. Supported TiO₂ of enhanced surface area

The fabrication methods investigated for the synthesis of thin films through spin coating of precursor sol-gels and thick films through novel electrophoretic deposition techniques involve the formation of flat materials with reduced available surface area relative to suspended powders. For this reason, immobilisation of titanium dioxide photocatalysts was done so as to enhance the surface area while maintaining the advantages of catalyst recoverability. The materials used for this purpose were sands. The main advantage and key driver behind this choice of support material was an economic one. The application of titanium dioxide photocatalysts for water purification applications requires use of materials on a large scale and thus the choice of catalyst support materials that are available in large quantities at low costs is critical for the applicability of such materials for real-world situations.

It was demonstrated that effective coverage of sand particles with TiO₂ coatings is achievable using alkoxide precursors. However, despite this accomplishment, photocatalytic activity was not shown to be sufficient for the justification of the use of such materials in large-scale water purification applications. Furthermore, the settling of coated sand particles into a packed bed impeded the realisation of the high surface areas exhibited by the support materials as the bulk of the material was not exposed to impinging irradiation and thus did not function as a photocatalyst.

While important steps have been made towards the use of sand as a cheap and readily available catalyst support material, the realisation of the potential of this approach to photocatalytic

materials fabrication requires further advances in application, design and execution as well as the fabrication of coatings exhibiting improved activity relative to the materials described in Chapter 9 of this thesis.

11.4. Phase composition

The phase composition and phase transformation behaviour of TiO_2 materials prepared during experimentation throughout the bodies of work presented in this thesis represent an important thread woven throughout the presented work.

11.4.1. Anatase to rutile phase transformation

Chapter 3 of this thesis presented an interpretative and predictive review into the anatase to rutile phase transformation. The concepts discussed in this chapter are relevant to phenomena reported in many published works involving the thermal treatment of anatase TiO_2 and indeed to the work involving the thermal treatment of anatase and/or brookite TiO_2 reported in the subsequent chapters of this thesis.

The effects of dopants were summarised and reported in Chapter 3 and these effects were seen to have consequences on the phase transformation behaviour observed in the various research efforts presented in other chapters of this thesis. The inhibition of the anatase to rutile phase transformation is a frequently observed result of common impurities and this was evident in titanium dioxide coatings formed on quartz substrates and on grains of sand (owing to silicon contamination) manifested in higher rutile formation temperatures.

11.4.2. Effects of mixed phase compositions on photocatalytic performance

The synergistic benefits of anatase-rutile mixtures are widely reported in the literature, as has been shown in greater detail in Chapters 2 and 3 of this thesis. For this reason, during the course of the experimentation reported in this thesis, emphasis was placed on obtaining mixed-phase materials through thermal treatments.

Despite the overwhelming cited evidence from the literature of the enhanced performance of mixed-phase TiO₂ photocatalysts relative to single-phase materials, the advantages of mixed-phase compositions with respect to photocatalytic performance are not unequivocally clear from the bodies of work reported in the present thesis. The performances of single- and mixed-phase materials are evident in the study of the decomposition of methylene blue and the inactivation of bacteria, as reported in Chapters 4, 6 and 9. From an examination of these studies, no clear advantage of mixed-phase material was observed. This was likely to be a consequence of low levels of surface area obtained in the materials studied and the low levels of irradiance used. This by no means detracts from the findings of enhanced performance of mixed-phase materials as reported in numerous publications. However, it does suggest that a particular morphological phase assemblage or interface morphology may be necessary for this enhancement to be evident to a greater extent.

11.4.3. Mineralogical analyses

The studies that have been presented here involve significant components of mineralogical analyses. In the majority of cases, these studies were carried out with the utilisation of laser Raman microspectroscopy and/or X-ray diffraction for the purposes of phase differentiation and quantification. It has been shown that both of these methods have benefits and drawbacks that

influence their suitability in different analytical situations. X-ray diffraction, in conjunction with quantitative analysis methods, were shown to be useful in determining overall phase compositions in thick films, powders and thin films, while Raman methods were shown to facilitate the differentiation of phases with respect to morphological observations as carried out in Chapters 4, and 10. Furthermore it was shown that laser Raman microspectroscopy allows the determination of phases present in coated surfaces of sand grains, where the diffraction peaks from the crystalline support materials prevent the use of XRD methods as these overwhelmed the signals resulting from the nanocrystalline coatings.

11.5. Assessment of photocatalytic performance

The efforts towards assessment of photocatalytic performance presented in this work yielded results showing lower levels of photoactivity relative to most studies reported in the literature, even though the approaches taken in the present thesis are appropriate for the assessment of photocatalytic materials designed for water purification applications. The inactivation of bacteria and decomposition of methylene blue are both standard analytical approaches owing to the simulation of such approaches of real-world pollutants, such as pesticides and microbial contaminants. Future efforts towards the assessment of photocatalytic performance should involve greater intensity of irradiation to achieve more significant results.

11.6. Future prospects

The bodies of work that have been presented here illuminate various potential trajectories for future research efforts and establish potential for future synergistic nexuses drawing on the findings made in the bodies of work which have been presented.

Prospective future paths may involve:

- **Rutilation without significant grain growth**

As discussed in various sections of this thesis, the use of dopants can be employed to lower the temperature at which rutile forms and give rise to the formation of this phase with lower levels of grain growth. Future work may involve employing rutile formation enhancing dopants and firing atmospheres in conjunction with fabrication methods and immobilisation techniques explored in this thesis to yield mixed phase materials through thermal treatment while maintaining higher levels of surface area.

- **Electrokinetic characterisation of amorphous TiO_2 powders and mixed phase powders**

The formation of amorphous TiO_2 and mixed anatase-brookite TiO_2 through the hydrolysis of titanium alkoxides was demonstrated in the work presented in Chapter 8. The electrokinetic characterisation of such powders using methods similar to those used in Chapters 5 and 7 would yield previously unreported findings and might pave the way for the use of such powders as precursor materials for the fabrication of thick films through EPD.

- **EPD of amorphous / mixed phase powders**

The use of mixed phase or amorphous powders such as those whose synthesis is reported in Chapter 8 for immobilisation through carboxylic acid facilitated anodic aqueous EPD, as reported in Chapters 5–7, may yield materials of improved phase composition and morphology relative to the use of commercially available anatase powder as reported in this work.

- **EPD on to alternative support materials of enhanced surface area**

Experimental procedures involving electrophoretic deposition carried out in this work exclusively involved the use of flat graphite substrates. Such substrates are good candidates for support material owing to the potential beneficial effects of carbon on photocatalytic performance of TiO_2 as discussed in Chapter 6, and the use of flat

conductive substrates facilitates rapid analysis of deposition kinetics. However, in future research efforts, alternative support materials, exhibiting enhanced levels of surface area relative to the flat substrates used in the present work may be sought. The use of alternative support materials as support materials for oxide semiconductor photocatalysts deposited through EPD would require the formulation of alternative deposition procedures, using appropriate parameters of voltage, solids loading, deposition time, and electrode configuration to achieve the desired outcome.

- **Thin film coating methods applied to hollow spherical particles**

The sand particles used as support materials for immobilised mixed and single phase TiO_2 materials, the fabrication of which is reported in Chapter 9, show merit for water purification applications as a result of their low cost and potentially advantageous aspect ratio, forming a compromise between powders and films, allowing easy recovery from treated water while yielding enhanced levels of surface area. Despite this, the use of sands as support materials is associated with significant drawbacks, as observed in the work which has been reported in this thesis. The settling of sands in a packed bed prevented the realisation of the effective surface area of the particles, as only the top layer of particles was subject to illumination.

An alternative support material conceived in the process of research presented here is the immobilisation of TiO_2 films on hollow spheres which would float on the surface of treated water. The surfaces of such spheres above the water level would become covered in a film of treated water (as a result of the previously discussed potential super-hydrophilicity of nano- TiO_2 coatings) while the surfaces of the spheres below the water level would be in contact with the bulk of the treated water. Furthermore, the floating layer of coated hollow spheres would form an evaporation barrier, reducing water losses.

- **Quantitative analysis of grain growth kinetics in AGG rutile**

The study reported in Chapter 10 presents novel findings of a previously unreported system of abnormal grain growth in titania. The mechanism through which the phenomenon is brought about was not conclusively determined and thus the work presented in Chapter 10 is an phenomenological introductory study, serving as an overture to bring this system to the attention of the scientific community. Further studies into AGG of titanium dioxide are warranted and such studies should include quantitative analysis of grain growth kinetics, utilising variant firing temperatures and firing durations in order to quantitatively observe this phenomenon. Further studies should involve the exploration of the properties imparted by AGG in TiO_2 systems, this may include mechanical properties of fracture toughness and compressive strength, which may be improved as a result of elongated rutile grains.

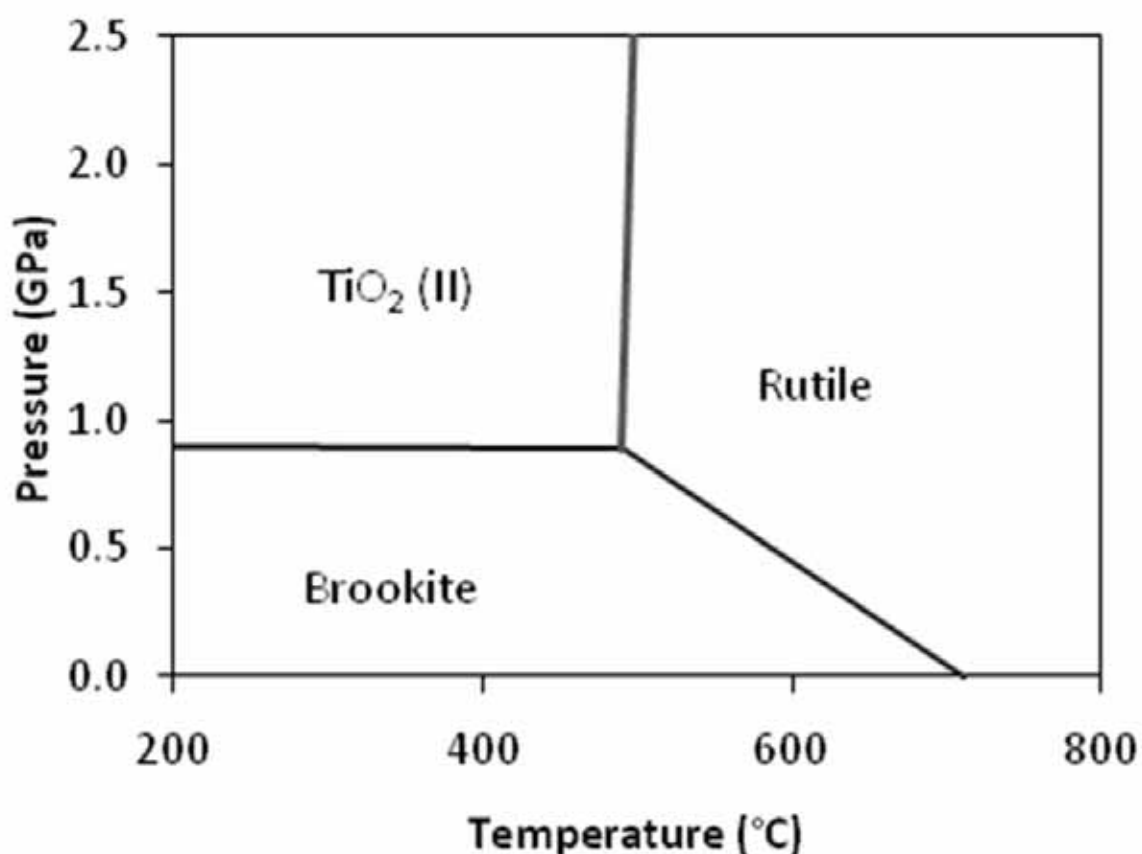
- **Sunlight driven photocatalysis**

The assessment of photocatalytic activity included in the Chapters 4,6 and 9 of this thesis involved the use of UV lamps and the measurement of irradiance through the use of a light-meter. In comparison with sunlight, levels of irradiance achieved in the framework of this work 2–3 orders of magnitude lower than what is achievable using solar irradiation on a clear summer's day. As the use of renewable energy resources, solar energy in particular, for water purification applications is highly desirable, future work could be designed to take place under bright midday sunlight, which may facilitate the obtainment of more significant levels photocatalytic performance, relative to those obtained by comparatively weak UV irradiance sources in the course of the present work.

Appendix

Presented in this appendix are figures and data not included in the chapters comprising the main body of the present thesis. These data are auxiliary and were not included in the analyses and discussions presented in the eight manuscripts included in this thesis.

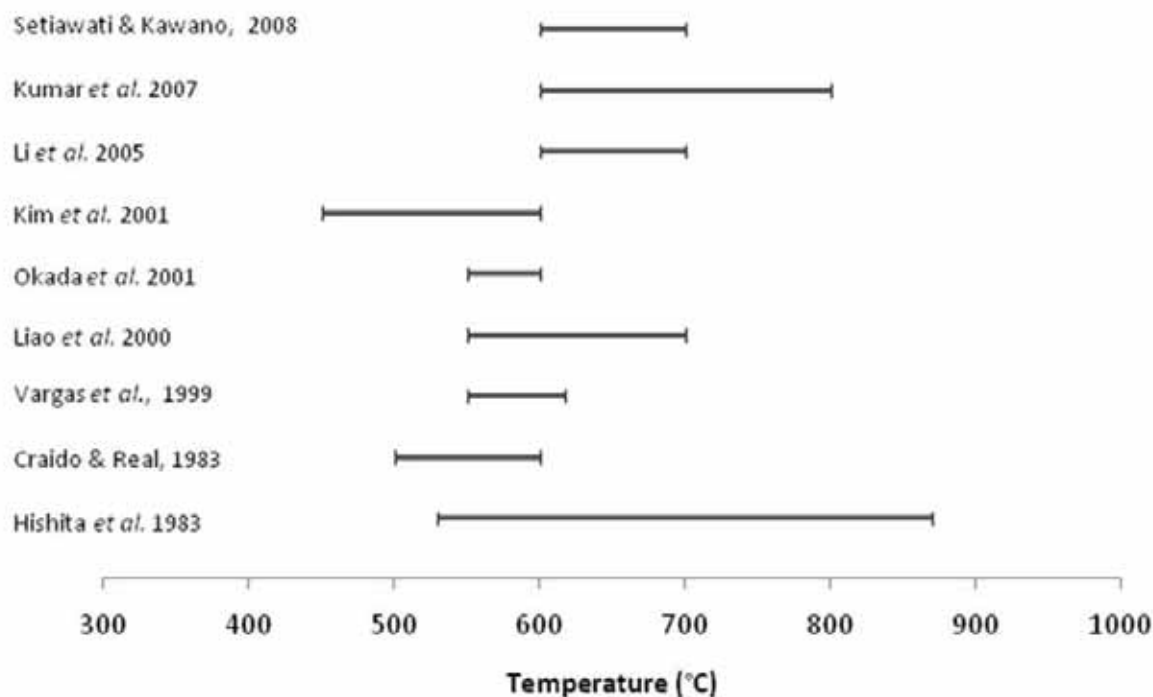
A1. Phase transformation reaction boundaries from Dachille et al. [1] when brookite is used as the initial phase. These results compliment the data shown in Fig. 3.8. which pertains to the anatase to rutile phase transformation. As the review presented in Chapter 3 focused on the anatase to rutile rather than the brookite to rutile phase transformation, this figure was not included in the main body of the manuscript.



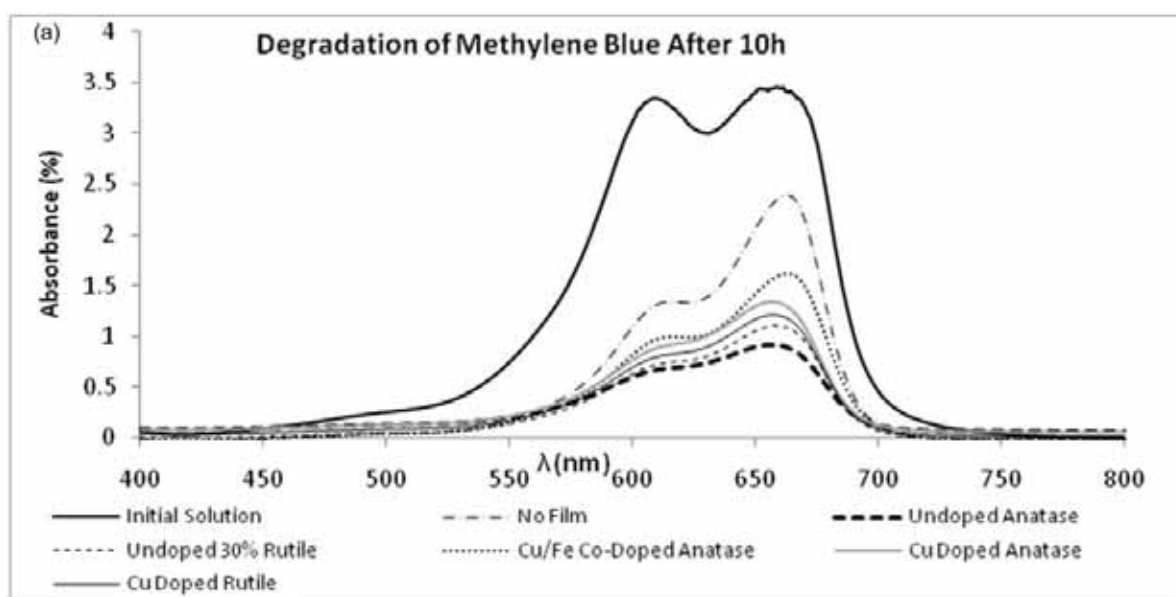
A2. Time line of phase transformation intervals

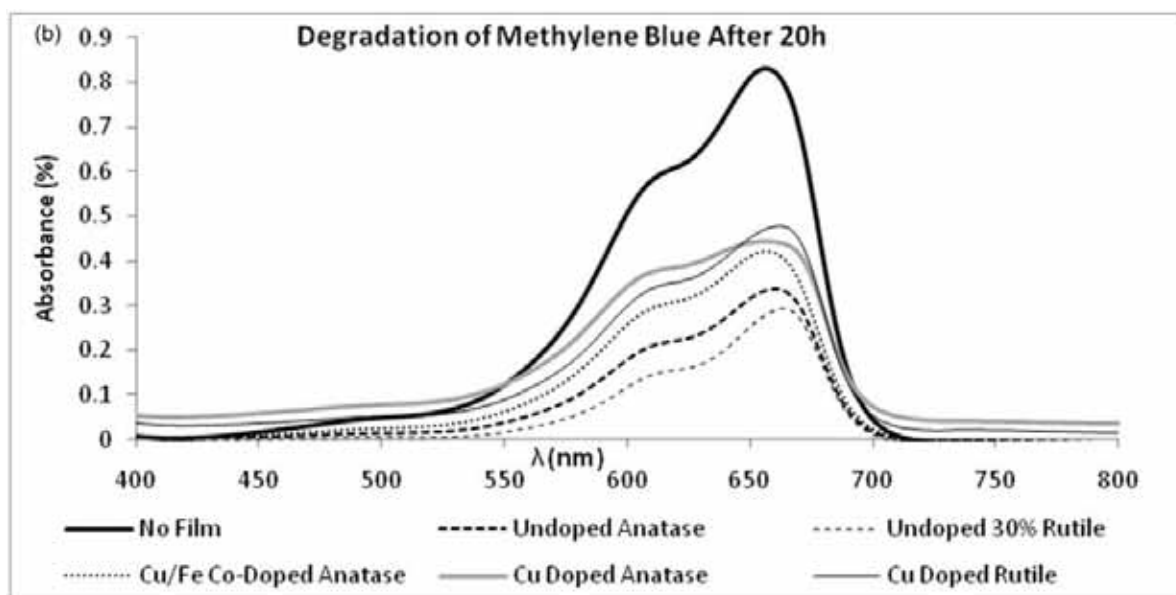
The onset temperature intervals shown in **A2** represent the intervals between the highest soak temperature at which rutile was not detected (left end-point of range) and the lowest soak temperature at which rutile formation was detected (right end-point of bar) by XRD. This figure does not take into account the differing firing durations employed by the various studies.

Rutile Formation in Anatase - Onset Temperature Intervals

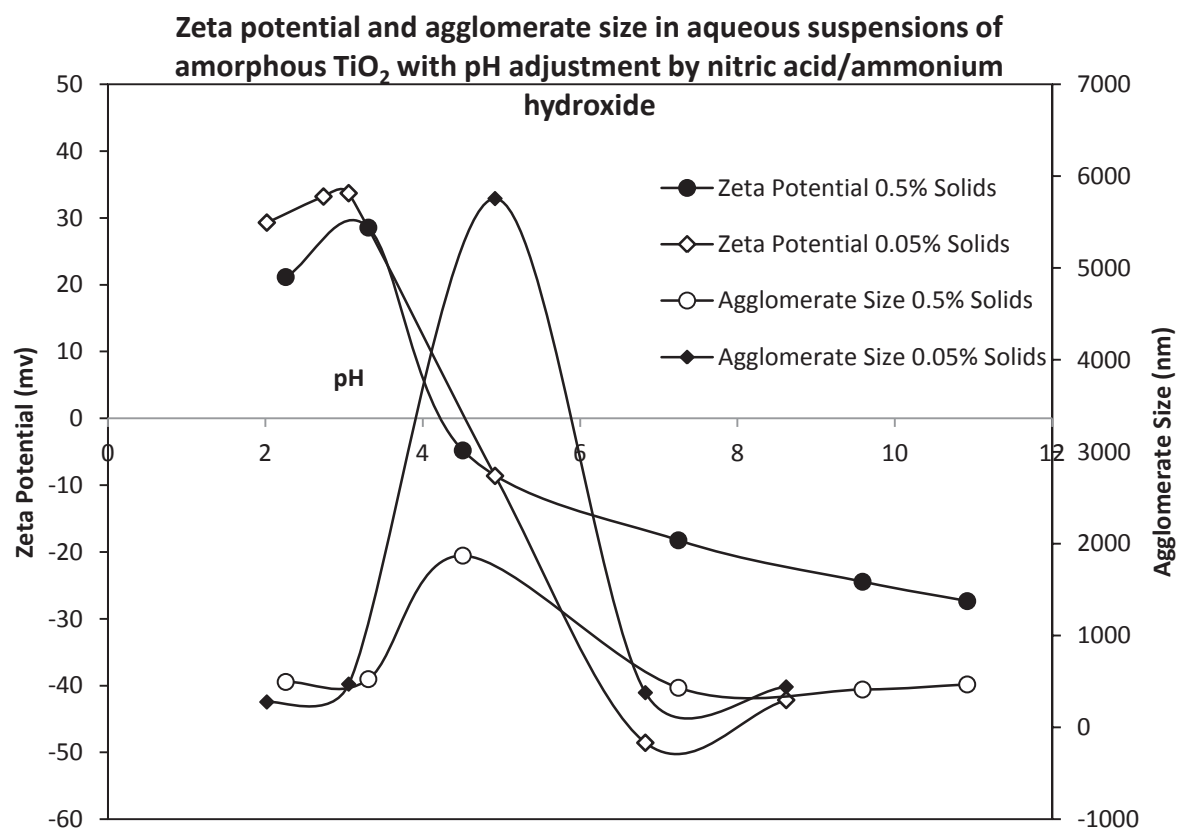


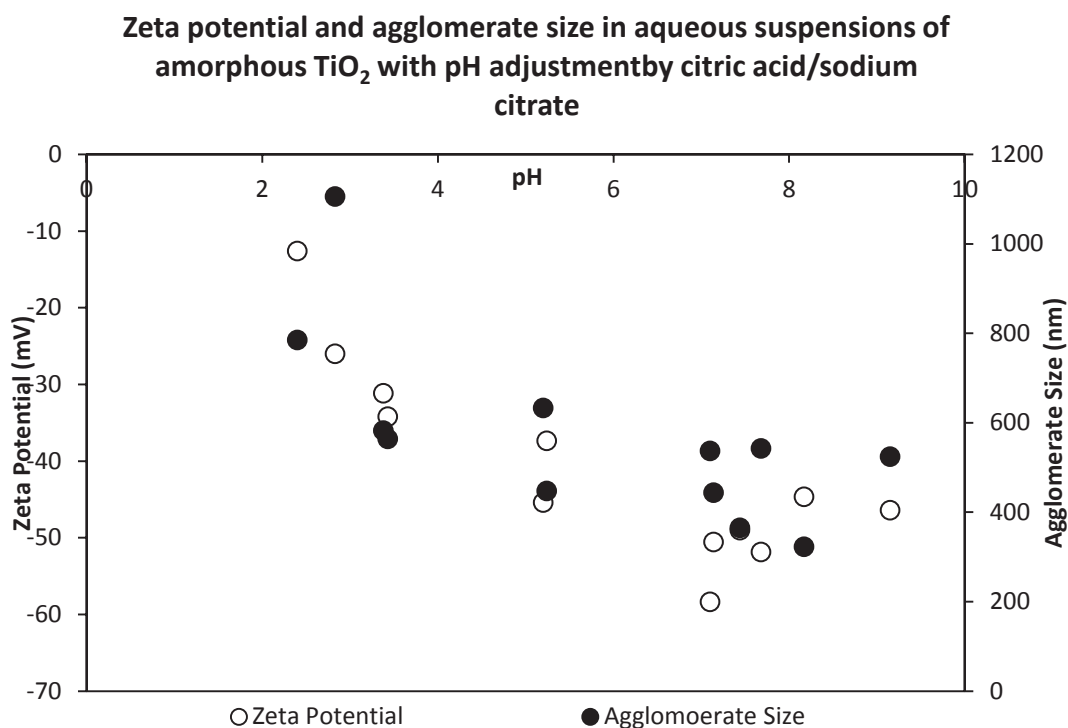
A3. UV-vis absorbance spectra used to determine the concentration of Methylene blue in experiments to determine the photocatalytic activity of quartz supported thin TiO_2 films as presented in Chapter 4 of this thesis. These spectra were used in conjunction with the calibration curve shown in Fig. 4.10 to obtain the data shown in Fig. 4.11.



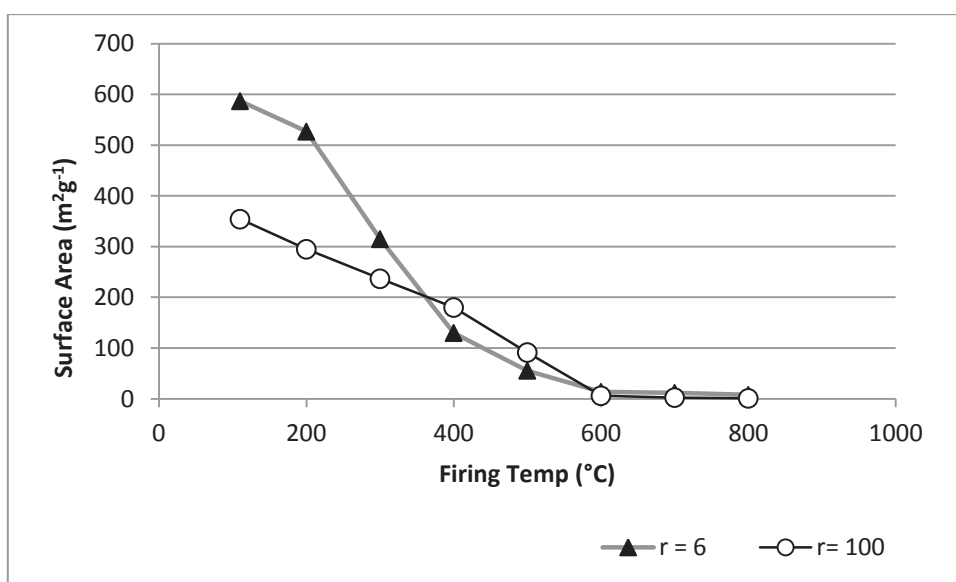


A4. Electrokinetic characterisation of suspensions of amorphous TiO_2 ($r=6$ powder from Chapter 8) showing zeta potential and agglomerate size behaviour as determined using the methods reported in Chapters 5 and 7. These data show that in similarity to crystalline TiO_2 and ZrO_2 powders, the use of citric acid brings about a significant drop in zeta potential and inhibition of agglomeration.

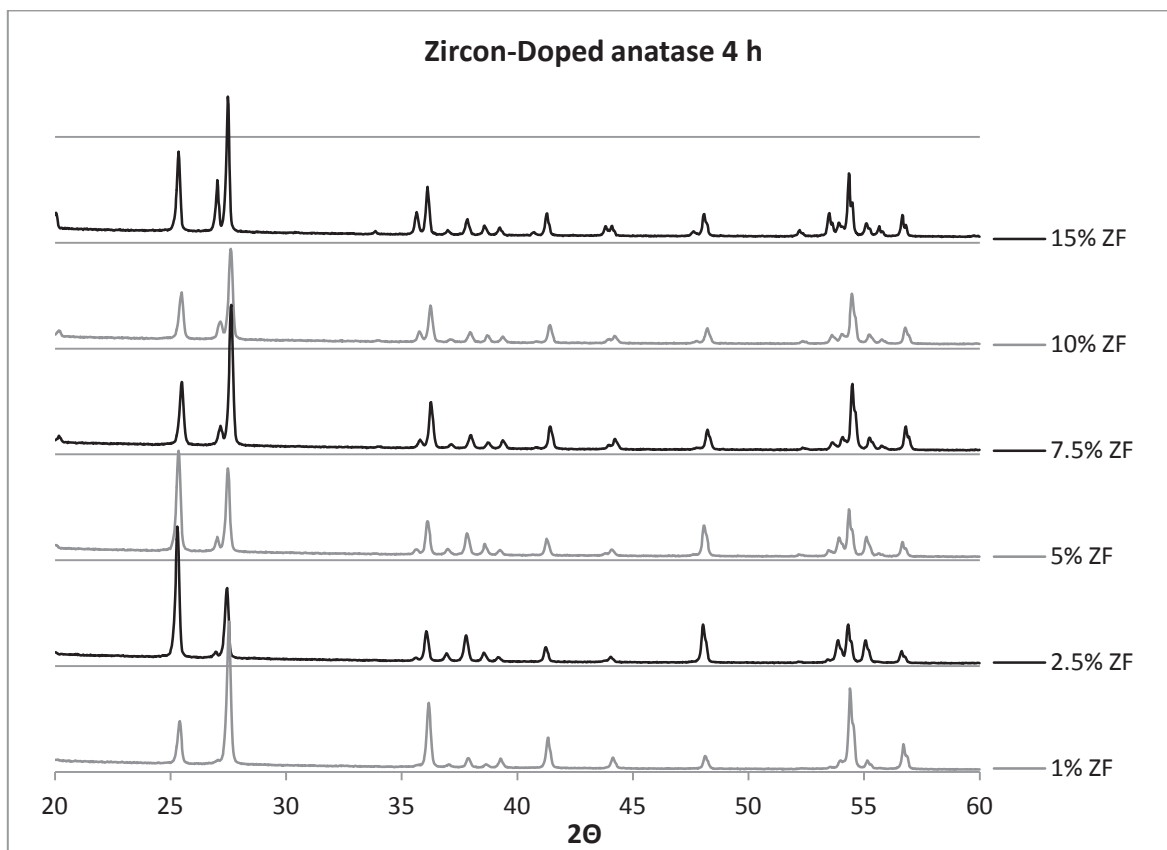




A5. Surface areas of powders from Chapter 8 as determined using Langmuir surface area analysis methods. Results are consistent with those determined using BET analysis as reported in Fig. 8.13



A6. XRD Patterns of TiO_2 compacts doped with varying weight fractions of zircon flour. Data presented here was used to calculate the values shown in figure 10.2.



[1] Dachille F, Simons PY, Roy R. Pressure-Temperature Studies of Anatase, Brookite, Rutile and TiO_2 -II. The American Mineralogist 1968; 53 1929–1939