Titania catalysts : crystal chemical insights and tailored functionalities

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TITANIA CATALYSTS:

**CRYSTAL CHEMICAL INSIGHTS AND
TAILORED FUNCTIONALITIES**

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Abstract

The functionality of titania in photocatalytic, photovoltaic and sensing applications is controlled by the morphology, microstructure, and phase assemblage of this semiconducting oxide. Many approaches have been reported to synthesize high purity titania nanomaterials, but soft chemical methods are favoured as crystalline products can be easily obtained after heat treatment. However, defective and amorphous titania variants have been less investigated, as the transition from the gel to the crystalline phase is frequently assumed to be straightforward. While it is possible, in principle, to determine the phase proportions by powder X-ray diffraction (XRD), the reliability of weight percentages extracted by Rietveld analysis can be compromised by microabsorption. Spectroscopic methods also provide valuable insights but may be surface sensitive, rather than representative of the bulk. This thesis describes the quantitative determination of titania phase assemblages, using X-ray, neutron and electron diffraction methods, for a range of catalysts of prescribed composition and architectures. In this manner, key linkages between crystal chemistry, microstructure and catalytic activity are established, leading to innovative tailored synthesis and morphological designs.

While the conversion of the titania dimorphs – anatase to rutile – is often implied to be a direct process obeying first-order kinetics, the transition must in a strict crystallographic sense must be reconstructive, rather than displacive. Moreover, refined neutron diffraction data reveals that anatase can be grossly nonstoichiometric and contain up to 10% titanium (Ti) vacancies when calcined at < 600°C. In addition, sol-gel synthesized titania is shown to contain a persistent amorphous phase (aperiodic titania) that coexists with rutile to relatively high temperature (1000°C). While neutrons are highly penetrating, diffracted X-ray intensities will be attenuated due to microabsorption. Studying the degree of attenuation as a function of energy by multiple wavelength X-ray diffraction, allows the evolution of the titania microstructure from the gel to be monitored. It is found that anatase disassociates to aperiodic titania before rearranging as rutile, with this amorphous phase enveloping the crystalline material and modifying

functionality. The findings are supported by X-ray absorption spectroscopy (XAS) where Ti coordination and order correlation are consistent with the appearance of aperiodic materials prior to rutile crystallization. The complete chain of transformations can be summarized as:

amorphous gel → nonstoichiometric anatase → aperiodic titania → rutile

This enhanced understanding of the relationships between titania variants has been exploited to more completely describe several environmental catalysts. Cobalt-doped titania and silica-titania core-shell composites were fabricated with chemistries and forms targeted to enhance the optical and electronic properties of these photocatalysts. The incorporation of cobalt retards crystal growth, and promotes the development of aperiodic titania as an anatase-to-rutile interphase. In silica-titania core-shell architectures, the thermal stability and surface area are significantly enhanced as titania crystal growth is inhibited, which delays rutile formation from ~ 600°C to 1000°C. This optimized core-shell support is further modified for environmental catalysis by decoration with nanosized gold via a deposition-precipitation (DP) method. By homogeneously dispersing the gold nanocrystals (3 nm) over the support, a robust catalyst of superior activity is obtained that allowed 100% CO oxidation at temperature as low as 35°C.

This research has demonstrated that characterization-in-depth is an indispensable tool for optimizing catalyst performance and creating new materials designs. A more complete understanding of titania phase relationships and transformations can direct the tailoring of chemistries and architectures. Future developments, such as magnetic core catalysts that can be readily collected and recycled, or noble metal alloy catalysts with high selectivity, will benefit from the insights provided by this research.

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- ⁵ Lim, S. H., Phonthammachai, N. Zhong, Z. Han, Y. F. & White, T. J. (2008). Robust Gold-Decorated Silica-Titania Pebbles for Low Temperature CO Catalytic Oxidation. *Langmuir*, under review.

Chapter 1

Introduction

Titania photocatalysts are used to remove pollutants from contaminated water and air, but the role of crystallographic defects and amorphicity in determining efficiency and specificity are poorly defined. Combining diffraction, microscopy, and spectroscopy with new testing protocols, leads to superior quality control and guides the development of novel catalytic chemistries and architectures.

1.1. Problem Statement

In the last 40 years, numerous permutations of titania nanomaterials preparation and fabrication have been developed to enhance their physical and chemical performance in photocatalytic and photovoltaic applications [1]. Finely divided titania is commonly synthesized by sol-gel methods, at relatively low temperatures, followed by calcination to remove organic residues. Such routes involve the sequential formation of a sol (hydrolysis and condensation), a gel (polymerization), an amorphous dry gel (removal of solvents $\leq 100^\circ\text{C}$), and finally the growth of titanium oxides (crystallization). However, the processes that occur during this last calcination stage are far from simple, and the recovered titania may contain:

- (i) Surface and bulk defects

The nature of titania defects, especially in nanopowders, is not yet completely defined. Oxygen vacancies (δ), in nonstoichiometric $\text{TiO}_{2-\delta}$, are commonly accepted, while titanium (Ti) vacancies are less well understood. Generally, surface defects of rutile single crystals, especially $\{110\}$ facets, are investigated by spectroscopic methods to probe (i) the reduction of $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$ accompanied by the formation of surface oxygen vacancies, and (ii) the migration of Ti^{3+} to a depth of several microns [2-3]. However, bulk defects are less easily confirmed due to the volumetric limitations of spectroscopic techniques, that often restrict detection to a few nanometers of the titania surface. Conductivity and ion mobility measurements also provide useful insights, but interpretation can be difficult for powders where interphase grain boundaries are numerous. Diffraction methods offer distinct advantages, with powder neutron diffraction (PND) able to deliver compositional information through Rietveld refinement of both titanium and oxygen sites, while X-ray diffraction can yield unit cell constants to high accuracy and monitor changes in titanium occupancy.

(ii) Amorphous phases

The crystallization of the amorphous gel as titania is usually assumed to be direct, and beyond the anatase-to-rutile transformation temperature ($\sim 600^{\circ}\text{C}$) thought to leave negligible amorphous content, at least as detectable by powder X-ray diffraction (XRD). However, the matter has not been examined systematically. Furthermore, the determination of non-Bragg diffracting content by Rietveld quantitative analysis may be comprised by X-ray microabsorption [4], and baseline contents are better obtained by neutron scattering.

For photocatalytic applications, chemical and topographical modifications of titania provide a means of narrowing the direct band gap to improve catalytic efficiency under visible light. Chemical enhancements include cationic and anionic doping into titania structure, but verification of successful substitution based on changes in lattice parameters or diffracted intensity can be inconclusive and sometimes misleading. Therefore, in addition to diffraction studies, differentiation of interstitial or substitutional replacements requires X-ray absorption spectroscopy (XAS), which can sensitively probe the local structure, chemical state and order-disorder of a material.

Finally, different titania architectures based on composites and spheres have been proposed to improve (i) activity and mass transfer, and (ii) the recovery and reuse of catalysts. For example, titania-coated silica spheres may provide superior catalytic properties, but their fabrication usually requires expensive ingredients, such as polystyrene spheres, cationic polyelectrolytes and surfactants to obtain monodisperse and homogeneous products. Although functionality can be optimized, their wide application may ultimately prove uneconomic.

1.2. Objectives & Scope

The objectives of this research are to

- (i) establish a comprehensive
- (ii) understanding of the gross crystallochemical defects and phase assemblages of catalytic titania, and
- (iii) use these new insights to design and fabricate optimized products for environmental applications.

To this end, the scope of this PhD work includes:

- (I) Comprehensive characterization
 - (I-i) Electron microscopy: The morphology and nanostructure of titania catalysts were examined by transmission electron microscopy (TEM) using bright field imaging and selected area electron diffraction (SAED). These methods allow direct observation of coherent crystallite size and aperiodicity in titania.
 - (I-ii) Powder diffraction: X-ray, fixed wavelength neutron and multiple wavelength (synchrotron) diffraction were employed to obtain crystallochemical information (unit cell parameters and composition), conduct quantitative phase analysis, and examine microstructural evolution during calcination.
 - (I-iii) Spectroscopy: The surface chemical states of titanium (Ti) and cobalt (Co), as a dopant, were determined using X-ray photoelectron spectroscopy (XPS), while bulk analyses were conducted using X-ray absorption spectroscopy (XAS) for assessing atomic-pair distributions and ultraviolet-visible spectroscopy (UV-vis) to estimate band gap energy.

(I-iv) Gas adsorption isotherms: By measuring the adsorption-desorption of nitrogen and applying the Brunauer-Emmett-Teller (BET) approach the specific surface areas of the catalysts were extracted.

(II) Titania catalyst fabrication

(II-i) Standard titania: Pure nanotitania powders were synthesized by an acid catalyzed sol-gel process. The precursor, titanium tetrabutoxide (TBT), was hydrolyzed and condensed to yield a homogenous sol, that formed a gel at room temperature. After vacuum drying, the amorphous product was heat treated to 1000°C.

(II-ii) Cobalt-doped titania: The chemical doping of titania was carried out by modifying the sol-gel synthesis developed in part (II-i). Anhydrous cobalt (II) chloride (CoCl_2) was chosen as the Co^{2+} dopant source to ensure that the ratio of water:alkoxide was unchanged.

(II-iii) Silica-titania core-shell structure: A simple sol-gel synthetic route was designed to produce a core-shell composite from inexpensive reagents (ethanol, distilled water and TBT). Titania shells of the desired thickness were coated onto the amorphous silica spheres by repeated hydrolysis and condensation of TBT.

(II-iv) Gold decorated silica-titania pebbles: A deposition-precipitation (DP) method was developed for decorating silica-titania pebbles with gold nanocrystals (< 5 nm diameter) to product a robust composite for the catalytic oxidation of carbon monoxide (CO). Homogeneous metal dispersion that delivers high activity was achieved by adjusting pH, reaction times and heat treatment parameters.

(III) Developing protocols for quality control and testing

(III-i) Photocatalytic oxidation (PCO) of environmental organic pollutants (methylene blue and formic acid): The photocatalytic activity of the catalysts was examined by monitoring the photodegradation of pollutant simulants as a function of illumination time using UV-vis spectroscopy (methylene blue) and capillary electrophoresis (formic acid). Since the UV-vis spectrum/electropherogram signals are proportional to analyte concentration, it proved essential to remove suspended solids to obtain reliable data. In addition, standard operating procedures were developed to calibrate the analytical instruments and minimize systematic errors.

(III-ii) Detection and exploitation of X-ray microabsorption: Powder X-ray diffraction can be significantly affected by microabsorption when the material contains an inhomogeneous phase distribution and/or a range of crystal sizes. Since microabsorption correlates to X-ray energy, a multiple wavelength experiment was conducted using synchrotron radiation to probe the microstructural changes accompanying the crystallization and phase transformations of alkoxide derived titania. Neutron data provided a baseline for assessing the reliability of the phase proportions extracted from the X-ray diffraction patterns.

1.3. Dissertation Overview

This dissertation contains two parts, where the first focuses on fundamental studies that assess (I) *the nature of catalytic titania* (Chapters 2-4), and the second describes the development of (II) *catalyst chemistries and architectures* (Chapters 5-8). The Introduction (Chapter 1) provides a rationale for the research and establishes the goals and scope that are directed towards developing a deeper understanding of the crystallochemical and architectural issues impacting upon the deployment of titania as a catalyst.

Chapter 2 reviews the literature of titania polymorphs, nanomaterials synthesis and catalytic applications. In addition, characterization methodology is discussed with respect to the strengths and limitations of the techniques for specific analytical tasks. New protocols developed for photocatalytic oxidation (PCO) testing with methylene blue and formic acid are also described, particularly to ensure the reliability of UV-vis and electrophoresis data collection.

Chapter 3 explores the challenge of conducting crystal structure refinements of powder diffraction data from sol-gel synthesized nanotitania using Rietveld methods. From these studies, a protocol for recognizing X-ray microabsorption is presented, with nonstoichiometry (metal vacancies) and amorphicity determined using a combination of neutron and synchrotron diffraction data. Rather than considering X-ray mass attenuation as a problem to be avoided, it is developed as a method for monitoring microstructural evolution. This quantitative assessment, that yields accurate phase proportions and crystal sizes, supports recent kinetic models for the crystallization of nanotitania.

Chapter 4 examines the derivation of titanium local environments in nanotitania from X-ray absorption spectroscopy pre-edge features and extended structures of the K and L edges. The correlation between amorphicity and short range disorder of titanium is highlighted, revealing the transformation from anatase to rutile is indirect, proceeding through an aperiodic intermediate, which is structurally distinct from the primary gel.

Chapter 5 describes the influence of cobalt (Co) doping on the crystal chemistry, metal coordination, band gap energy and catalytic activity of nanotitania. The extended region of Co K-edge absorption was carefully analyzed to establish that $\text{Co}^{2+/3+}$ incorporation is substitutional, but quite limited, with CoTiO_3 appearing as a second phase. Moreover, the introduction of cobalt is possibly deleterious towards catalytic activity, even though the band gap appeared to undergo a bathochromic shift.

Chapter 6 provides a method for the fabrication of silica-titania core-shell structures via a simple sol-gel route without the need for polystyrene spheres, polyelectrolytes and surfactants. By optimizing the experimental parameters (titanium tetrabutoxide concentration, solvent ratio, and repetition of coating cycle), a product with an activity, durability and recyclability superior to the titania nanopowder was obtained. Maximal catalytic activity appeared to correlate with the greatest abundance of aperiodic material.

Chapter 7 presents the synthesis and testing of nanogold decorated silica-titania pebbles for catalytic oxidation of carbon monoxide (CO). A process for decorating the pebbles with gold using a deposition-precipitation method was developed. The size, shape and distribution of gold nanocrystals were adjusted by varying the reaction pH, aging time and calcination temperature. For the optimized material, 100% CO oxidation was attained at temperatures as low as 35°C.

Chapter 8 proposes future materials designs, that exploit the deeper understanding of titania phase and microstructural evolution developed in the thesis. These new architectures address specific technological issues concerning the recovery and reuse of the catalysts especially after wastewater treatment, and include magnetic cores, or decoration with noble metals/metal alloys.

The objectives of this research have been met by:

- (i) establishing clear insights into the formation of bulk defects and an aperiodic phase during the microstructural evolution of titania using neutron and synchrotron diffraction techniques; and
- (ii) demonstrating simple methods for fabricating silica-titania core-shell architectures and the decoration of these pebbles with gold to enhance the efficiency of these environmental catalysts.

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Part I:

The Nature of Catalytic Titania

Chapter 2

Semiconductor & Reducible Catalysts

Methylene Blue

The titania dimorphs – anatase and rutile – are the most important variants of this semiconducting oxide for environmental catalysis. Differentiating these chemically equivalent, but structurally distinct forms, is challenging, especially when crystal sizes are nanoscaled. To ensure the collection of reliable data the methodologies for characterization and validation must be integrated.

2.1 Literature Review

2.1.1 The Titania Polymorphs

Pure titania is an n-type semiconductor that naturally occurs in three forms – anatase, brookite and rutile (Table 2-1). Anatase and rutile are readily fabricated to desired sizes (from micro to nano scale) [1, 2], morphologies (spheres, rods, wire and tubes) [1, 3-4], and dimorphic mixtures [1-2, 5], however brookite is far more difficult to obtain as a single phase product. Large rutile crystals are the common thermodynamically stable phase [6]. All the titania polymorphs are composed of distorted TiO_6 octahedra (Figure 2-1). In rutile, the octahedra are connected by edges and corners to form [001] chains; two Ti-Ti pairs (2.959 Å, Table 2-1) are found in the second coordination shell. In anatase, each octahedron of the crystal structure has 4 edges and 4 corners shared, which also gives the highest Ti-Ti coordination (4) (Figure 2-1). Therefore, the distortion of anatase octahedra is more significant due to greater cation-cation repulsions that increase the Ti-Ti distance (3.039 Å, Table 1) [1, 6]. Consequently, the mass density, refractive index and band energy of anatase are distinct from rutile (Table 2-2). In brookite, zigzag chains form and Ti-Ti coordination is less crowded than anatase (2.944 and 2.974 Å, Table 2-1) [9] as the octahedra are linked to each other through 3 shared edges and 6 shared corners in an orthorhombic structure.

Anatase is metastable, and must be prepared at relatively low temperatures. Both brookite and anatase transform to rutile at higher temperatures ($\geq 400^\circ\text{C}$), with the transition accelerated or retarded depending on the method of synthesis, the atmosphere and presence of substrates [1, 10-13]. While the transformation is irreversible in the bulk, it has been established experimentally, and shown through thermodynamic simulations [14], that anatase is the stable phase for small crystals ($< 11\text{ nm}$) [1]. This observation is also consistent with calorimetric measurements [15]. While the band energy (E_{bg}) of anatase (3.20 eV) and rutile (3.02 eV) are well established, that of brookite is not well defined, although a direct E_{bg} of 3.4 eV [16] and indirect E_{bg} of 1.9 eV [17] have been reported.

Table 2-1 Crystallography and applications of the titania polymorphs.

Crystal System*	Space Group*	Bond distance (Å)*		Application
		Ti-O	Ti-Ti	
		(1 st shell)	(2 nd shell)	
anatase	tetragonal (ICSD-63711)	<i>I4₁/amd</i> a = 3.784 Å c = 9.514 Å	1.934 1.980	3.039 A photocatalyst widely used in wastewater treatment and photodegradation of organic and inorganic contaminants.
rutile	tetragonal (ICSD-63710)	<i>P4₂/mnm</i> a = 4.594 Å c = 2.959 Å	1.949 1.980	2.959 A brilliant white pigment used in paints, coatings, papers, inks, foods and cosmetic.
brookite	orthorhombic (ICSD-56155)	<i>Pbca</i> a = 9.184 Å b = 5.477 Å c = 5.145 Å	1.924 1.933 1.946 1.957 1.980 1.987	2.944 2.974 A rarely occurring form that is sometimes observed as a transient structure during the anatase to rutile transformation.

* Data extracted from the Inorganic Crystal Structure Database (ICSD) for anatase [6], rutile [6] and brookite [9].

Figure 2-1 Clinographic crystal structure projections of the titania polymorphs emphasizing the TiO_6 octahedra: (a) rutile, (b) anatase and (c) brookite.

Table 2-2 Material and electronic properties of anatase and rutile.

	Density (g cm^{-3})	Refractive Index ($\lambda_D = 589.3 \text{ nm}$)[8]	Band Gap Energy, E_{bg} (eV)
Anatase	3.84 [6]	$n_e = 2.49$, $n_o = 2.56$	3.20 [1]
Rutile	4.26 [6]	$n_e = 2.61$, $n_o = 2.90$	3.02 [1]
Brookite	4.17 [7]	$n_\alpha = 2.58$, $n_\beta = 2.58$, $n_\gamma = 2.70$	Not clearly defined

2.1.2 Catalytic Applications

Titania has been extensively explored for the remediation of polluted air and water [2, 5, 18-22], photocatalytic water splitting [23-27], photovoltaic [28-32] and sensing [33-35] applications, electrochromic devices [36-38] and hydrogen storage [39-41]. These versatile functionalities are controlled by tailoring morphology, microstructure and phase assemblage [3, 42-43]. When deployed as a heterogeneous catalyst, titania properties can be enhanced by (i) employing different synthetic routes, including sol-gel, hydrothermal and micelle methods [1]; (ii) introducing noble metals (Pd, Rh, Pt and Ag) as co-catalysts [44-46]; (iii) fabricating ceramic composites, e.g. $\text{SiO}_2\text{-TiO}_2$, $\text{Al}_2\text{O}_3\text{-TiO}_2$, $\text{WO}_2\text{-TiO}_2$ and

ZrO₂-TiO₂ [47-50] to enhance durability and recyclability; (iv) cationic substitutions (Co²⁺, Mn²⁺, Cu²⁺, Cr³⁺, Fe³⁺, and V⁵⁺, W⁶⁺) [1, 51-55] to create active sites and mobility and modify E_{bg} ; and (v) anionic doping (F⁻, N³⁻, C⁴⁻ or S²⁻) that enhances visible light absorption [1, 56-59]. In addition, titania is often used as a catalyst support due to its low cost, adjustable porosity and favourable surface behaviours, that allow strong connection to WO_x, NbO_x, trifluoromethanesulfonic acid (CF₃SO₃H), MoO_x, PMoV and Au amongst others [60-65].

2.1.2.1 General Mechanism of Titania Photocatalysis

Figure 2-2 Scheme of the photoexcitation processes occurring in a titania semiconductor under light illumination: (1) photogeneration of charge carriers (e^-/h^+ pair) by a photon with energy $\geq E_{bg}$; (2) surface recombination of e^-/h^+ with heat liberation; (3) oxidation of donor initiated by a VB hole (h_{vb}^+); (4) reduction of donor initiated by a CB electron (e_{cb}^-); (5) further photodecomposition process (involving one or more radicals or intermediate species, e.g. $\cdot OH$, O_2^- , H_2O_2 , or O_2) to yield mineralization products; (6) formation of Ti^{3+} due to e_{cb}^- trapping in a dangling surface bond; (7) h_{vb}^+ trapping at a surface titanol group [Adapted from 1, 43, 74].

The electronic band structure of titania is characterized by a filled valence band (VB) and an empty conduction band (CB) with a band gap energy, E_{bg} that is strongly dependant on morphology (size and shape) and microstructure (phase composition and disposition, chemical doping, and metal loading) [1, 43].

Photoreactions over titania (as in other semiconductors) are initiated by photon absorption, followed by the formation of electron-hole (e^-h^+) pairs, and finally photodegradation of adsorbed contaminants by the photogenerated radical(s) or active species (Figure 2-2).

Rutile particles are usually catalytically inferior to anatase as they are larger, yield lower specific surface areas, and offer fewer surface active sites. Although anatase shows a larger band gap (E_{bg}) (Table 2), which should limit photoexcitation, it is often reported as the superior photocatalytic phase in undoped [11, 19, 21-22, 66-68], doped [18, 20, 69] and mixed phases (anatase/rutile) [5, 42]. This has been attributed to greater hydrophilicity of the surface [69-72], or the extension of charge transfer lifetimes, especially when quantum size effects appear at sub-nanometre scales (≤ 2 nm) [73]. Subsequently, electron-hole (e^-h^+) recombination (process 2, Figure 2-2) can be delayed if the charge carriers are trapped in the wider E_{bg} resulting in a blue shift of the absorption spectrum [1-2, 28].

2.1.2.2 Environmental Catalysis

The environmental applications of titania catalysts focus on the detoxification of air and wastewater pollutants, which encompass (i) photocatalytic remediation of organic contaminants, for example chlorinated hydrocarbons (carbon tetrachloride, CCl_4 and chloroform, $CHCl_3$), carboxylic acids (glyoxylic acid, $HCOCO_2H$ & acetic acid, CH_3CO_2H), pesticides (isoproturon, $C_{12}H_{18}N_2O$ and pentachlorophenol, C_6Cl_5OH , PCP), dyes (methylene blue, $CH_{16}H_{18}N_3ClS$ and methyl orange, $CH_{14}H_{14}N_3NaO_3S$) and polymer (polyvinylpyrrolidone, PVP) [41, 74-75]; (ii) photochemical transformation of inorganic species, such as ammonia (NH_3), azide (N_3^-), nitrate (NO_3^-), nitrite (NO_2^-), sulphur, iron, chromium and manganese species [29]; (iii) catalytic oxidation of pollutants by Au/Pt/Pd/Ru-supported titanias, such as carbon monoxide (CO), propane (C_3H_8), formic acid (HCO_2H), acetic acid (CH_3CO_2H) and phenol (C_6H_5OH) [76-80]; (iv) reductive deposition of heavy metals, for instance Pt^{4+} , Pd^{2+} , Au^{3+} , Rh^{3+} , Cr^{4+} from aqueous solution to surfaces [43]; (v) photocatalytic sterilization of titania films toward bacteria, including *Escherichia coli*, *Bacillus cereus*, *Pseudomonas aeruginosa*,

Enterococcus faecalis, *Salmonella choleraesuis* subsp., *Listeria monocytogenes* [24, 81-82]; and (vi) anti-fogging and self-cleaning coatings of optical glass/mirrors, exterior windows, walls and windshields due to the superior photocatalytic oxidizing and superhydrophilic properties of titania (particularly anatase) [22, 83-84].

2.2 Characterization Methodology

The characterization of nanomaterials is not straightforward, as the probe volumes of different techniques (microscopic, spectroscopic, analytical and so on) are often distinct, leading to apparently contradictory results. For example, surface enrichment of a metal would be readily detected by X-ray photoelectron spectroscopy (XPS), but may be entirely overlooked by diffraction methods. Conversely, X-ray diffraction would readily detect a two-phase assemblage of isostructural and compositionally similar compounds, that could not be easily differentiated using XPS. Therefore, it is essential to examine nanomaterials by several techniques and correlate the results to obtain consistent descriptions. Nanosized titanias prove particularly challenging to characterize as they are polymorphic, frequently non-stoichiometric, and may contain amorphous and crystalline forms. Therefore, in this work, a complimentary suite of tools were selected to provide high assurance that the interpretation of data was unambiguous. Here, the strengths and limitations of each technique are reviewed, while later chapters provide specific information concerning their application for the analysis of different titanias.

2.2.1 Transmission Electron Microscopy (TEM)

TEM is a powerful and efficient tool for microstructural and electron diffraction characterization of materials. The resolution of a TEM extends down to atomic scales and is obtained by operating at high voltages (100-400kV). Hence, it is very useful for direct observation of crystal/particle size, shape, structure and lattice orientation in nanomaterials [85-86]. However, collecting images and diffraction patterns requires care as: (i) electron beam damage may accumulate,

especially when field emission guns (FEGs) are used; (ii) thin specimens, that may not be wholly representative of the sample, are essential; and (iii) misleading interpretations of 2D transmission images arising from 3D specimens can be problematic [85]. In this work, the materials were lightly ground, dispersed ultrasonically in water to minimize particle aggregation, and several drops of the suspension deposited onto holey-carbon coated copper grids before TEM examination. A high-contrast objective aperture (20 μm) was employed to optimize image quality, which corresponds to a nominal point resolution of 1.9 Å.

2.2.2 X-ray Techniques

2.2.2.1 Powder X-ray Diffraction (XRD)

XRD is an analytical tool used to determine phase assemblages and transitions, crystallinity, cell constants and crystallite size. By spiking with an internal standard (NIST X-ray references), these parameters can be extracted quantitatively, and additional crystallochemical information, such as thermal displacement parameters and metal vacancies obtained somewhat less routinely using Rietveld analysis. Sample preparation is, in principle, a simple process of manual or mechanical grinding before packing into a circular or rectangular-shaped holder. However, to obtain reliable diffracted intensities, particle sizes must be homogeneous and $< 0.1 \mu\text{m}$ or absorption within particles will be significant. These fundamental requirements are often overlooked in materials science experiments that do not have diffraction as a core component.

2.2.2.2 X-ray Synchrotron Powder Diffraction

Although microabsorption can be avoided by powder neutron diffraction (see Section 2.2.3), not all the materials of interest can be measured with this technique, as accessibility to neutron sources is quite limited. As another option, multiple wavelength synchrotron experiments were conducted to systematically study microabsorption effects as a function of X-ray energy. The dependence of diffraction intensity on mass absorption for titania particles of various diameters

can be studied to understand the nature of the microstructural changes that accompany the phase transformation of anatase to rutile. While the resolution of the diffraction patterns collected with monochromatic radiation is excellent [86], for nanotitania the diffraction line width is controlled by the crystal size. Microabsorption correlates with X-ray energy through the mass absorption coefficient, and can profoundly affect the determination of amorphous content during quantitative analysis.

2.2.2.3 X-ray Absorption Spectroscopy (XAS)

The electronic properties of titania are directly linked to the local structure of titanium (Ti). When titania is chemically doped or topographically modified, the surroundings of Ti will be subtly altered in ways that are most readily probed by XAS. The Ti pre-edge and near-edge absorption regions (XANES) (5-150 eV), which correspond to the transition of $1s \rightarrow 3d$ and $1s \rightarrow 4p$, provides information of concerning oxidation state, coordination and geometric distortions. Furthermore, structural information (coordination number, bond distances and disorder) can be accurately extracted from the analysis of the extended region (EXAFS) which usually ranges from 500-1000 eV in Ti K-edge absorption spectra [86]. XAS is especially useful for monitoring the quantity of aperiodic structures, and consequently, is a primary tool for examining the reconstructive phase transformation from anatase to rutile as described in Chapter 4. The sensitivity of XAS to low metal dopant concentrations, also proved indispensable for determining the oxidation state cobalt in titania.

2.2.2.4 X-ray Photoelectron Spectroscopy (XPS)

The chemical states of surface cobalt and titanium were evaluated by X-ray photoelectron spectroscopy (XPS), which is a quantitative spectroscopic technique with a lower limit of detection of a few atomic percent. Since the surface and bulk chemistries of titania can be different (especially for anatase) the combined analysis of XAS and XPS ensures that data interpretation is unambiguous. To obtain reliable spectra, specimens should be completely dry and stored in a clean environment prior to the measurement to avoid surface contamination. Each

element is directly identified by its characteristic XPS peaks, which correspond to the electron configuration within atoms (e.g. 1s, 2s, 2p, 3s, 3d, etc), at specific values. These binding energies are sensitive to charging, and therefore are calibrated against adventitious carbon (1s) before collecting (i) survey scans (0-1000 keV) and (ii) multiplex scans of specific transitions.

2.2.3 Powder Neutron Diffraction (PND)

In fixed wavelength neutron diffraction, elastic scattering arises from the direct interaction of the neutron beam (generated by a nuclear reactor) with the nucleus of an atom. Since neutrons weakly interact with materials, and are highly penetrating, the microabsorption effect, which can powerfully attenuate X-rays, is negligible. Therefore, PND provided baseline data concerning nonstoichiometry and the determination of amorphicity in titania. A disadvantage of PND, is that large amounts of sample (> 1g) are required to increase the scattering intensity, and minimize measuring times.

2.2.4 Ultraviolet-Visible Spectroscopy (UV-vis)

UV-vis spectroscopy is used to investigate electronic transitions over the energy range 200 to 800 nm. For nanotitania and cobaltiferous titania, E_{bg} were estimated directly from the absorption spectra, by extrapolating to the visible region, such that

$$E_{bg}(eV) = \frac{h \cdot c}{\lambda}$$

(Equation 2.1)

where E = band gap energy (eV), h = Planck's constant (6.626×10^{-34} J s), c = light speed (3×10^{17} nm s⁻¹), and λ = wavelength (nm) [87].

2.2.5 Thermal Analysis and Infrared Spectroscopy

Thermo gravimetric analysis – differential gravimetric analysis (TGA–DGA) can be used to establish decomposition and crystallization temperatures, thermal stability, and phase transformations of the dry titania gels. The titanias studied here were heated to 1000°C (5°C per min) with nitrogen used as both the balance and sample gas at a flow rate of 50ml per min. Separately, Fourier transform infrared spectrometry (FTIR) was used to detect organic residues in the samples calcined from 200°C up to 800°C after being well-ground with potassium bromide (KBr, IR grade, Merck) and pressed into pellets (10 mm diameter) [88].

2.2.6 Specific Surface Area Measurement

The specific surface area of the catalysts was determined using the BET physisorption method. Prior to collection of the final isotherm, a clean surface was prepared by degassing the powders overnight at 250°C under vacuum. For those materials calcined at 200°C, the degassing temperature was reduced to 150°C to avoid alteration. In this measurement, nitrogen is used as the adsorbed gas molecule due to its well studied molecular size and inertness. The adsorption/desorption isotherm plots were collected at liquid nitrogen temperature (-196°C) [89].

2.3. Protocols for Photocatalytic Testing

Generally, the photocatalytic activity of a catalyst is determined from the rate constant for the degradation of an organic pollutant under UV or visible light. In one protocol developed for these studies (see Section 2.3.1), the photodecomposition of methylene blue (MB) was monitored as a function of illumination time using UV-Vis spectrometry after removal of suspended catalyst particles that scatter light and modify the spectral background (Figure 2-3). Therefore, pre-treatment with NaCl (aq) was employed to settle catalyst particles in the analyte solution.

Figure 2-3 UV-Vis spectra of photodegradation of methylene blue (a) before and (b) after the pre-treatment of 1M NaCl (aq.) to remove of P25 catalysts in a preliminary test.

In the capillary electrophoresis (CE) protocol described in Section 2.3.2, the decomposition of formic acid (FA) is followed by the decrease of formate (HCOO^-) peak area as a function of irradiation time. In these experiments, HCl (aq) was added to maintain the suspension pH at 3 while the Cl^- ion is used to internally calibrate the peak area of formate in the electrophoregram.

2.3.1 Photocatalytic Oxidation (PCO) of Methylene Blue

The PCO apparatus shown in Figure 2-4a allowed separation of the bottom portion for cleaning, while a water jacket maintained isothermal conditions (20°C) during the experiment. Either UV or visible lamps could be inserted into the centre of the reaction vessel. The radiance of the UV-light measured at 254 nm was $14\text{--}15 \text{ mW/cm}^2$. The intensity of the cold white light lamp measured between 450 nm and 550 nm was $8000\text{--}8500 \text{ lumen/m}^2$. The volume of the reaction vessel was relatively large (1 L) to ensure that the ratio of catalyst to solution did not change significantly during sampling (5 ml aliquots).

Figure 2-4 (a) Schematic of photocatalytic reactor; (b) flow sheet for PCO of methylene blue protocol.

Catalyst powders suspended in methylene blue (MB) were pumped through the reactor at the rate of 300 mL/min while entirely enclosed in a light-tight cabinet to forestall catalytic or photochemical decomposition. During reaction, the solution was aerated at a rate of 1.2 L/min. Degradation of the MB dye as a function of reaction time was monitored using UV-visible spectroscopy. As reconnaissance experiments showed that signals could be substantially attenuated due to scattering by colloidal particles, a standard procedure was developed to obtain reproducible data.

In the MB protocol, 0.1 g/L of photocatalyst powder was ultrasonically mixed with distilled water for 30 mins then stored in the dark for ~12 hrs to equilibrate (Figure 2-4b). MB solution (0.89 mL of 5000 ppm) was added immediately before PCO testing and the suspension treated ultrasonically for 30 minutes before being poured into the reactor. During mineralization with UV light, aliquots were collected every 5 mins for the first 30 mins, and thereafter each 15 mins for a total of 1 hr. For visible light experiments, the sampling time was extended to 6 hours. Before UV-visible spectroscopy, suspended solids were removed by introducing 1 M NaCl to the analyte in a 1:30 ratio. This mixture was well shaken and centrifuged and the clear solution stored in a light-tight cabinet prior to spectroscopy. Degradation of MB was monitored by tracking the intensity of absorption bands at ~ 664 nm using a Shimadzu UV 2501PC UV recording spectrometer (Figure 2-3).

2.3.2 PCO of Formic Acid

Formic acid (FA) decomposition was conducted in a light-tight 100 ml jacketed glass reactor, fitted with a transparent quartz window, sealed by a Teflon cap that held an oxygen gas bubbling tube, a dissolved oxygen probe, and a pH electrode with temperature sensor (Figure 2-5a). Either a high-pressure mercury short arc UV-light lamp (OSRAM), or a xenon short arc visible-light lamp (USHIO) was centrally aligned with the quartz window (3 cm diameter) and the temperature of the stirred suspension maintained at 20°C. The radiance of the UV-light measured from 320 and 400 nm at the quartz window entrance was 543.5 mW/cm². The

radiation from the xenon lamp was attenuated by an infrared filter to prevent excessive heating, and a 400nm UV filter (Chroma Technology) yielded a flux of 51.6 lumen/cm² between 380 and 760 nm at the quartz window entrance. In this protocol, stock suspensions containing 25 g/L photocatalyst were prepared and buffered at pH 3 to ensure that the $\text{HCOOH} \leftrightarrow \text{H}^+ + \text{HCOO}^-$ equilibrium was driven strongly towards the left. The reactor was loaded with 0.1 mL HCOONa (1 mM), 100 ml of HCl (2 mM) and 0.4 ml of photocatalyst stock that was well stirred for at least 30 minutes then purged with oxygen before irradiation. Aliquots (2 mL) were collected at 5 min intervals for the first 30 mins and 10 min intervals to 1 hr during UV and visible light experiments.

FA decomposition was monitored as a function of photocatalytic reaction time using capillary electrophoresis (CE) (Hewlett-Packard; model G1600AX-3D). By recording the rate of electro-osmotic flow of ionic species in buffer-filled (pH 5.5 for organic acids), narrow-bore capillaries (72 cm long by 75µm inner-diameter), concentration-dependent electropherograms were generated that connect migration time with UV-visible absorption. In this study, the concentration of formate (HCOO^-) was used as a proxy for FA with a ppm lower limit of detection. Errors in the measurement of the peak areas for 1 mM Cl^- were correlated with those of calibrated formic acid concentrations established by >10 replicates at each concentration. In this way, the observed formic acid peak areas were adjusted according to the simultaneously observed chloride peak areas to minimize systematic errors. The combined errors of the photocatalytic experiment and CE measurement are <5% over the calibrated concentration range of formic acid (1000 - 30 µM). To avoid cross-contamination, the capillary was flushed consecutively with 0.1 M HCl, milli-Q water, and organic acid buffer for 45 mins (Figure 2-5b) between sample injections.

Figure 2-5 (a) Schematic of photocatalytic reactor; (b) flow sheet for PCO of formic acid protocol.

2.4 Integrated Synthesis, Characterization and Testing

In this work, sol-gel techniques were employed to synthesize bulk nanotitania, cobalt-doped titania and silica-titania core-shell architectures. The influence of the alkoxide/water ratio and gelation duration on the phase assemblages and crystal sizes of nanotitania has been reported earlier [90]. This research systematically varied a range of synthesis parameters to adjust the crystal chemistry and morphology of titania including: (i) comparison of alkoxide (titanium tetrabutoxide, titanium ethoxide or isopropoxide), and (ii) modification of heat treatment temperature/time to investigate the kinetics of phase transitions. Since sol-gel syntheses were unusually sensitive processes, the experimental parameters are varied singly to determine their influence on the end product. During gold decoration (Chapter 7), the deposition-precipitation aging temperature was adjusted to alter the dispersion and morphology of gold nanocrystals. In this case, both pH and aging time required optimization to achieve a high dispersion of gold on the silica-titania support.

In addition, nuclear magnetic resonance (NMR) and density functional theory (DFT) are particularly valuable for studying reaction kinetics and nonstoichiometry. Combined ^{18}O and $^{47,49}\text{Ti}$ solid state NMR can probe titanium (Ti) coordination, microstructural evolution and phase distribution as the titania gel crystallizes [91-94]. Recently, Grey & Wilson [95] combined the XRD analysis of sol-gel synthesized anatase with DFT calculations to show that up to 20% Ti vacancies were present. DFT simulations are also consistent with the vacant sites being charge balanced through the introduction of protons (H), $n\text{Ti}^{4+} \leftrightarrow 4n\text{H}^+$. While NMR, DFT and other methods were not used in this research, care were taken to ensure that the interpretation of published data was consistent with diffraction and imaging results obtained here to establish a complete, and where possible, unambiguous linkages between materials processing, characterization and functionality.

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Chapter 3

Crystal Structure Refinement & Quantitative Phase Analysis

Titania evolution during calcination involves dehydroxylation of the gel precursor, crystallisation of nonstoichiometric anatase, deconstruction of anatase, and growth of rutile. Powder neutron diffraction can be used to extract phase contents and compositions, while multiple wavelength X-ray diffraction shows systematic changes in Bragg intensities that correlate with alterations in microstructure.

3.1 Nonstoichiometry & Amorphicity of Titania

It is commonly stated that photocatalytic titanias for the mineralization of pollutants are adequately represented as stoichiometric TiO_2 (generally anatase or rutile), or nearly so, and that the excitons which reduce (e^-) or oxidize (h^+) absorbed molecules arise solely in the ordered dimorphs. Yet it has long been recognized that multiphase assemblages containing anatase, rutile and amorphous material offer superior quantum yields [1]. Investigations of non-crystalline titania are not extensive, and largely restricted to analysis of anatase crystallization from *chimie douce* precursors [2-4], with the intervening aperiodic titania which appears during the high temperature transformation to rutile not considered explicitly. Quantitative phase analyses using spectroscopic and diffraction methods invariably arrive at dissimilar dimorph contents, that are ascribed to differences in volumetric sampling of the techniques, but in general, appear consistent with the formation of anatase-rutile core-shell morphologies or the appearance of structurally modified surface regions [1, 5, 6].

The anatase-to-rutile transformation is irreversible in the bulk [7]. During this phase change single crystals retain their faceting [8] and topotaxial interfaces are occasionally observed directly by high resolution electron microscopy [1, 9], leading to the conclusion that the structural rearrangements proceed via the near cubic close-packed $\{112\}_{\text{anatase}}$ and hexagonal close-packed $\{100\}_{\text{rutile}}$ oxygen planes [8, 10] (Figure 3-1). Formally, the conversion of anatase ($I4_1/amd$) to rutile ($P4_2/mnm$) must obey first order kinetics as these structures are not symmetrically hierarchical [11], but the observed rates of nucleation and growth cannot be readily explained in this manner [12-15], with discrepancies normally attributed to differences in precursor chemistry or oxygen fugacity. Zhang and Banfield [14, 15] suggest that for pure titania treated at low temperatures (e.g. 450°C) interface nucleation dominates, with surface nucleation more significant at intermediate temperatures (e.g. 650°C), and bulk nucleation governing growth at the highest temperatures (e.g. 1150°C). Madras et al. [11] advocate a formally derived kinetic model for the transformation where the population of anatase particles combined with surface nucleation accounted for time-dependant crystal growth. This

approach was also consistent with the preservation of anatase to higher temperatures when diluted with Al_2O_3 [14] or La_2O_3 [5] particles that separated the crystalline interfaces.

Figure 3-1 (a) Rutile and (b) anatase represented as ideal TiO_6 octahedra and emphasizing the relationship between the close-packed planes that allow topotaxial interfaces, but which play an indirect role during phase interconversion as the transformation is mediated by an aperiodic intermediate compound. (Compare with real structures in Figure 2-1).

While the TiO_6 octahedra are common to the dimorphs, interconversion is reconstructive because the Ti-Ti coordination is reduced from 4 to 2 in passing from anatase to rutile, in a mechanism classified as intermediate topotaxy [8]. In classical studies, powder X-ray diffraction (XRD) is often the primary tool for establishing the onset and termination of the phase change, with the integrated intensities of anatase (101) and rutile (110) reflections used to determine the extent of the transformation (α) such that $\alpha = 1/(1 + 0.884(I_{\text{anatase}}/I_{\text{rutile}}))$ where the correction factor (0.884) was derived from mixtures of finely divided polymorphs [16]. Although the dimorphs are readily distinguished by XRD from levels as low as 1 wt%, depending on crystal size, the value of α will be significantly affected by X-ray microabsorption in sol gel derived titanias [17] and the modulation of diffracted intensity (especially (101) anatase) arising from Ti nonstoichiometry (18). Nor is there a direct correlation of α with photocatalytic activity, as co-crystallized titania phase assemblages prove superior to mechanically-mixed anatase and rutile. Recent experimental and computational studies have revealed gross titanium nonstoichiometry in chemically-derived anatase crystals, especially at low temperatures ($< 400^\circ\text{C}$), with up to 20% metal vacancies accommodated as $[\text{Ti}_{1-x}\square_x][\text{O}_{2-4x}\text{X}_{4x}]$ where $\text{X} = \text{OH}, \text{Cl}$ [17-21]. It has been thought that the amorphous content of nanotitania sintered near the transition temperature is negligible, with precursor gels or powders rendered substantially crystalline. This assumption was considered reliable because in powder XRD the broad X-ray scattering feature, characteristic of amorphicity, was generally absent after low temperature treatments. However, quantitative XRD and X-ray absorption spectroscopy (XAS) found that aperiodic titania (several tens of percent) coexists with the dimorphs, even after the complete removal of anatase [Chapter 4-5, 18, 22], as recognized in early electron microscope studies [1]. It is now apparent that a significant non-Bragg diffracting portion is retained without the telltale amorphous hump, and that a new aperiodic phase, distinct from the amorphous precursor, appears in the crystallization sequence:

with the temperatures of the phase transformations dependant on chemistry and form. Moreover, the photocatalytic degradation of methylene blue may correlate with the maximum amorphous content [22]. This might be due to the relatively high surface areas afforded by the intervening aperiodic material, or the modification of the space-charge potential at the disordered interfaces and the creation of localized electronic states.

While the progression from gel to rutile is certain, the absolute quantity of aperiodic titania determined by Rietveld analysis of powder X-ray diffraction data ($\text{Cu K}\alpha$) remained doubtful as attenuation of Bragg diffraction by microabsorption proved difficult to eliminate, leading to an overestimation of amorphous content [22]. In this chapter, we extract the non-Bragg diffracting content in sol-gel derived titania powders as a function of calcination temperature using neutron diffraction, where absorption is expected to be negligible, and multiple-wavelength X-ray diffraction, to monitor the energy dependence of microabsorption and evaluate the evolution of microstructure. Finally, kinetic models describing the phase transformation are considered with respect to these accurate measurements of dimorph proportions and crystal size.

3.2 Preparation of Nanotitania Powder

Nanosized titania powder was synthesized using an acid catalyzed sol-gel method (Figure 3-2). Titanium tetrabutoxide (TBT, Aldrich, 97%) was diluted with a half portion by volume of absolute ethanol (EtOH , Merck, > 99.9%). A mixture containing EtOH , hydrochloric acid (HCl , Merck, 37 %) and deionized water was introduced dropwise to the diluted TBT with the molar ratio of TBT: EtOH : HCl : deionized water fixed at 1: 15: 1: 0.3. The sol was stirred at room temperature for 30 mins, followed by gelation for 5 days. The wet gel was vacuum dried at 60°C and then heat-treated in air ($200 - 1000^\circ\text{C}$) for 2 hrs.

Figure 3-2 Flow chart of nanotitania sol-gel synthesis.

3.3 Materials Characterization

3.3.1 Quantitative Phase Analysis

The absolute phase proportions and cell metrics were calibrated against 20 wt% of $\alpha\text{-Al}_2\text{O}_3$ [24] as an internal standard that was introduced with manual grinding (20 mins) using an agate mortar and pestle to improve homogeneity, but not perturb the microstructure. The diffraction patterns were analyzed using the Rietveld method as implemented in Topas V3.0 to ascertain the weight percents (wt%) of anatase, rutile and amorphous titania [17] after including a correction of 8.25 wt% amorphous intrinsic to the $\alpha\text{-Al}_2\text{O}_3$ [24].

3.3.2 Fixed Wavelength Neutron Powder Diffraction

Neutron diffraction data was acquired at the Institute Laue-Langevin (ILL) Grenoble (France) using the high resolution D1A diffractometer with a wavelength of 1.91 Å, a 2-theta range of 0°–157.9° and scan steps of 0.1° at room temperature. The diffractometer is equipped with a focusing Ge monochromator at a take-off angle of 123° and 25 standard ^3He counter detectors. A cylindrical sample container (0.9 cm diameter) was used during the measurement. All neutron data was analyzed using Topas V3.0 with the refinement parameters of zero shift, cell parameters, fractional occupancies and thermal factors. The atomic coordinates and thermal parameters of anatase [25], rutile [25] and corundum [26] were fixed at the reported values. The peak profile was fitted with a pseudo Voigt function where the parameters U, V, W (0.12, -0.21, 0.17) were fixed to values supplied by ILL to model size broadening of the diffraction peaks (Figure 3-3a).

3.3.3 Multiple Wavelength Powder Diffraction

Synchrotron diffraction experiments were conducted at the Singapore Synchrotron Light Source (SSLS) with the Helios 2 storage ring running at 700 MeV and using a 4.5 T bending field to deliver a typical stored electron beam current of 200 mA. Data were collected on the X-ray Demonstration and Development (XDD) beamline fitted with a Huber 4-circle system 90000-0216/0 diffractometer with high-precision step size (0.0001°) for the 2-theta circle. The distance from entrance slit to sample centre was 688 mm and that from sample centre to detector slit 680 mm [27]. Powder diffraction patterns were collected at energies near the $K\alpha_1$ emission lines of Cr, Mn, Fe, Co, Ni, Cu and Zn (5.368-8.641 keV) selected by a Si (111) channel-cut monochromator (CCM), with a typical step size of 0.02° and counting time of 1 sec/step. Lower energies were not selected to avoid anomalous absorption near the titanium edge and to increase count rates. The X-ray beam was confined to 1.00 mm width vertically and 3.50 mm horizontally by the collimating mirror and slit system. The detector slit was 1 mm vertical and essentially infinite in the horizontal direction. This set-up typically yields an X-ray beam with $\sim 0.006^\circ$ divergence ($\Delta E/E \approx 5.3 \times 10^{-4}$ at 8.048 keV). Data were

analysed using Topas V3.0 and included refinement of source wavelength, zero shift, cell parameters and thermal factors. The patterns were fitted using a modified pseudo Voigt Thompson-Cox-Hasting profile with parameters established with respect to α - Al_2O_3 collected at 8.641 keV (Figure 3-3b).

Figure 3-3 Rietveld plots for sol gel derived titania fired at 600°C for 2 hours and spiked with 20 wt% alumina as an internal standard. (a) Neutron data collected at $\lambda = 1.911 \text{ \AA}$. (b) Synchrotron X-ray data collected at $\lambda = 1.435 \text{ \AA}$.

3.4 Protocol for Detection of Microabsorption

3.4.1 Nonstoichiometry and Crystal Growth

The refined neutron and X-ray diffraction data show the anatase c-axis dilates with increasing calcination temperature (Figure 3-4a, Table 3-1) in tandem with the filling of the titanium sites, such that occupancy rises from 0.90 at 300°C to almost unity at 600°C at the onset of the transformation to rutile. These observations are consistent with earlier reports [18, 28] where elimination of hydroxyl and the filling of titanium vacancies (V_{Ti}) ($V_{Ti} + 4OH^- \rightarrow Ti^{4+} + 4O^{2-}$) leads to greater Ti-Ti repulsion between the [001] edge-sharing TiO_6 octahedra. In contrast to anatase, rutile is stoichiometric within the limits of the diffraction data, however the a- and c-axes contract and dilate slightly with increasing heat treatment temperature (Figure 3-4b), suggestive of the concomitant creation of titanium vacancies [29]. The crystal sizes determined by analysis of the peak widths confirm that anatase ($\sim 7 - 64$ nm) and rutile ($\sim 122 - 351$ nm) grow larger at higher temperatures (Figure 3-4c), with the values obtained from X-ray data considered more reliable due to the availability of standard data to fix the peak shape parameters.

3.4.2 Amorphicity and X-ray Microabsorption

In a homogeneous, mixed-phase assemblage the Rietveld scale factors will be independent of incident X-ray energy providing the crystals are sufficiently small to allow equal penetration of all components (crystalline and non-crystalline). According to Brindley [30], microabsorption is negligible if the product of the linear absorption co-efficient (μ) and the diameter of a single-phase particle (D) is less <0.01 (Table 3-2). In a two-phase assemblage this analysis will breakdown if one phase encapsulates, and effectively shields, the other from the X-ray flux. In this circumstance, the diffracted intensity will not truly indicate the relative phase proportions (Figure 3-5a), leading to an energy dependence of the scale factors. Moreover, it is essential to differentiate the crystal size (derived from analysis of the Bragg diffraction peak width) from the diffracting particle size (collections of

crystals), as the latter can compromise quantitative phase analysis even if the individual coherent scattering volumes satisfy $\mu D < 0.01$ (Figure 3-5b).

Figure 3-4 Temperature dependence of titania lattice metrics. (a) Nonstoichiometric $[\text{Ti}_{1-x}\square_x][\text{O}_{2-4x}\text{OH}_{4x}]$ anatase with $0.90 \leq x \leq 0.98$ approaches the ideal composition (TiO_2) as removal of water leads to greater electrostatic Ti-Ti repulsions and the dilation of the c-axis. (b) Rutile is stoichiometric, within the limits of the Rietveld method, and the unit cell shows minor contraction at higher temperature possibly as a result of greater crystal perfection or the creation of Ti vacancies. (c) Anatase crystals grow in tandem with unit cell volume expansion as the calcination temperature increases.

Table 3-1 Crystallochemical parameters for anatase and rutile.**Neutron Data ($\lambda = 1.911 \text{ \AA}$)**

Calcination n ($^{\circ}\text{C}$)	Anatase				Rutile		
	a ($\text{\AA}$)	c ($\text{\AA}$)	Ti Occupancy	Crystallite Size (nm)	a ($\text{\AA}$)	c ($\text{\AA}$)	Crystallite Size (nm)
300	3.7892(2)	9.4870(9)	0.90	13	-	-	-
400	3.7865(1)	9.5011(4)	0.92	20	-	-	-
600	3.7844(1)	9.5139(2)	0.98	64	4.5944(1)	2.9585(1)	153
1000	-	-	-	-	4.5922(1)	2.9601(1)	351

X-ray Data ($\lambda = 1.4306 \text{ \AA}$)

Calcination ($^{\circ}\text{C}$)	Anatase				Rutile		
	a ($\text{\AA}$)	c ($\text{\AA}$)	Ti Occupancy*	Crystallite Size (nm)	a ($\text{\AA}$)	c ($\text{\AA}$)	Crystallite Size (nm)
300	3.7857(5)	9.5003(2)	0.90	7	-	-	-
400	3.7850(4)	9.5052(2)	0.92	10	-	-	-
500	3.7858(6)	9.5088(6)	"0.95	19	-	-	-
600	3.7844(1)	9.5144(5)	0.98	40	4.5941(2)	2.9587(3)	122
800	-	-	-	-	4.5927(1)	2.9596(1)	330
1000	-	-	-	-	4.5920(1)	2.9598(1)	large

* Neutron values used

" Average between neutron 400 and 600 $^{\circ}\text{C}$

Figure 3-5 (a) Variation in diffracted intensity as a function of X-ray energy ($E_1 > E_2 > E_3$) and penetration ($P_1 > P_2 > P_3$) into a particle of diameter (D) with a core phase region (B) shielded by a shell phase region (A). (b) Influence of crystal size on relative diffracted intensity (I/I_0) in a core-shell particle. For quantitative phase analysis to be valid the diffracting particle must be sampled volumetrically by the incident X-rays, and in multiple wavelength experiments, variation in I/I_0 with incident energy can be used to infer microstructural phase distributions.

Table 3-2 Linear absorption co-efficients for anatase (an), rutile (ru) and amorphous (am) titania as a function of X-ray energy. Following Brindley [30] it is expected that polycrystalline diffracting particles experience excessive microabsorption that will invalidate quantitative phase analysis when $\mu D > 0.01$. The combination of X-ray energy and particle diameter where reliable Rietveld scale factors can be extracted, provided the phases are distributed homogeneously, is shaded.

Energy (keV)	Mass absorption co-efficient (cm ² .g ⁻¹)*		Linear absorption co- efficient (cm ²)**			D (nm)			
						400	200	100	50
	Ti	O	μ_{an}	μ_{ru}	μ_{am}	$\mu_{an}D$ (for anatase)			
5	683.8	47.9	1707.9	1823.77	1587.75	0.068	0.034	0.017	0.009
6	432.3	27.7	1076.43	1149.46	1000.7	0.043	0.022	0.011	0.005
7	317.3	19.67	789.02	842.55	733.51	0.032	0.016	0.008	0.004
8	202.3	11.63	501.23	535.23	465.97	0.020	0.010	0.005	0.003
9	156.5	8.79	359.73	384.13	334.42	0.014	0.007	0.004	0.002
10	110.7	5.95	273.62	292.18	254.37	0.011	0.005	0.003	0.001

* <http://physics.nist.gov/PhysRefData/XrayMassCoef/tab3.html>

** Titania densities used: anatase (an) 3.98 g.cm³; rutile (ru) 4.25 g.cm³; amorphous (am) 3.70 g.cm³

For each phase, absorption contrast is expressed as

$$I/I_0 = e^{-\mu t} \quad (\text{Equation 3-1})$$

where t is the crystal thickness [30], and in this treatment, considered distinct from D in multicrystal diffracting particles. Assuming each particle is composed of a single phase then a map of calculated I/I_0 versus energy can be constructed (Figure 3-6) using the parameters given in Table 3-2. By superimposing experimental values of I/I_0 , obtained from the Rietveld derived crystal sizes (Table 3-1) and relative phase proportions (Table 3-3), discrepancies with the calculated map are evident, as practically, the diffracting volumes are never single phase or homogeneous (Table 3-4). For the material calcined at 300°C, microabsorption is negligible and attenuation is constant across the X-ray energy range (6.40 – 8.64 keV). However, as crystal growth and particle accretion continues with increasing temperature, attenuation becomes more evident with I/I_0 falling away more obviously at lower incident energies. Indeed, for the largest rutile crystals μD will

be so large that the diffracted intensity, and hence the Rietveld scale factors must be unreliable in an absolute sense as the X-rays are not sampling these materials volumetrically.

Figure 3-6 A map showing the dependence of diffraction intensity (I/I_0) on mass absorption for titania particles with thicknesses (t) ranging from (10 - 400nm) derived from the $e^{-\mu t}$. The map is overlaid by I/I_0 derived from the relative Rietveld proportions, normalized against the wt% for the highest energy (8.64 keV) (Table 3-4), then placed on an absolute scale by assuming the crystal size derived from peak broadening corresponds to the particle size. At the lowest calcination temperature the titania powders show no energy difference of the phase content and microabsorption is negligible. Mass attenuation is more evident at higher calcination temperatures but I/I_0 generally shows less energy dependence than expected. This is consistent with the diffracting particles containing aperiodic material of lower density than anatase or rutile.

Table 3-3 Quantitative phase analysis, inclusive of the non-diffracting component that was derived from the refined weight percent of a standard alumina spike (20 wt%).

Calcination (°C)	λ (Å)	Non-diffracting (wt%)	Anatase (wt%)	Rutile (wt%)
300	neutron	10.0 ₆	89.9 ₄	0
	1.436	7.2 ₁	92.7 ₉	0
	1.541	6.8 ₀	93.2 ₀	0
	1.659	11.0 ₅	88.9 ₅	0
	1.789	12.3 ₄	87.6 ₆	0
	1.948	13.8 ₇	86.1 ₃	0
	neutron	7.7 ₃	92.2 ₇	0
400	1.436	8.3 ₁	91.6 ₉	0
	1.542	5.7 ₉	94.2 ₁	0
	1.659	12.5 ₀	87.5 ₀	0
	1.789	14.0 ₇	85.9 ₃	0
	1.938	19.1 ₅	80.8 ₅	0
	2.102	21.0 ₄	78.9 ₆	0
	2.290	22.3 ₈	77.6 ₂	0
500	1.436	15.0 ₅	84.9 ₅	0
	1.542	18.1 ₀	81.9 ₀	0
	1.659	22.7 ₇	77.2 ₃	0
	1.790	23.0 ₄	76.9 ₆	0
	1.938	24.1 ₁	75.8 ₉	0
	2.102	24.4 ₉	75.5 ₁	0
	2.291	33.7 ₆	66.2 ₄	0
600	neutron	8.8 ₂	72.5 ₄	18.6 ₄
	1.435	30.6 ₇	55.7 ₅	13.5 ₈
	1.540	32.2 ₈	54.9 ₀	12.8 ₂
	1.658	35.2 ₉	52.4 ₅	12.2 ₆
	1.790	41.5 ₁	46.9 ₄	11.5 ₅
	1.936	45.9 ₁	43.6 ₀	10.4 ₈
	2.102	47.1 ₆	42.0 ₃	10.8 ₁
800	2.291	51.4 ₆	40.2 ₉	8.2 ₅
	1.436	44.1 ₄	0	55.8 ₆
	1.241	47.1 ₁	0	52.8 ₉
	1.659	52.1 ₉	0	47.8 ₁
	1.790	56.0 ₄	0	43.9 ₆
	1.938	59.1 ₀	0	40.9 ₀
	neutron	10.2 ₈	0	89.7 ₂
1000	1.435	49.1 ₁	0	50.8 ₉
	1.541	53.9 ₁	0	46.0 ₉
	1.658	57.7 ₂	0	42.2 ₈
	1.789	61.5 ₇	0	38.4 ₃
	1.937	64.3 ₃	0	35.6 ₇
	2.101	68.3 ₁	0	31.6 ₉
	2.290	71.4 ₅	0	28.5 ₅

Table 3-4 Attenuation of anatase and rutile wt% derived from the Rietveld scale factors as function of X-ray energy. For each temperature, the absolute attenuation was estimated from the $I/I_0 = e^{-\mu t}$ for crystals fixed to the Rietveld refined size determined at $E = 8.64$ keV, and this correction applied for all energies.

Calcination (°C)	Rietveld Crystal Size (nm)	E (keV)	λ (Å)	Anatase			Rutile		
				wt%	Rel. Atten.	Abs. Atten.	wt%	Rel. Atten.	Abs. Atten.
300	7	6.40	1.936	78.46	0.996	0.996			
		6.93	1.790	78.70	0.999	0.999			
		7.48	1.658	78.15	0.992	0.992			
		8.05	1.540	79.22	1.005	1.005			
		8.64	1.453	78.81	1.000	1.000			
400	10	6.40	1.936	76.23	0.968	0.967			
		6.93	1.790	78.55	0.997	0.996			
		7.48	1.658	78.53	0.997	0.996			
		8.05	1.540	79.38	1.007	1.006			
		8.64	1.453	78.79	1.000	0.999			
500	19	6.40	1.936	75.85	0.974	0.964			
		6.93	1.790	76.09	0.977	0.967			
		7.48	1.658	76.33	0.980	0.970			
		8.05	1.540	77.21	0.992	0.982			
		8.64	1.453	77.85	1.000	0.990			
600	40/122	6.40	1.936	56.16	0.936	0.916	13.61	0.925	0.861
		6.93	1.790	57.09	0.952	0.932	14.18	0.963	0.899
		7.48	1.658	59.43	0.991	0.971	13.99	0.950	0.886
		8.05	1.540	60.18	1.003	0.983	14.14	0.961	0.897
		8.64	1.453	59.99	1.000	0.980	14.72	1.000	0.936
800	330	6.40	1.936				64.07	0.904	0.740
		6.93	1.790				65.72	0.927	0.763
		7.48	1.658				67.58	0.954	0.790
		8.05	1.540				69.54	0.981	0.817
		8.64	1.453				70.86	1.000	0.836
1000	400	6.40	1.936				60.84	0.883	0.764
		6.93	1.790				62.62	0.909	0.789
		7.48	1.658				64.87	0.942	0.822
		8.05	1.540				66.69	0.968	0.848
		8.64	1.453				68.90	1.000	0.881

Table 3-5 Linear absorption co-efficients for anatase and rutile. Mass attenuation was calculated using a fixed particle size (D) of 0.01 micron and plotted against the Rietveld phase proportion (Figure 3-7). Changing D altered the spread of the wt% as a function of energy, but did not change the intercept when $\exp^{(\Delta\mu)D} = 1$ and microabsorption was absent. For the core-shell microstructures observed $\Delta\mu$ is negative for the shielded phases (anatase and rutile) and positive for the accessible phase (primary gel or aperiodic intermediate).

Conversely, in neutron diffraction all the titania samples will experience an equal flux of neutrons, irrespective of heat treatment, leading to scale factors unaffected by microstructural irregularities arising from different particle sizes and distributions. Therefore, the neutron data collected at four calcination temperatures (300, 400, 600, 1000°C) were used to provide reference phase contents for comparison with the multiple wavelength X-ray analysis (Table 3-5). As expected on the basis of the analysis in Figure 3-6, the agreement between the neutron and X-ray data (collected at the shortest wavelength of 1.436 Å) is reasonable for the materials calcined at 300 and 400°C, but differences grow ever more evident at the higher temperatures. In particular, the non-diffracting content of samples treated at higher temperatures is significantly over estimated by X-ray diffraction as the aperiodic material forms an overlayer covering the larger rutile crystals.

Neutron diffraction shows that the primary non-diffracting portion (the gel) initially decreases ($10.0_6 - 7.7_3$ wt%) as anatase crystallizes, then increases to 8.8_2 wt% (as anatase reconstructively transforms to rutile), and finally remains as a persistent co-component (10.2_8 wt%) with rutile, at least after soaking at 1000°C for 2hr. This variation in amorphous content is consistent with other XRD studies (Chapter 5) and X-ray absorption spectroscopy (see Chapter 4), but the absolute quantity is lower.

3.4.3 Phase Evolution and Microstructure

In microabsorption, phases that are preferentially exposed to X-rays will give greater diffracted intensity, while those that are shielded will diffract less strongly (Figure 3-5). For all the titanias examined, the proportions of the crystalline phases (anatase and rutile) increase with X-ray energy, while those of the amorphous phases decline, indicating that the dimorphs are enveloped in aperiodic material. The energy-dependent absorption contrast is readily calculated from the linear absorption co-efficients for anatase ($\rho = 3.98 \text{ g.cm}^3$) and rutile (4.25 g.cm^3), but can only be estimated for amorphous titania. Here, it is assumed that the

amorphous phase has a density of 3.70 g.cm³, which is 7% less dense than anatase, although the precise value is not critical in the following analysis. Adapting the ideas of Brindley for examining mixtures of coarse and fine particles it follows that when anatase (an) is encapsulated in amorphous material (am)

$$\frac{I_{an}}{I_{ano}} = e^{(\mu_{am} - \mu_{an})D} \quad (\text{Equation 3-2})$$

where D is the diameter of a spherical diffracting aggregate containing the both phases (Figure 3-5). As a consequence of density differences and shielding it follows that $(\mu_{am} - \mu_{an})$ must be negative and the observed relative intensity of anatase increases at high X-ray energies. Conversely, for the amorphous phase the matching equation is

$$\frac{I_{am}}{I_{amo}} = e^{(\mu_{an} - \mu_{am})D} \quad (\text{Equation 3-3})$$

where $(\mu_{an} - \mu_{am})$ is positive and the measured proportion of non-diffracting titania decreases as the X-ray sampling becomes more nearly volume representative rather than from the surface. Similar equations can be written for rutile (ru). As the I/I_o ratios are extracted from the Rietveld scale factors and wt% phases, a plot of $e^{(\Delta\mu)D}$ versus wt% of the phases can be extrapolated to zero absorption contrast (where $e^{(\Delta\mu)D} = 1$) to estimate the true phase content.

Treating all the data in this manner confirmed the preferential interaction of the amorphous phases (both the gel and the reconstructive product of anatase) with the X-rays (Figure 3-7). Agreement between the neutron and X-ray data was only reasonable for the lower temperature calcination where $\mu D < 0.01$ (Table 3-5). In the plots shown, the diameter of the mixed phase particles was fixed at 100 nm,

and, while varying this parameter changes the spread of the contrast ($e^{(\Delta\mu)D}$), the extrapolated intercept is unaffected. Similarly, changing the density of the amorphous phase did not change the phase proportions in the absence of X-ray contrast. The three phase assemblage at 600°C is particularly notable, as the Rietveld extracted anatase wt% is evidently more energy dependant than for rutile, where the extrapolated value (15.1%) is in reasonable agreement with the neutron data (18.6%). This suggests that rutile forms preferentially nearer the surface of the particles. However, at 800-1000°C as the individual rutile crystals grow larger the discrepancy between the X-ray and neutron results becomes substantial due to mass absorption in the former.

By monitoring the variations in mass attenuation as a function of X-ray energy insights are gleaned into titania evolution. For low calcination temperatures (300°C) the microstructure of the diffracting particle can be schematically represented as a homogeneous dispersion of anatase crystals unaffected by self-absorption or shielded by the amorphous gel (Figure 3-8). From 400 - 500°C the particle structure stays the same, but the anatase crystals grow and agglomerate with self-attenuation becoming significant. However, at 600°C, and the onset of the phase transformation, the aperiodic titania intermediate component develops as the anatase transforms reconstructively to rutile, with the latter less shielded from X-rays and near the exterior of the diffracting aggregates. The rutile crystals are 2-3 times larger than anatase consistent with the phase transition proceeding via crystal pair interactions. However, crystal growth must take place through the aperiodic intermediate, rather than directly via the close-packed planes, although topotaxial interfaces will ultimately be favorable. Finally, at the highest temperatures, the particles consist of large rutile crystals (> 120 nm) interspersed with a persistent amorphous phase. Here the determination of phase proportions by X-ray diffraction is unreliable due to microabsorption ($\mu D \gg 0.01$).

Figure 3-7 Quantitative phase analysis using multiple wavelength X-ray diffraction and neutron diffraction as a function of calcination temperature. As the X-rays become increasingly energetic, sampling of the diffracting particle is more nearly volumetric, and the apparent relative proportion of the shielded phase increases, while that of the accessible, surface phase decreases. The discrepancies between the neutron and X-ray data become significant when larger crystals appear in the phase assemblages and $\mu D > 0.01$.

Figure 3-8 Microstructural models for the diffracting titania particles can be derived from multiple wavelength X-ray diffraction and the Rietveld wt% proportions. For titania calcined at 300°C there is no energy dependence of the phase proportions implying that anatase is homogeneously distributed through the primary gel. At the phase transformation temperature (600°C) accreted pairs of anatase particles nearly spontaneously rearrange as rutile via an aperiodic intermediate arising from anatase disorganization, with the high temperature dimorph somewhat enriched at the exterior of the crystalline core. At 1000°C the rutile crystals are very large, coated in a non-diffracting phase, and the X-ray Rietveld scale factors are significantly in error as the material is no longer sampled homogeneously. In this case, neutrons are required for quantitative phase analysis.

3.5 Kinetic Implications

The kinetic model of Madras et al [11] divides the phase transformation into two parts – a reconstructive re-arrangement that takes place independently in each anatase crystal, and a coarsening step, where there is coalescence of the rutile crystals. Furthermore, hydration is invoked as a means of separating anatase crystals and restricting crystal growth. The current data are supportive of this analysis in several respects.

While transformation of the gel to anatase is rapid, hydration persists internal and external to the crystals, such that at lower temperatures (300-500°C) the hydrated gel isolates the anatase and slows crystal growth, with residual hydrocarbons playing a similar role when alkoxide precursors are used. As calcination continues, additional water and carbon dioxide are released during growth and the initially non-stoichiometric anatase approaches TiO_2 . This is comparable to the concept of Madras [11] where each particle, consisting of a mixture of crystalline and amorphous titania is ‘behaving as a large molecule cluster’. At higher temperatures, the transformation to rutile is delayed when the anatase particles are separated, say by the introduction of Al_2O_3 [14] or La_2O_3 [5], implying the crystals must be in contact for crystallographic rearrangement to occur. The present data suggest that agglomeration proceeds when the aperiodic structure (accounting for ~ 7-10 wt% of the entire assemblage) (Table 3) primes anatase crystal pairs to almost instantaneously consolidate as a single rutile crystal. The difference in size between the largest anatase (~ 62 nm) and smallest rutile (~ 120 nm) are consistent with the phase transformation proceeding by (i) growth of anatase to a critical size (~ 60 -70 nm); (ii) overlap of the aperiodic altered surfaces of two adjacent anatase crystals, and (iii) rapid rearrangement to rutile encapsulated in residual amorphous titania that persists to 1000°C. Confirmation of this mechanism would require in situ powder neutron diffraction experiments where the evolution phase contents, crystallization rates and crystal sizes are examined dynamically as function of heating rate, and also atmosphere, to control the loss of organics.

It is generally recommended that powders for X-ray diffraction be reduced to homogeneous solids that minimize mass absorption effects. However, in the present experiments the microstructure of the titania was preserved by using light manual grinding to enable the exploration of microabsorption effects that provide guidance for examining phase evolution and transformations. While the crystallization of photocatalytic titania from alkoxide precursors is undoubtedly complex, a more complete picture of the nature of this process has emerged from this work, that is inclusive of changes in local chemistry, the evolution of crystal sizes, the inclusion of non-crystalline components of the phase assemblage, and the preconditions for phase transformation. Moreover, this study has established

quantitatively the evolution of compounds when calcined in air for 2 hrs, and demonstrated how the combination of neutron and X-ray diffraction delivers a reliable measure of phase content and microstructural distributions. The presence of an enveloping aperiodic titania (either gel remnants or a product of anatase disorganization) implies that the dimorphs themselves are never the primary surface in contact with contaminated water or air. Evidentially, more work is required to understand both the formation of e^-/h^+ pairs and/or the transport of excitons through this material. It is noted that titanias containing a mixture of anatase and rutile frequently offer higher quantum yields and/or catalytic activity and such assemblages are likely to contain a significant quantities of aperiodic material.

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Chapter 4

Atomic Scale Order Correlation

The local structure of titanium undergoes distinct changes in second nearest neighbour coordination number and order correlation during titania crystallization and phase transformation. X-ray absorption spectra of the Ti-K and L edges show the temperature dependance of these structural adjustments can be modified by the introduction of dopants or the deposition of titania on an amorphous silica substrate.

4.1 Understanding of Ti Local Structure

It was noted in Chapters 1 and 2 that nanosized titania is fabricated in a variety of forms to deliver materials of prescribed physical, optical and electronic functionality. The tuning of size-dependent parameters, such as specific surface area and quantum confinement, is essential in photocatalysis [1-7] and requires control of morphology and composition at near unit cell scales. Nanotitania can be prepared as: (i) thin films using chemical / physical vapor deposition (CVD / PVD) [8-9] and molecular beam epitaxy (MBE) [10]; (ii) crystalline aggregates by sol-gel routes [4, 11]; and (iii) fine powders via mechanochemical milling [12]. To enhance visible light photocatalysis, a large surface area is a beneficial, but insufficient, requirement to maximize quantum yield, because the relatively wide band gap of titania ($\sim 3.0 - 3.2$ eV depending on polymorph) inhibits exciton production, and the excited states that do form, are rapidly annihilated. Modification of titania by cationic substitution [Chapter 5, 13-14] or anionic doping [15-16], composite fabrication [Chapter 6, 17-18], and noble metal decoration [Chapter 7, 2, 19], in a variety of combinations, can induce bathochromic band gap shifts, delay electron-hole recombination and create more accessible active sites.

Powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) can probe the crystallinity and surface chemistry of titania photocatalysts, while X-ray absorption spectroscopy (XAS) is especially valuable for accessing order-disorder phenomena. In early work, Ti K [20-22] and doublet Ti $L_{2,3}$ [20, 23-26] X-ray pre-edge and near-edge (XANES) absorption in anatase and rutile were modelled by the one electron golden-rule approximation, muffin-tin approximation or many-body effects. The subsequent development of multiple-scattering theory provided a unified treatment for both extended X-ray absorption fine structure (EXAFS) spectra and XANES, with contemporary methods including a Debye-Waller factor (σ^2) and anharmonic corrections in EXAFS simulations providing more nearly quantitative spectral interpretations [27]. Recent studies of titania have emphasized the pre-edge and XANES features of ‘amorphous’ [28-29] and nanostructured forms [30-32], together with EXAFS of metal-doped titanias [29,

33-36]. The titanium pre-edge and XANES regions, which arise from $1s \rightarrow 3d$ and $1s \rightarrow 4p$ [20-22] transitions respectively, provide characteristic fingerprints of coordination number, chemical state and geometrical distortions [28-32]. In metal-doped titanias, the short-range coordination environment of the dopant can be deduced from EXAFS [30-32].

In the previous chapter, it was shown that nanosized titania synthesized by soft chemical methods is more correctly described as $[\text{Ti}_{1-x}\square_x][\text{O}_{2-4x}\text{OH}_{4x}]$ with $0 \leq x \leq 0.1$. In addition, the amorphous content (in this context regarded as the non Bragg-diffracting component) can amount to more than 10 wt%, especially around the reconstructive anatase-to-rutile transformation [37]. In view of these new quantitative insights, it was timely to re-examine the local structure of Ti and its correlation with amorphicity and photocatalytic activity. This chapter presents comparative XAS of three nanocrystalline titania photocatalysts having distinct chemistries and morphologies - sol-gel synthesized titania (synthesis details in Chapter 3), cobalt-doped titania powders (Chapter 5), and silica-titania core-shell materials (Chapter 6) – to associate systematic changes in bond length, coordination number and order correlation of Ti with amorphicity and photocatalytic activity.

4.2 Characterization Strategy

4.2.1 Nanostructure and Phase Analysis

The materials were examined by transmission electron microscopy (TEM) at 200 kV with a JEOL JEM 2100F microscope equipped with double-tilt holder. The samples were lightly ground, dispersed ultrasonically in water and several drops of the suspension deposited onto holey-carbon coated copper grids, prior to image collection using a high-contrast objective aperture (20 μm).

Powder X-ray diffraction (XRD) patterns were collected over the angular range 10° – 140° 2θ using Bragg-Brentano geometry ($\text{Cu-K}\alpha$ source, primary and secondary soller slits, 0.1 mm divergence slits, 0.3 mm receiving slit, secondary

graphite monochromator) with a Shimadzu Lab-XRD-6000 instrument. The diffractometer was calibrated against a LaB₆ standard using the fundamental parameters approach implemented in TOPAS V3.0 [38]. For quantitative phase analysis, 20 wt% of Al₂O₃ [39] was introduced as an internal standard with manual grinding (20 min) using an agate mortar and pestle to improve homogeneity and minimize the effects of X-ray microabsorption [37]. The amorphous content of SRM 676 has recently been corrected from 2% to 8.25% [24] and the calculations adjusted accordingly. The XRD patterns were analyzed using the Rietveld method to ascertain the wt% of anatase, rutile and amorphous titania [37] by employing the following refinement strategy: 1/x background function and a Chebychev polynomial of order 4; lattice constants (a and c) of alumina fixed at 4.75919 and 12.99183 Å provided by NIST [39] and atomic parameters according to Toebe et al. [40]; zero shift, sample displacement, lattice parameters, scale factors and crystallite size of anatase, rutile and ilmenite optimized in turn. The atomic co-ordinates (Table 4-1) and thermal parameters of anatase [41] and rutile [41] were fixed at reported values.

Table 4-1 Coordination shells for anatase [41] and rutile [41].

Coordination	Anatase		Rutile	
	Bond	Bond Length (Å)	Bond	Bond Length(Å)
First Shell	(Ti – O1) × 4	1.937	(Ti – O1) × 4	1.948
	(Ti – O2) × 2	1.966	(Ti – O2) × 2	1.980
Second Shell	(Ti – Ti1) × 4	3.040	(Ti – Ti1) × 2	2.959
Third Shell	(Ti – Ti2) × 4	3.785	(Ti – O3) × 4	3.487
			(Ti – O4) × 4	3.560
	(Ti – O3) × 8	3.867	(Ti – Ti2) x 8	3.569

4.2.2 X-ray Absorption Spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) of titania, cobaltiferous titania and silica-titania core-shell photocatalysts was conducted at the Singapore Synchrotron Light Source (SSLS) [42], using the X-ray Demonstration and Development (XDD) beamline which provides a focused 2.5 ~ 10 keV source selected using a Si (111) monochromator. The Ti and Co K-edges were measured at room temperature in transmission mode, with intensity normalized against two ionization chambers recording the incident and transmitted X-ray intensities simultaneously. Each sample was ground to a fine powder (400 mesh) that was coated on scotch tape and folded to form multiple layers (for Ti K-edge collection) or pressed into thin pellets (for Co K-edge data). For samples prepared in this manner, the absorption edge jump was ~ 1 for the Ti K-edge, and 0.05-0.2 for the Co K-edge. Multiple scans were performed to improve the counting statistics with energy calibrated against K-edge absorption of pure Ti and Co foils leading to a reproducibility of ± 0.15 eV between scans. The absorption spectra were collected from -150 to 900 eV (for Ti) and -150 to 700 eV (for Co) relative to the metal K-edges. XAS of commercial CoO, Co₂O₃, Co₃O₄, a benchmark photocatalytic titania (P25 Degussa), and anatase and rutile standards were also collected.

Data analysis followed a standard procedure using WinXAS [43]. The absorption spectra were normalized by employing a linear and second polynomial fit to the pre-edge and post-edge regions, respectively. Subsequent processing included transforming from energy to momentum (k) space, a 7-segment (6-segment for Co) spline fit to the post-edge region, and Fourier transformation (FT) from k space to real (R) space. In this manner, EXAFS over the range of 3.1-15 Å⁻¹ (Ti edge) and 2.1-11 Å⁻¹ (Co edge) in k space were extracted, then k³ weighted and a Bessel window function applied. The data fit was performed in R space using the theoretical phase shift and backscattering amplitude extracted from the anatase and rutile models. For Co-K edge fitting, the model presumes Co substitutionally displaced Ti in anatase. The inelastic factor, S_0^2 , was determined by fitting to standard references and fixed at 0.89 for the Ti K-edge (anatase and rutile) and 0.92 for the Co K-edge (anatase).

In addition, Ti L-edge absorption measurements of the dry gel and calcined nanotitanias (200, 400, 600 and 1000°C) were performed using the Surface, Interface and Nanostructure Science (SINS) beamline at SSLS. This soft X-ray beamline is equipped with 4 spherical gratings in a modified dragon-type monochromator covering a spectral range from 50 eV– 1.2 keV [44]. The powder samples (passed through a 400 mesh sieve) were pressed into pellets (10 mm diameter). An argon sputter-cleaned poly-gold reference was used to calibrate the energy of the absorption edges. The absorption spectra were collected in vacuum using the sample drain current in total electron yield (TEY) mode with a photon energy resolution of 0.1 eV. The TEY signal contains all electrons escaping from the specimen, including photoelectrons, Auger electrons and secondary electrons originating in the cascade decay process [45].

4.3 Ti K-edge

The Ti K-edge spectra for titania and the reference materials are divided into pre-edge (A), XANES (B-D) and EXAFS (E-I) regions (Figure 4-1). The features B, C₂, C₃, D, E and F are characteristic of rutile while C₁, C₃, H and I are typical of anatase. The absorption spectra of the powders calcined from 300-600°C and 700-1000°C are similar to commercial anatase and rutile respectively, in agreement with XRD [46]. The dried gel and powder treated at 200°C were less crystalline and the absorption spectra poorly correlate with the anatase reference.

4.3.1 Ti Pre-edge Region

Subtle variations in the pre-edge reflect changes in the nearest neighbour geometry of Ti and are sensitive to heat-treatment (Figure 4-1b). The pre-edge crests (A₂ and A₃) of the precursor gel progress to higher energies with increasing calcination temperature (200, 400 and 600°C), while a third feature (A₁), typical of anatase, appears for the 400°C and 600°C materials. According to Grunes et al. [20] and Farges et al. [22] the more intense A₂ and A₃ peaks are consistent with

lower coordination and the absence of a centre of symmetry in a solid figure described as “tetrahedral”. A reduction in the intensity of A_1 - A_3 at higher temperatures (400°C and 600°C) matches the spectrum of the anatase ($I4_1/amd$) reference and is therefore ascribed to octahedral coordination with $4\bar{m}2$ point symmetry, while from 700°C the pre-edge features gain intensity due to removal of the centre of inversion (mmm point symmetry) in rutile ($P4_2/mnm$) [28]. For the third common polymorph, brookite, the point symmetry of Ti is the identity (1), therefore the intensity is predicted to be higher than for anatase and rutile. The absence of A_1 [20-22] in the pre-edge of titania calcined from 700°C - 1000°C (Figure 4-1c: for clarity 700°C data are excluded) is consistent with near complete replacement of anatase by rutile, as demonstrated by XRD [37]. As the A_2 and A_3 peaks are less intense than in the calcined materials compared to the rutile reference, there may be greater crystallographic strain in this coarse grained material.

4.3.2 Ti Extended Edge Analysis

In both dimorphs, the FT plots of the first coordination shell of Ti contains six oxygen near neighbours (TiO_6), together with four (or two) Ti as second nearest neighbours for anatase (or rutile) (Table 4-1). The most intense feature at ~ 1.96 Å arises from the Ti-O bonds, followed by Ti-Ti coordination (3.05 or 2.92 Å) (Figure 4-2). The third peak in the FT is due to Ti-Ti and Ti-O interactions in outer coordination shells and contributions from multiple scattering paths. The radial distribution plots become sharper at higher calcination temperatures in tandem with increasing crystal size. Because the precursor gel is largely amorphous the match to the anatase reference is poor.

Figure 4-1 (a) The Ti K-edge absorption spectra for nanotitania and the reference materials with enlargement of the pre-edge regions (A) to identify (b) anatase and (c) rutile as a function of calcination temperature.

Figure 4-2 Fourier transform plots of Ti K-edge EXAFS data for nanotitania.

Figure 4-3 The change of (a) Ti coordination environment, (b) Ti-O and Ti-Ti bond distance, and (c) individual Debye-Waller factors (σ^2) for nanotitania with calcination temperature. The expected coordination numbers and bond distances of anatase and rutile references are indicated by dashed lines. The amorphous gel showed the greatest disorder ($\sigma^2_{\text{Ti-O}} = 0.0179$ and $\sigma^2_{\text{Ti-Ti}} = 0.0123$) among the synthesized materials. The error for the coordination number, bond length, and the Debye-Waller factor are estimated to be 10%, 0.01 Å and 10% for the first Ti-O shell, and about 20%, 0.02 Å and 20% for the second shells [47]. The error for the second shells is larger due to the wider spread of Ti-Ti distances.

4.3.3 Structural Information of Titania Polymorphs

The coordination numbers of Ti-O (CN = 6) and Ti-Ti (CN = 4 in anatase and 2 in rutile) in the first two shells of radial density are slightly lower than expected, especially for materials calcined at $< 400^{\circ}\text{C}$ (Figure 4-3a), however the step change in Ti-Ti coordination after rutile crystallization is clear. The dry gel gave a very low Ti-Ti coordination number reflecting very short range order in this material. The Ti-O bond distance is reasonably constant (1.95 to 1.96 Å) except in the amorphous gel (1.92 Å) where Ti-OH bonding is significant and can lead to a slight contraction in bond length (Figure 4-3b) [41]. The Ti-Ti distances are close to the expected values of 3.050 ± 0.010 Å (anatase) and 2.925 ± 0.005 Å (rutile). The Debye-Waller factor (σ^2) progressively shows superior order as anatase crystallizes, but this trend reverses in samples calcined beyond 600°C at the onset of the anatase-to-rutile transition (Figure 4-3c).

Figure 4-4 The absorption spectra of the Ti L-edge 1s for nanotitania as a function of calcination temperature.

4.4 Ti L-edge

The titanium L_3 edge ($2p^{3/2}$), contains three peaks (a_1 , b_1 and c) at lower energy and the L_2 edge ($2p^{1/2}$) shows two features (a_2 and b_2) at higher energy (Figure 4-4) [25, 48]. There was no significant change in the peak position with increasing temperature but the intensity of b_1 diminished with respect to c . The dry gel contains a single peak (b_1) at ~ 460 eV that may be characteristic of “tetrahedrally” coordinated Ti [48]. The broadening of b_1 with calcination temperature (200 – 600°C) is attributed to the formation of TiO_6 octahedra [25-26, 48] that accompanies increasing abundance of anatase. The splitting of b_1 gives an additional peak, c , arising from greater octahedral distortion in the larger and more perfect crystals [25, 48], that becomes more apparent as the phase transformation proceeds. Once rutile is dominant (700-1000°C), b_1 and c have near equal intensity, as distinct from other studies where $c > b_1$ in rutile [25-26, 48], $c < b_1$ in anatase [25-26, 48] and $c \sim b_1$ in brookite [25], TiO_2 -II [26] and Ti_2O_3 [48]. Presently, the origin for these differences is not well understood.

In summary, the crystallization of sol-gel synthesized titanias proceeds via four phases - gel $\rightarrow$ nonstoichiometric anatase $\rightarrow$ amorphous titania $\rightarrow$ rutile – where composition and form determine the transformation temperatures. The trends in coordination number and σ^2 of Ti in nanotitania determined by XAS agree with the relative amorphicities established by quantitative XRD and PND. During calcination, σ^2 decreases as the gel yields to anatase, then increases as anatase transforms reconstructively to rutile. Nanotitania powder retains an abundant amorphous phase and persistently high σ^2 in sample calcined at 1000°C that is at odds with the commonly held view that titania will completely transform to rutile.

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Part II:

Catalyst Chemistries and Architectures

Chapter 5

Cobaltiferous Photocatalytic Titania

Cobalt doping of nanotitania promotes nonstoichiometry in anatase and delays the onset of rutile crystallisation. Solid solubility is limited with CoTiO_3 appearing at higher cobalt concentrations and elevated firing temperatures. Photocatalytic activity was not enhanced in cobaltiferous titania as surface accumulation of Co^{3+} reduced the number active sites, and Co^{2+} may accelerate the annihilation of excitons.

5.1 Optimization through Chemical Doping

Effective photoexcitation requires irradiation at wavelengths < 400 nm, where photon energies are similar to the semiconductor band gaps anatase and rutile [1-2]. Consequently, while excitation is efficient under ultraviolet sources, it is rather less so when exploiting the $\sim 5\%$ ultraviolet (UV) fraction of sunlight. One method to induce red shifts of the band gap is to chemically dope with cations (A) including $\text{Co}^{2+,3+}$, Ag^+ , Pt^{6+} , W^{6+} and V^{5+} to form $\text{Ti}_{1-x}\text{A}_x\text{O}_{2-\delta}$ compounds [2-8]. In all these cases, superior catalytic activity is generally taken to indicate that crystallochemical modification of titania has been achieved through aliovalent or intervalent substitutions such as $\text{Ti}^{4+} \leftrightarrow \text{Co}^{4+}$, $\text{Ti}^{4+}\text{O}^{2-} \leftrightarrow \text{Co}^{3+}\text{F}^-$, or $\text{Ti}^{4+}\text{O}^{2-} \leftrightarrow \text{W}^{6+}\text{C}^{4-}$. However, direct evidence of such replacements is not usually presented, as small crystallite sizes, low dopant concentrations, and the difficulties of conducting microanalysis makes verification particularly challenging. Nor has the role of amorphous content received significant attention.

It has been reported that cobalt doping of titania will enhance photocatalytic properties. Barakat et al. [7] found that titania containing 0.036 mol% cobalt rapidly photo-oxidised 2-chlorophenol, with greater or lesser amounts proving less active. While it was not possible to conclude if cobalt was entering titania substitutionally, or present as a discrete oxide, it was shown that after high temperature firing rutile (TiO_2) and ilmenite-type $\text{Co}^{2+}\text{Ti}^{4+}\text{O}_3$ co-existed. Broadly similar results were obtained by Iwasaki et al. [8] who studied the degradation of acetaldehyde. Although cobalt doped titania is frequently reported as $[\text{Ti}_{1-x}\text{Co}_x]\text{O}_2$, this formulation is evidently only correct for tetravalent cobalt (a rare valence state), whereas both experiment [7] and theory [9] suggest di- or tri-valency are prevalent and a more correct crystallochemical description is $[\text{Ti}_{1-x}\text{Co}_x]\text{O}_{2-\delta}$ [10]. Additionally, these idealized formulas neglect the possibility of significant metal vacancies as described in Chapter 3, and identified by Sancez et al. [11] and Grey & Wilson [12].

In a previous investigation of sol-gel derived titania prepared by hydrolysis of titanium butoxide, it was confirmed that crystallographic data derived from Rietveld analysis of powder X-ray diffraction patterns correlated with that from high resolution transmission electron microscopy, and a blue shift in band gap arises from with increasing quantum confinement in nanosized crystals [13]. In this chapter, these techniques are used to characterize titanias as a function of cobalt loading and sintering temperature. In addition, the chemical, crystallographic and physical states of cobalt are considered, with particular attention given to the abundance and role of X-ray amorphous materials. The performance of cobaltiferous titania was benchmarked against pure titania prepared under identical conditions, and the manner in which cobalt loading influences the anatase to rutile transformation, crystal growth, and specific surface area quantified.

5.2 Chemical Modification of Titania

Oxides of nominal composition $(\text{Ti}_{1-x}\text{Co}_x)\text{O}_{2-\delta}$ were synthesized via a sol-gel technique with $x = 0.001, 0.005, 0.01, 0.02$ and 0.05 (Figure 5-1). Titanium tetrabutoxide $[\text{Ti}(\text{O-Bu})_4, 97 \%, \text{Aldrich}]$ was dissolved in absolute ethanol ($\text{EtOH}, > 99.9 \%, \text{Merck}$) prior to hydrolysis, with cobalt introduced by adding a solution of absolute EtOH , anhydrous CoCl_2 (Merck), HCl (37 %, Merck) and deionized water dropwise. The molar ratio of EtOH , deionized water and HCl was fixed at 15, 1 and 0.3 for all the cobalt-doped titanias. The sol was homogenized by stirring for 30 minutes at room temperature followed by gelation for 5 days. The gel was vacuum dried at 60°C then calcined at selected temperatures from 200°C to 1000°C for 2 hours. The heat-treated samples were washed with hot water to remove chloride before using as a photocatalyst. The sample codes are collated in Table 5-1.

Figure 5-1 Flow sheet for photocatalyst synthesis.

Table 5-1 Metals content of (Ti_{1-x}Co_x)O_{2-δ} compounds.

Sample Code	Nominal Composition		
	Co(x)	Ti	Co/Ti
Co001	0.001	0.999	0.0010
Co005	0.005	0.995	0.0050
Co01	0.01	0.99	0.0101
Co02	0.02	0.98	0.0204
Co05	0.05	0.95	0.0526

5.3 Materials Characterization

X-ray diffraction patterns were collected in the usual manner (see Section 4.2.1). Quantitative phase analyses using the Rietveld method included refinement of the background, surface roughness according to Suortti [14], cell constants, scale factors, titanium occupancy (anatase) and crystallite size. All atomic co-ordinates

and thermal parameters were kept fixed to the values of the starting models of the crystalline phases that included anatase [15], rutile [16] and CoTiO_3 [17]. The mass of amorphous material and the relative values of the cell parameters were determined by adding 30 wt% of Al_2O_3 (NIST SRM 676) as an internal standard. The amorphous content of SRM 676 (8.25%) was corrected [18] and the calculations adjusted accordingly. Every sample was homogenized with the Al_2O_3 standard by 20-minutes of manual grinding in an agate mortar to avoid the need to apply a correction for microabsorption. The refinement strategy detailed in Section 4.2.1 was employed [18-19]. The isothermal parameters of all phases were constrained to literature values. For anatase, the titanium occupancy was refined, following the approach of Grey and Wilson [12]. However, this earlier study used the atomic form factor of Ti^{2+} , rather than Ti^{4+} to model the vacancies, as this gave a better match for well-crystallized anatase where full titanium occupation was presumed. In the present refinements, the form factor of Ti^{4+} was used throughout.

Powdered samples deposited onto holey carbon coated copper grids were analyzed using transmission electron microscopy (TEM) performed at 200 kV on a JEOL JEM 2100F microscope, equipped with double-tilt holder. Field limiting apertures used for selected area electron diffraction (SAED) were 5, 20 and 60 μm in diameter and images collected using a high-contrast objective aperture.

The chemical states of surface cobalt and titanium were evaluated by X-ray photoelectron spectroscopy (XPS) using a PHI 5600 instrument and a magnesium anode. Survey scans covered the binding energy from 0 to 1000 keV calibrated against adventitious carbon, and the multiplex spectra processed using Computer Aided Surface Analysis (CASA) software [20].

For TGA–DGA, samples were heated to 1000°C at a rate of 5°C per min, with nitrogen used as both the balance and sample gas at a flow rate of 50ml per min. Fourier transform infrared spectrometry (FTIR) (Perkin Elmer GX) was used to detect organic residues in the samples calcined from 200°C up to 800°C after being well-ground with potassium bromide (KBr, IR grade, Merck) and pressed

into pellets (10 mm diameter). Specific surface area was determined using the Brunauer-Emmett-Teller (BET) physisorption method (Micromeritics ASAP 2020).

Photocatalytic activity of cobalt-doped titania was investigated by monitoring the photodegradation of methylene blue and formic acid as a function of reaction time under UV and visible light. Two protocols were established for the photooxidation of methylene blue (Section 2.3.1) and formic acid (Section 2.3.2) with NaCl (aq) introduced in the former to remove the influence of colloidal scattering UV-visible spectroscopy measurement. In the later, data calibration by chloride was carried out after each capillary electrophoresis measurement.

5.4 Crystal Chemistry

5.4.1 Phase Transition

The X-ray amorphous dry gel powders begin to crystallize as anatase when heated to 200°C and subsequently convert to rutile at higher calcination temperatures such that the onset of the phase transition increases to 700°C with cobalt doping (Figure 5-2) as compared to a previous study of pure titania (600°C) [17]. In addition, ilmenite-type $\text{Co}^{2+}\text{Ti}^{4+}\text{O}_3$ appears at the highest cobalt concentrations and firing temperatures. On the basis of diffraction peak broadening, anatase crystals obtained at 200°C have thicknesses of ~ 5 nm that expand to 20-30 nm at 600°C with growth suppressed marginally at higher cobalt levels. For calcination at 800°C, Co01 ($x = 0.01$) contained trace CoTiO_3 (1.75 wt%, ~ 76 nm) with substantially more found in Co05 (9.9 wt %, ~ 97 nm). As expected, the ‘a’ unit cell parameter of Co-doped titanias decreased from 3.787(4) Å to 3.783(1) Å, with annealing temperature and crystallite size, while ‘c’ increased from 9.478(4) Å to 9.522(5) Å (Figure 5-3). The ‘c’ dilation is closely related to crystal growth with the expansion slowing as the crystallite size approaches 100 nm.

Figure 5-2 The evolution of wt % of anatase and rutile in (a) Co01 and (b) Co05 versus calcinations temperature shows the suppression of rutile crystallization at higher cobalt loadings.

Figure 5-3 The evolution of anatase unit cell parameters, a and c , in Co001 versus crystallite size and annealing temperature. The similarity to Figure 3-4(a) should be noted.

Figure 5-4 TGA – DGA curves of (a) Co001 and (b) Co05.

Thermal analyses were consistent with the diffraction data showing clear differentiation between high cobalt doped titanias ($x \geq 0.01$) and those containing lower concentrations. The weight loss (40 %) and exothermic peaks below 400°C reflect the oxidative elimination of organic residues and water, while the exothermic reactions between 450 – 550°C, arise from rapid crystallization of anatase and removal of trace organic compounds. The formation of CoTiO_3 for $x = 0.01, 0.02$ and 0.05 corresponds to the exothermic transitions at $\sim 650^\circ\text{C}$ and

770°C. The transformation of anatase to rutile took place in a broad band between 700 – 900°C (Figure 5-4).

Prior to calcination, FTIR spectroscopy confirmed the presence of physisorbed H_2O with characteristic absorption at 1620 cm^{-1} (Figure 5-5) [13, 21]. Other features include: i) free and bounded hydroxyl (O—H) groups of tert-butanol that absorb strongly from $3650 - 3200\text{ cm}^{-1}$; ii) out-of-plane bending of the bonded O—H group in the range $769-650\text{ cm}^{-1}$; iii) a single band at 1384 cm^{-1} caused by the O—H in-plane bending vibration of the tertiary alcohol [22]; and iv) C—O stretching absorptions from the band range of $1023 - 1114\text{ cm}^{-1}$. After calcination at 200°C , Co001 showed strong C—H stretching absorption bands of — CH_3 at 2853 , 2923 and 2951 cm^{-1} and a corresponding disappearance of the O—H group due to the removal of tert-butanol (with a boiling point of 83°C). Treatment at 400°C leaves trace organics that disappear at 500°C in agreement with the TGA-DGA observations.

Figure 5-5 FTIR spectra of Co001 calcined at different temperatures.

5.4.2 Phase Assemblage

In addition to anatase, rutile and ilmenite, significant amorphous content was present at all calcination temperatures. Particularly at high temperatures the existence of non-diffracting content is not intuitively obvious as a characteristic “amorphous hump” is absent (Figure 5-6). Quantitative Rietveld analyses, which leads to an overestimation of amorphous content due to microabsorption (Chapter 3), showed that samples treated at 200°C contain 53 wt% amorphous matter, that upon higher temperature treatment initially decreases to 4 - 25 wt% (Figure 5-7). A further increase of calcination temperature leads to a massive augmentation in amorphicity with a maximum of 41 - 53 wt% at 800°C when the anatase completely disappears and rutile is the only crystalline phase. In the case of Co001 heating was continued to 1000°C which reduced the non-diffracting phase to 29 wt%. While these weight percentages are high, it is believed that the relative proportions are reliable, and confirm the formation of aperiodic titania at the phase transformation. The phase composition of Co001 and Co01 calcined at different temperatures are summarized in Table 5-2a-b. The proportion of Ti-vacancies was refined for anatase. At 200°C a titanium occupancy of 83(5) % was found which increased to 97(7) % at 300°C and reached 100 % at 500°C. There was no indication of metal deficiency in rutile. In this case, cobalt incorporation can be neglected as a secondary effect due to the low concentration of the metal. The sum formula of the deficient anatase can be given as $\text{Ti}_{1-x}\text{O}_{2-4x}\text{OH}_{4x}$ under the assumption that bulk titanium is tetravalent and charge balance is maintained by the substitution of O^{2-} by OH^- , rather than by oxygen defects.

Figure 5-6 Quantitative Rietveld refinements of CoO1 and 30 weight % of SRM 676 added for the determination of the amorphous content calcined at (a) 400°C and (b) 700°C.

Figure 5-7 Temperature dependence of amorphous content: (a) Co001 and (b) Co01. The shaded bar indicates the temperature range over which the anatase to rutile transformation takes place.

Table 5-2a Phase content of Co001 as a function of annealing temperature. Note the amorphous content is overestimated due to microabsorption.

Temperature (°C)	Anatase	Rutile	Amorphous
200	47.1	0.0	52.9
300	53.7	0.0	46.3
400	56.6	0.0	43.4
500	64.2	0.0	35.8
600	74.2	0.0	25.8
700	65.6	3.6	30.8
800	0.0	47.1	52.9
1000	0.0	71.1	28.9

Table 5-2b Phase content of Co01 as a function of annealing temperature.

Temperature (°C)	Anatase	Rutile	ilmenite	Amorphous
200	46.9	0.0	0.0	53.1
300	54.0	0.0	0.0	46.0
400	59.8	0.0	0.0	40.2
500	70.5	0.0	0.0	29.5
600	75.3	0.0	0.0	24.7
700	57.0	39.3	0.0	3.6
800	0.0	57.3	1.2	41.5

5.5 Microstructure and Nanostructure

The material calcined at 200°C contains nano-crystalline anatase having a mean diameter of ~ 5 nm (Figure 5-8), a statistically smaller value compared to the 6-10 nm reported previously for nanotitania without cobalt doping [17]. The crystals grew to 10-12 nm at 400°C, and further increased from 25 nm at 600°C to 95 nm at 800°C. Selected area electron diffraction (SAED) patterns contained featureless rings attributed to anatase at 400°C, which became progressively differentiated at higher temperatures due to enhanced crystal growth. Of particular interest are

results for the sample Co01 calcined at 800°C for 2 hours (Figure 5-9). The analyses indicate co-existing i) sub-micron idiomorphic rutile crystal assemblages (Figure 5-9a, b, c), and ii) smaller non-idiomorphic rutile crystals (20-25 nm) encapsulated in amorphous material as confirmed by the SAED (Figure 5-9d, e). HRTEM shows well-defined crystal habit and irregular surfaces where smaller rutile nano-crystals aggregate (Figure 5-9c, d).

The BET surface areas of the Co-doped titanias are summarized in Figure 5-10. As noted previously, calcination at 200°C initiates crystallization of anatase while most organic compounds are oxidized completely after 400°C. Both processes cause shrinkage, and the loss of CO₂ and H₂O vapour create a sponge-like structure of specific surface areas ranging from 200 m²/g (200°C) to 80 m²/g (400°C). The isotherm was characterized as Type IV [23] indicating that these materials are mesoporous. A rapid decrease of specific surface area from 300°C onwards is a consequence of crystallization and growth of anatase. At calcination temperatures > 700°C, the specific surface areas were < 1 m²/g [24].

Figure 5-8 (a) Lattice image of Co05 calcined at 400°C and (b) SAED patterns of powders calcined from 200°C to 800°C.

Figure 5-9 (a) Bright field images of Co01 calcined at 800°C; SAED and HRTEM images of sub-micrometre idiomorphic rutile crystal assemblages (b & c) and nano-crystals of rutile embedded in amorphous material (d & e).

Figure 5-10 BET surface areas of Co001, Co01, Co02 and Co05.

5.6 Surface Chemistry

XPS showed that surface titanium in pure and cobalt-doped titania existed primarily as Ti^{4+} with less Ti^{3+} that decreased with cobalt loading and sintering temperature ($>500\text{ }^{\circ}\text{C}$) (Table 5-3). Cobalt could not be detected at low concentrations ($0.001 \leq x \leq 0.01$) but for Co01 calcined at 800°C a $\text{Co } 2\text{p}^{3/2}$ peak at 780.1 eV was evident (Figure 5-11, Table 5-3). The strong paramagnetic satellite peaks are consistent with CoO , Co_2O_3 or mixed-valent Co_3O_4 [25], but the chemical states of cobalt could be confirmed unambiguously as the binding energies of Co^{2+} and Co^{3+} could not be differentiated. At higher cobalt doping the $\text{Co } 2\text{p}^{3/2}$ spectral lines of Co02 and Co05 were shifted to 780.9 and 781.5 eV . The intensity of $\text{Co } 2\text{p}^{3/2}$ peak increased with the concentration of cobalt. Under the synthesis conditions used, the miscibility of cobalt in titania is limited with CoTiO_3 the preferred form, especially at higher temperatures ($> 700\text{ }^{\circ}\text{C}$).

Figure 5-11 Co XPS multiplex scan of Co01, Co02 and Co05 calcined at 800°C .

Table 5-3 Chemical states of surface titanium and cobalt

Material		Ti 2p ³²			Co 2p ³²	
Cobalt Content, x	Firing Temperature	Chemical State	Binding Energy (eV)	Atomic %	Chemical State	Binding Energy (eV)
0	400 °C	Ti ³⁺	456.8	32.9		
		Ti ⁴⁺	458.7	67.1		
0.001	400 °C	Ti ³⁺	456.8	27.2		
		Ti ⁴⁺	458.7	72.8		
	500 °C	Ti ³⁺	456.8	18.3	less than lower limit of detection	
		Ti ⁴⁺	458.0	81.7		
	800 °C	Ti ³⁺	456.8	14.0		
		Ti ⁴⁺	457.7	86.0		
0.01	800 °C	Ti ³⁺	456.8	14.0	Mixed Co ²⁺ & Co ³⁺	780.1
		Ti ⁴⁺	458.7	86.0		
0.02	800 °C	Ti ³⁺	456.8	14.3	Mixed Co ²⁺ & Co ³⁺	780.9
		Ti ⁴⁺	458.8	85.7		
0.05	800 °C	Ti ³⁺	456.8	14.1	Mixed Co ²⁺ & Co ³⁺	781.5
		Ti ⁴⁺	458.7	85.9		

5.7 Optical Band Gap

The absorbances of pure titania and Co-doped titania powders in the ultraviolet and visible regions (Figure 5-12) suggested the band gap energy of the former calcined at 400°C is 2.97 eV which is lower than the reported value for anatase (3.2 eV) when quantum confinement is operative [2, 7]. After cobalt doping the band gaps narrow, although at the highest loadings ($x = 0.05$) it could not be satisfactorily estimated by extrapolation of the spectrum. It is noted that the Co05 powder was green. However, because at least two phases – crystalline and amorphous - are invariably present the estimation of the band gap energy is of limited value, as the data contains a convolution of absorbances.

Figure 5-12 UV-Vis spectra of nanotitania and Co-doped titania powders calcined at 400°C.

5.8 Order and Disorder of Ti and Co

5.8.1 Ti K-Edge

The XAFS absorption spectra of $(\text{Ti}_{1-x}\text{Co}_x)\text{O}_{2-\delta}$ are similar to nanotitania calcined at 400°C (Figure 5-13a). The anatase phase is dominant regardless of doping concentration, however, the crystallinity compared to nanotitania was reduced (Section 4.3). The Ti-O coordination was confirmed as octahedral since the intensity of the pre-edge feature is relatively small. In contrast, the commercial catalyst Degussa P25 contains a mixture of anatase (75%) and rutile (25%), and consequently, the spectra were dominated by anatase features (A, C₁, C₃, H and I).

5.8.2 Ti Extended Edge Region

The FT of the cobaltiferous and P25 photocatalysts are sharper, but correspond well to the anatase reference as the smaller crystals retain less strain (Figure 5-13b). The coordination of Ti-O (~ 6) and Ti-Ti (~ 4) for the cobaltiferous material also accords with anatase, however, the Debye-Waller factors are slightly higher than P25 and the anatase reference (Table 5-4).

Figure 5-13 (a) The XAFS spectra and (b) Fourier transform curves of the Ti K-edge for cobaltiferous titania and the reference materials (Degussa P25, anatase and rutile). The nanotitania, Co01, Co02 and Co05 were calcined at 400°C.

Table 5-4 Structural information for nanotitania and cobaltiferous titanias calcined at 400°C and compared with the Degussa P25, and the rutile and anatase reference materials.

Material	Coordination number		Bond Distance (Å)		Debye-Waller Factor	
	Ti-O	Ti-Ti	Ti-O	Ti-Ti	Ti-O	Ti-Ti
Nanotitania	4.8	2.9	1.962	3.058	0.0058	0.0049
Co01	6.0	4.0	1.964	3.054	0.0065	0.0062
Co02	6.0	3.8	1.964	3.052	0.0063	0.0055
Co05	5.9	3.8	1.964	3.051	0.0064	0.0060
P25	6.2	3.8	1.964	3.044	0.0059	0.0055
Anatase	6.0	3.7	1.962	3.052	0.0054	0.0043
Rutile	6.2	2.8	1.963	2.925	0.0071	0.0076

5.8.3 Co K-Edge

The Co01 XANES yields a spectrum identical to CoO indicating only Co^{2+} is present (Figure 5-14a), while Co02 and Co03 also host minor Co^{3+} , as the absorption is shifted to a slightly higher energy. XPS results (Section 5.6) show that the solid solution limit is reached when $x > 0.01$ in $(\text{Ti}_{1-x}\text{Co}_x)\text{O}_{2-\delta}$, beyond which Co^{2+} is excluded then oxidized to Co^{3+} on the titania surface. Because XANES has a superior lower limit of detection for cobalt compared to XPS, it was possible to identify $\text{Co}^{2+/3+}$ throughout the bulk, in addition to the surface accumulation. Coupled with the XRD observation that cobalt delays the conversion of anatase to rutile, it is possible that the disarrangement of anatase and crystallization of rutile from the amorphous intermediate are both impeded through ready charge balancing during dehydroxylation ($\text{Co}^{2+} + \text{OH}^- \rightarrow \text{Co}^{3+} + \text{O}^{2-}$) and the incorporation of oxygen vacancies ($2\text{Co}^{3+} + \text{O}^{2-} \rightarrow 2\text{Co}^{2+} + \square_{\text{O}}$).

5.8.4 Co Extended Edge Region

A simulated FT curve was calculated for a simple $(\text{Ti}_{1-x}\text{Co}_x)\text{O}_{2-\delta}$ anatase model where the Ti central metal absorber was replaced by Co (Figure 5-14b). The experimental data from the cobaltiferous titania do not strongly correlate with the simulation because second shell Co-Ti features is absent, and distortion around the Co dopant, that leads to broader peaks, are not included. The fitted Co-O bond length ($2.00 \sim 2.02 \text{ \AA}$) is longer than Ti-O ($1.96 \text{ \AA}$) as Co^{2+} ($\text{IR} = 0.745 \text{ \AA}$) is larger than Ti^{4+} ($\text{IR} = 0.605 \text{ \AA}$) (Table 5-5). Considerable weakening of the peak at $\sim 2.9 \text{ \AA}$ indicates substantial variation in second-nearest neighbour Co distances relative to the cobalt oxide references. This is expected, since altermvalent replacement of Ti^{4+} by Co^{2+} will necessarily require the introduction of oxygen vacancies or the condensation of oxygen octahedra by edge-sharing to maintain neutrality.

Figure 5-14 (a) The Co K-shell near edge absorption spectra and (b) Fourier transform representation of the Co K-edge EXAFS data for the calculated substitutional model $(\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta})$, Co01, Co02, Co05 and cobalt references.

Table 5-5 Variation of the Co coordination environment in Co01, Co02 and Co05 prepared at 400°C, together with the bond distances and coordination numbers of the standards (Co₃O₄, Co(OH)₂, CoO).

	Coordination number	Bond Distance (Å)	Debye-Waller Factor
Co01	5.0	2.010	0.0094
Co02	5.0	2.000	0.0107
Co05	5.6	2.020	0.0115
Co ₃ O ₄ [26]	5.3	1.926	-
Co(OH) ₂ [27]	6.0	2.100	-
CoO [28]	6.0	2.130	-

5.9 Photocatalytic Oxidation

5.9.1 Methylene Blue (MB)

A blank test using ultraviolet light partially bleached ($C/C_0 = 0.7$) methylene blue over 60 minutes, but in the presence of pure titania and Co001 catalysts calcined at 400°C, the suspension was rendered achromatic. For $x > 0.001$ photocatalytic efficiency decreased with the concentration of cobalt, but for all compositions a linear decay of $\ln(C/C_0)$ with irradiation time was consistent with pseudo first order kinetics.

Experiments in visible light yielded rate constants reduced by a factor $10^{-3} - 10^{-4}$ from that in ultraviolet light. In relative terms, doping failed to produce enhancement in visible light activity. Pure titania calcined at 400°C performed best during photo-mineralization of methylene blue under visible light irradiation, with the rate constant of Co001 (which performed well in ultraviolet light) being much lower. However, when calcined at 500°C superior visible light catalysis was observed, possibly because of better crystallization of anatase with surfaces enriched with Ti^{3+} (Table 5-6).

5.9.2 Formic Acid (FA)

A blank test demonstrated ~ 20 % photolysis after 60 minutes UV irradiation and a pseudo first order rate constant of 0.004 min^{-1} (Table 4), with pure nanotitania calcined at 400°C being more effective (0.186 min^{-1}). Co001 calcined at 400°C degraded formic acid most effectively among the Co-doped materials delivering a rate constant of 0.150 min^{-1} , however catalytic activity deteriorated at higher cobalt levels, with the $x = 0.05$ material calcined at 400°C least effective. Unlike the PCO of methylene blue, the degradation rate of formic acid was not influenced by longer calcination times to 10 hours at 400°C . The rate constants of nanotitania and Co001 calcined for 2 hours and 10 hours were similar, but calcination at 500°C reduced the rate constant to 0.101 min^{-1} .

Under visible light there was negligible degradation of formic acid, and nanotitania calcined at 400°C had the highest rate constant of 0.001 min^{-1} . There was little improvement in the PCO of formic acid using Co-doped materials calcined at 400°C and 500°C (both at 0.001 min^{-1}) (Table 5-6). For nanotitania and Co001 calcined at 400°C with a 10-hour holding time, the degradation rate was negligible.

Table 5-6 Degradation rate constants of methylene blue and formic acid over nanotitania and cobalt-doped titania.

Composition (x)	Heat Treatment	Degradation Rate Constant (min^{-1})			
		Methylene Blue		Formic Acid	
		Ultraviolet	Visible	Ultraviolet	Visible
Blank		0.005	Negligible	0.004	Negligible
0	$400^\circ\text{C}/2 \text{ hrs}$	0.067	0.002	0.186	0.001
	$400^\circ\text{C}/10 \text{ hrs}$	0.077	0.001	0.169	0.000
	$500^\circ\text{C}/2 \text{ hrs}$	0.035	0.001	0.092	0.001
0.001	$400^\circ\text{C}/2 \text{ hrs}$	0.075	0.001	0.150	0.001
	$400^\circ\text{C}/10 \text{ hrs}$	0.070	0.001	0.151	Negligible
	$500^\circ\text{C}/2 \text{ hrs}$	0.038	0.001	0.101	0.000
	$600^\circ\text{C}/2 \text{ hrs}$	0.037	0.001	-	-
	$700^\circ\text{C}/2 \text{ hrs}$	0.032	Negligible	-	-
0.01	$400^\circ\text{C}/2 \text{ hrs}$	0.046	0.001	0.088	0.001
0.05	$400^\circ\text{C}/2 \text{ hrs}$	0.025	0.000	0.055	0.001

5.10 Influence of Cobalt Doping

5.10.1 Crystal Chemistry

While it is generally agreed that sol-gel syntheses yield more amorphous material than conventional solid state synthesis, it was presumed that these quickly crystallize during calcination. Therefore, a substantial non-diffracting component even after sintering at 1000°C was unexpected. Moreover, the relatively high reactivity and/or sorption capacity of aperiodic structures raises questions concerning their role during photocatalysis, and the need to control their quantity, and quantify their influence. Small anatase particles have been shown to exhibit significant concentrations of titanium vacancies [12, 29], with charge balance maintained by introducing H^+ through conversion of O^{2-} to OH^- in the emptied octahedra (Figure 5-15). The resulting sum formula can be written as $Ti_{1-x}O_{2-4x}(OH)_{4x}$ and this possibility has been included in these calculations. However, a detailed analysis of the X-ray refinements showed a strong correlation between amorphicity and the titanium occupancy. Both the lattice parameters a and c dilate with increasing crystal size (Figure 5-3) as the shortest titanium-titanium contact (3.04 Å) anatase propagates in the c -direction with the strong repulsion between Ti^{4+} cations compensated for by shortening of the shared edges ($O-O = 2.66$ Å) and expansion of unshared edges ($O-O = 2.79$ and 3.04 Å). Introducing metal vacancies reduces titanium-titanium repulsions, leads to a contraction of the octahedra, and reduces the length of the c -axis.

The c -axis behavior in cobaltiferous titania is comparable to the undoped materials [12-13], but the a -axis trend is subtly different from the data by Li et al. [13] who reported a slight decrease (3.795 to 3.790 Å) in pure titania, while in this study ' a ' is practically constant (3.783 ± 0.002 Å). This was also observed by Barakat et al. [24] in cobalt doped material. However, as the changes are small (< 0.001 Å) and quickly diminish as the crystallite size increases beyond 10 nm, systematic errors arising from differences in data treatment cannot be discounted. For example, Grey and Wilson [12] used a split Pseudo-Voigt function to model diffraction peak profiles, while this study employed a profile shape based on the

fundamental parameter approach. As the empirical function models peak asymmetry without accounting for the shift in peak position, and the fundamental parameters considers both shape and position, the lattice parameters obtained from these methods are slightly different. Differences in the implementation of the Rietveld method in the various programs should also not be discounted.

5.10.2 Surface Chemistry and Catalytic Activity

The dependence of lattice parameters on metal vacancy concentrations precludes establishing a simple correlation with cobalt incorporation. The substitution of Ti^{4+} ($r = 0.605 \text{ \AA}$) by Co^{3+} ($0.61 \text{ \AA}$) or Co^{2+} ($0.745 \text{ \AA}$) would lead to dilation, but this effect if present, is masked by increasing cation-cation repulsions as occupancy rises and explicit evidence for replacement of titanium by cobalt in anatase could not be established. However, a combination of surface analysis and catalytic performance is consistent with limited miscibility of cobalt in anatase under the current synthesis conditions.

Figure 5-15 [010] projection of the structure of anatase featuring the distorted TiO_6 -octahedra and titanium-titanium contacts.

It has been reported that Ti^{3+} defects, generated by annealing or ion sputtering, may be charge balanced through the creation of oxygen vacancies in a manner that enhances photocatalytic activity [30]. It remains unclear if Ti^{3+} is formed on titania surfaces during processing, or is created via photogeneration of electrons (Ti^{3+} species) and holes (O^- species) during UV radiation [30]. Lee et al. [6] also found that the surface concentrations of Ti^{3+} and OH^- in titania thin films controlled hydrophilicity during photocatalysis, and Liu et al. [31] reported that Ti^{3+} plays an important role as an electron trapping center at the liquid-solid interface in silver-loaded titania powder water suspensions. In this case, it is believed that oxygen radicals transfer electrons to Ti^{4+} and generate Ti^{3+} .

The Co $2p^{3/2}$ XPS peak at 780.1-781.5 eV is attributed to mixed 2+/3+ valences. It is suggested that the appearance of Co^{3+} is due to the air exposure of surface Co^{2+} ions precipitated from the titania that had migrated to the surface during thermal treatment. Illumination may result in the following reversible photoexcitation processes that occur on the titania surface in the present of Co^{2+} and Co^{3+} [32]:

(1)	Electron-hole pair generation:	$(\text{Ti}^{4+} - \text{O}^{2-}) \xrightarrow{h\nu} (\text{Ti}^{3+} - \text{O}^-)$
(2)	Recombination:	$\text{Co}^{3+} + h\nu \rightarrow \text{Co}^{2+} + h_{\text{VB}}^+$
(3)	Photoionization:	$\text{Co}^{2+} + h_{\text{VB}}^+ \rightarrow \text{Co}^{3+}$
(4)	Trapping :	$\text{Co}^{2+} + h\nu \rightarrow \text{Co}^{3+} + e_{\text{CB}}^-$

The recombination process of Co^{3+} shown in equation (2) can limit the availability of photogenerated electrons (Ti^{3+} species) and holes (O^-). By displacing Ti^{3+} and scavenging electrons that would otherwise be available for photocatalysis, surface enrichment in Co^{3+} degrades catalytic activity. Consequently, cobaltiferous catalysts were generally less effective notwithstanding the apparent narrowing in band gap energy. This phenomenon is more significant at higher concentrations ($x > 0.01$) where the majority of cobalt is divalent and partitions to CoTiO_3 , and for these compositions heat treatment above the anatase to rutile transition temperature completely removed activity.

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Chapter 6

Silica-Titania Core-Shell Photocatalysts

↓
Calcined
at 600°C

Monodispersed silica-titania core-shell pebbles can be fabricated via a simple sol-gel route without the need of pH adjustment, cationic polyelectrolytes or surfactants. The core-shell composite is optimised by repeated coating and heat treatment. The efficiency of the pebbles towards the photodegradation of methylene blue exceeded that of unsupported nanotitania powders. Pebbles are also more readily collected by filtration for reuse.

6.1 Need for Composite Architectures

For advanced photocatalytic oxidation of pollutants, titania morphologies can be tailored in a number of ways, including the synthesis of hollow titania spheres [1] or loading titania on inert supports [2-8] that include zeolites, porous silica, glass fibers and beads, carbon fibers, and alumina. These architectures create numerous accessible photocatalytic sites while simultaneously enhancing the adsorption of organic toxins. Durability is a critical property, and titania thin films are deactivated after multiple photocatalytic oxidation campaigns with effective regeneration strategies yet to be developed [4]. In fixed bed systems, it is supposed that film functionality degrades in tandem with a reduction of effective surface area [3-5]. In general, many factors contribute to catalytic activity and the interplay between these remains poorly understood [4-6].

Solid colloidal silica spheres encapsulated in titania have been investigated as photocatalysts [9] and photonic devices [10-14], as these can be prepared prescriptively with respect to the size and composition of the support (core) and the coating thickness (shell). For example, Wilhelm & Stephan [9-10] synthesized silica-titania core-shell materials by heterocoagulation with pH adjustment and a fixed concentration of titania sol, but the photocatalytic oxidation of rhodamine B was found to be less complete as compared to powder due to sedimentation. Subsequently, Nakamura et al. [11-12] prepared closed-packed titania-coated silica spheres using a layer-by-layer (LBL) templating method in a complex synthesis route involving alternating lamination of cationic polyelectrolytes and anionic titania sheets on monodisperse silica spheres and polystyrene latex particles. Holgado et al. [13] deposited uniform titania coatings on three-dimensional silica sphere arrays, but the shell thickness was variable and the spheres partially agglomerated. Liu et al. [14] and Kim et al. [15] controlled the hydrolysis rate of titanium alkoxides to avoid agglomeration of the coated silica spheres but this proved less successful than other methods [8, 11, 13].

The synthesis of silica-titania core-shell architectures can be complicated and expensive when surface grafting agents and polystyrene latex particles are

involved, which is inconsistent with the principle of using titania (anatase) as an economic photocatalyst for water purification and degradation of air pollutants. This chapter describes a simple procedure for the preparation of monodispersed titania-coated silica spheres using low cost materials (ethanol, water, ammonia, tetraethyl orthosilicate and titanium tetrabutoxide) by a sol-gel process that avoids the need for pH controlled core grafting, cationic polyelectrolytes or surfactants. Rather, homogeneous titania coverage was achieved by repeated impregnation with titanium tetrabutoxide followed by incubation at room temperature and finally condensation of the oxide using an ethanol/water solvent. In this way, the shell thickness could be specified and agglomeration reduced. The optimum synthesis conditions were established by systematically varying the concentrations of titania sol and solvent, while photocatalytic activity was monitored using the decolourization of methylene blue (MB). The crystal chemistry and amorphicity of the shells were comprehensively characterized with high resolution transmission electron microscopy, BET specific surface area measurement, quantitative X-ray diffraction and X-ray fluorescence spectrometry.

6.2 Simple Route to Monodispersed Core-Shell Fabrication

6.2.1 Fabrication of silica cores

Mono-dispersed silica spheres with diameters ranging from 150-160 nm were synthesized via the Stöber method [16]. Tetraethyl orthosilicate (TEOS, $\geq 97\%$, Merck) was used as the precursor in the sol-gel process (Figure 6-1) to prepare colloidal silica in the presence of absolute ethanol ($>99.9\%$, Merck), water (Milli-Q water), ammonia (25%, Merck) and ammonium hydroxide (28-30%, International Scientific Pte Ltd). The volume ratio of an ethanol : water : ammonia : ammonium hydroxide : TEOS mixture was fixed at 34.0:1.2:1.0:1.5:2.2 and stirred vigorously at room temperature for 2 hrs to obtain a white turbid suspension. The precipitate was collected by centrifuging at 8000 rpm for 10 mins, washed several times using water, and a stock suspension prepared by ultrasonic re-dispersion in ethanol at the weight ratio of 1:4 (silica:ethanol).

Figure 6-1 Flow chart for synthesis of silica spheres.

Table 6-1 Key synthesis parameters: the volume ratio of ethanol-water solvent, concentration, and stirring time of titania sol.

Concentration of Titania sol (% v/v)	Volume Ratio of TBT and Ethanol		Stirring Time (Hour)	Volume Ratio of Solvents	
	TBT	Ethanol		Ethanol	Water
10	1	9	3	1	1
25	1	3	0.5	1	1
25	1	3	1	1	1
25	1	3	3	1	1
50	1	1	3	1	0
50	1	1	3	1	1
50	1	1	3	0	1

6.2.2 Titania Coating

The coating procedure is summarized in Figure 6-2. A titania sol was prepared by hydrolyzing titanium tetrabutoxide ($\text{Ti}(\text{OBu})_4$, 97%, Aldrich) in absolute ethanol according to the concentrations shown in Table 1. The silica stock (1.2 ml) was separated from the ethanol centrifugally and homogenized with the titania sol by ultrasonic treatment (10 mins) and magnetic stirring (30 mins), followed by incubation using either (i) magnetic stirring, or (ii) orbital shaking at room temperature (150 rpm). The coating process was continued for 16 hrs after which the mixture was centrifuged (8000 rpm, 15 mins) to remove excess titania sol. The separated spheres were condensed with ethanol, water or ethanol:water (1:1) solvent (Table 6-1), magnetically stirred for 2 hrs at room temperature, then treated ultrasonically (1 hr) to minimize agglomeration of the coated spheres. The solvent was removed by centrifugation (8000 rpm, 10 mins) before repeating the coating process up to four times. The coated spheres (ST-2x, ST-3x and ST-4x) were re-dispersed in 3 ml of water and left for 2 hrs in an ultrasonic bath with a 30 min rest before calcination. The final suspension was heat-treated from 200°C to 1000°C in intervals of 100°C. The ramp rate was set to 1°C min⁻¹ with a 2 hrs holding time for each calcination temperature.

6.3 Materials Characterization

High resolution transmission electron microscopic (HRTEM) and bright field images were collected using a Jeol JEM-2100F TEM operated at 200kV. The pre-calcined specimens were prepared by dipping a holey carbon-coated copper grid into the dilute suspension. After calcination, the materials were ground gently and dispersed ultrasonically in water and several drops of the suspension deposited onto the grid. The electron diffraction pattern of anatase was simulated using JEMS Electron Microscopy Software [17].

Powder X-ray diffraction (XRD) patterns were collected according to Lim et al. [18] and Rietveld analysis employing the fundamental parameters approach

implemented in TOPAS V3.0. Diffracted intensity arising from amorphous silica spheres was included by introducing a single peak (refined at $20\text{--}23^\circ$) [19]. The atomic co-ordinates and thermal parameters of anatase [20] and rutile [20] were fixed at the reported values. Mass balance of the core-shell structure was established using X-ray fluorescence spectrometry (XRF) collected with a Philips PW2400 instrument in combination with XRD. The absolute mass of amorphous titania was determined by adding 20 wt% of Al_2O_3 (NIST SRM 676) [21] as an internal standard with the correction reported in Lim et al. [18]. To improve the refinement statistics and avoid microabsorption, each sample was homogenized by 20 min manual grinding in an agate mortar before XRD powder patterns was collected. In this way, the wt% amorphous silica, anatase, rutile and amorphous titania were ascertained.

Figure 6-2 Flow chart for synthesis of the silica-titania core-shell photocatalysts.

The specific surface areas of the coated spheres were determined using the Brunauer-Emmett-Teller (BET) physisorption method (Micromeritics ASAP 2020). The calcined core-shell structures were degassed overnight and heated at 200°C for 3 hrs before carrying out the analysis, with the treatment temperature for the coated spheres calcined at 200°C reduced to 150°C to avoid alteration.

Catalytic activity under ultraviolet (UV) illumination was monitored through the photodegradation of methylene blue (MB). The protocol and experimental apparatus for photocatalytic oxidation (PCO) are detailed in Section 2.3.1.

6.4 Optimization of Coating Process

6.4.1 Incubation

The incubation process used either (i) magnetic stirring or (ii) orbital shaking, with the latter yielding coatings that were smoother and thicker. Keeping other parameters constant, a 16-hr incubation by magnetic stirring resulted in the pristine silica spheres (Figure 6-3a) being covered by uneven titania shells (ST-2x) (Figure 6-3b), while homogeneous shells (thickness of ~20 nm) were obtained by orbital shaking (Figure 6-3c). Therefore, the latter method was chosen for optimization.

Figure 6-3 Morphological changes of (a) silica cores and ST-2x catalysts prepared from 30 min stirred 50% v/v titania sol using (b) magnetic stirring and (c) orbital shaking incubation.

6.4.2 Condensation Solvents

The solvent used in condensation primarily controls the thickness and surface roughness of the titania. By fixing at 50% v/v of titania sol, the effect of solvent selection on coating during condensation was examined (Table 6-1). Absolute ethanol yields the smoothest surfaces that are thin due to slower condensation (Figure 6-4a), whereas when water was used as the solvent, the shells became thick and rough (Figure 6-4b). It was found that an ethanol:water ratio of 1:1 gave a superior product with contiguous shells of constant thickness (~15 nm) (Figure 6-4c).

6.4.3 Homogeneity of Titania Sol

The homogeneity of the titania sol also influences shell thickness. A 25% v/v titania sol was magnetically stirred for 30 mins, 1 hr and 3 hrs before orbital shaking incubation. At the shortest time, some titania aggregates were observed (Figure 6-5a), and these were removed by increasing the stirring time of the titania sol to 3 hr (Figure 6-5b). By stirring the titania sol alone (3 hrs), the coated spheres showed minor agglomeration and could not be well separated unless the sol concentration was reduced to $\leq 10\%$ v/v. This suggests that aggregate formation is attributable to excess hydrolyzed $\text{Ti}(\text{OBu})_4$.

Figure 6-4 Titania shell on ST-2x catalysts synthesized using 3 hr stirred 50% v/v titania sol that was condensed from (a) ethanol, (b) water and (c) ethanol-water as the solvent.

Figure 6-5 Titania aggregation was present in (a) uncalcined ST-2x catalyst produced when a 25% v/v titania sol was stirred for only 30 mins before incubation. Aggregation could be substantially eliminated by (b) increasing the stirring time to 3 hrs.

6.4.4 Concentration of Titania Sol

By adjusting the titania sol concentration from 10 – 50% v/v, it was found that high metal content gave the thickest coatings (~ 15 nm), but resulted in progressively more agglomeration (in Figure 6-3c). Although reducing the concentration (25 and 10% v/v) limited agglomeration, the coating thickness decreased. It was concluded that the 10% v/v titania sol delivered dispersed core-shell material (ST-2x) with negligible agglomeration (Figure 6-6a).

The coating cycle process was optimized using a well stirred (3 hrs) 10% v/v titania sol during orbital shaker incubation, and condensation with an ethanol:water (1:1) solvent with 2 hr magnetic stirring. These procedures were repeated once for ST-3x and twice for ST-4x and ended with a 2 hr ultrasonic treatment. The coating thickness increased with repeated treatments. The bright field image of the coated spheres in Figure 6-6b confirmed that monodispersity was maintained and homogenous titania shells (~ 13 nm in ST-4x) achieved using the optimal coating process described.

6.5 Optimization of Materials Properties

6.5.1 Titania Shell Morphology

Homogeneous and highly dispersed titania nanocrystals were clearly obtained at all calcination temperatures (200°C-1000°C) (Figure 6-7). Lower crystallinity of titania is observed for material calcined at 200°C with substantial organic residues still present according thermal gravimetric analysis. Selected area electron diffraction (SAED) patterns of materials calcined at $> 600^{\circ}\text{C}$ confirmed that anatase had crystallized (Figure 6-8f). Titania crystals become larger with increasing temperature resulting in greater surface roughness (Figure 6-8d-e and g).

Figure 6-6 Bright field images of uncalcined (a) ST-2x and (b) ST-4x catalysts where the titania shell was deposited using 10% v/v titania sol.

Figure 6-7 (a) Monodispersity and (b) homogenous coatings of ST-4x catalyst (prepared as in Figure 6-6b) were retained after calcination at 600°C.

Figure 6-8 ST-4x catalyst prepared from 10 % v/v titania sol and calcined at (a) 200°C, (b) 600°C and (c) 800°C. Magnified images (d), (e) and (g) confirmed that the materials were crystalline, while (f) SAED patterns could be indexed as anatase.

6.5.2 Titania Crystallinity

Powder XRD showed that in addition to anatase, an intense broad reflection is attributable to the amorphous silica core (Figure 6-9a). XRF confirmed the mass of amorphous silica showed little variation (86.6 to 89.0 wt%) with calcination temperature (200°C – 1000°C) as expected, while XRD could not detect any silica polymorphs. In the shell, the mass of crystalline and amorphous titania were differentiated using Rietveld quantitative analysis. By subtracting the wt% amorphous silica core from the total amorphous content, the crystallinity of the titania shell was determined (Figure 6-10a). The highest anatase content was found in the material calcined at 600°C (Figure 6-10b), beyond which it disordered ahead of transformation to rutile. The sharpening of anatase reflections in Figure 6-9a verified that crystallinity increased with temperature, and that the transformation to rutile was delayed to 1000°C as compared to 600°C – 800°C normally observed for doped [18] and undoped titania powders [22-23]. Previously, it has been suggested that anatase thermal stability is greater if the crystallite size is small [24-25], and in this case, the anatase crystals are (<10 nm) even at 900°C (Figure 6-9b). The lattice parameter, a , decreased from 3.792(4) to 3.787(2) Å with increasing calcination temperature and crystallite size, while c dilated from 9.498(5) to 9.517(6) Å, as expected due to the expulsion of OH⁻ [18] and the filling of titanium vacancies [26]. At low calcination temperatures (< 600°C) both lattice constants contract due to the loss of water and crystallization.

6.5.3 Specific Surface Area

The surface areas of titania coated spheres (ST-4x) calcined at 400°C – 600°C ranged from 107.5 to 44.3 m²/g (Table 6-2), whereas, the bare silica spheres calcined at 400°C have a surface area of 31.4 m²/g. Compared to nanotitania powders synthesized previously [22], the thermal stability of anatase (the active photocatalytic phase) improved greatly as a result of its adhesion to the silica cores. In addition, the surface area of the titania shell (44.3 m²/g) calcined at 600°C was substantially more than for the free powder (3.8 m²/g) (Table 6-2).

Figure 6-9 (a) Powder XRD patterns and (b) the refined crystallite sizes and lattice parameters of ST-4x as a function of calcination temperature. In the shaded region (200 – 500°C), the lattice parameters constrict due to loss of volatile components. Beyond 500°C the c-parameter dilates because Ti-Ti repulsions become stronger as the titania approaches TiO_2 stoichiometry. (See also Figure 3-4 and Figure 5-3).

Figure 6-10 The crystalline and amorphous contents of (a) the entire core-shell assembly, and (b) shell alone of ST-4x as a function of calcination temperature.

Table 6-2 Specific Surface Areas as a function of morphology and calcination temperature.

		Surface Area (m ² /g)
Nanotitania [33]	400°C	90.1
	500°C	50.0
	600°C	3.8
Bare Silica Spheres	400°C	31.4
	400°C	107.5
ST-4x	500°C	48.6
	600°C	44.3

6.6 Order Correlation of Ti

6.6.1 Ti K-Edge

The XAFS spectra of the core-shell structures (600 – 1000°C) are consistent with the anatase reference, especially the characteristic C_1 and C_3 peaks (Figure 6-11a). The absorption spectrum for the material calcined at 1000°C did not show rutile features, although XRD showed the anatase-to-rutile phase transformation had commenced (the wt % of anatase and rutile are 74.5 and 2.1 respectively) (Figure 6-10b). In Figure 6-12 the pre-edge region is plotted together with the anatase reference and nanotitania powder calcined at 600°C, and suggests the TiO_6 polyhedra are less distorted in the latter, demonstrating that interactions between the titania shell and amorphous silica core are strong enough to modify the electronic states of Ti associated with the $1s \rightarrow 4p$ transition.

Figure 6-11 (a) Ti K-edge absorption and (b) Fourier transform plots for core-shell ST-4x calcined from 600°C to 1000°C compared with reference anatase and nanotitania calcined at 600°C

Figure 6-12 The Ti-K pre-edge absorption spectra for calcined core-shell ST-4x (600°C, 800°C and 1000°C), anatase reference and nanotitania calcined at 600°C.

Figure 6-13 The change of (a) Ti coordination environment, (b) Ti-O and Ti-Ti bond distance, and (c) individual Debye-Waller factors (σ^2) for nanotitania and core-shell ST-4x with calcination temperature. The expected coordination numbers and bond distances of anatase and rutile references are indicated by dashed lines. (d) The amorphous content determined using XRD Rietveld analysis correlate qualitatively with σ^2 .

6.6.2 Ti Extended Edge Region

The coordination numbers of Ti-O (~ 6) and Ti-Ti (~ 4) are consistent with anatase and persist to 900 - 1000°C due to a substantial delay in the phase transformation (Figure 6-13 a,b). First and second nearest neighbour order correlations (σ^2) are markedly poorer than nanotitania at comparable temperatures due to the combined effects of high surface exposure of Ti atoms on smaller crystals and interaction with the silica core (Figure 6-13c)

6.6.3 Amorphicity and Order Correlation

At lower temperatures the glassy gel crystallizes as anatase by displacement of protons and the concomitant introduction of Ti into vacant metal sites ($\square_{\text{Ti}} + 4\text{OH}^- \rightarrow \text{Ti}^{4+} + 4\text{O}^{2-}$), and at higher temperatures, there is deconstruction of anatase prior to the formation of rutile (Figure 6-13c,d). XRD and XAS strongly correlate, with XAS σ^2 factors providing a compelling argument that XRD amorphicity are manifested primarily as second nearest neighbour Ti variance. Ding et al. [27] observed that the stability of anatase loaded on silica gel was substantially enhanced and ascribed this to Si-O-Ti bonding. The present study offers direct evidence that in the intermediate aperiodic phase, the TiO_6 octahedra over silica are less distorted (Figure 6-12), show higher Ti-Ti coordination (Figure 6-13a), and poorer spatial correlation (Figure 6-13c). Taken together these factors substantially slow anatase coarsening which removes the thermodynamic drivers towards the crystallization of rutile [28]. This mechanism seems distinct from studies where inert Al_2O_3 [29] and La_2O_3 [30] particles were mixed with titania gels to separate anatase nuclei and delay growth.

In summary, the transformation of the dry gel to the titania dimorphs is indirect, because the conversion of anatase to rutile is a reconstructive, rather than displacive process (Figure 6-14). Quantitative phase analysis by XRD has confirmed the presence of amorphous phases throughout calcination, that first decrease due to gel crystallization as anatase, increase during the reconstruction of anatase as rutile, and then are slowly consumed during rutile growth. In

nanotitania, amorphicity increases rapidly from 500°C once anatase crystals become thermodynamically unstable [22, 28-29], and reaches a maximum at ~700°C. The introduction of cobalt retards anatase dissociation, possibly by a redox mechanism that accommodates oxygen vacancies. In the core-shell structure, amorphous content begins to accumulate from 600°C and is stabilized by the underlying silica which delays the appearance of rutile. In an earlier microscopic investigation [31], it was shown that smaller anatase crystals were less likely to transform to rutile, which is consistent with the present study where the smallest anatase crystals occurred in the core-shell structures. However, it is now believed that the property-limiting feature is the surrounding amorphous phase that is thermally resilient and delays rutile crystallization until ~1000°C.

Figure 6-14 Phase transform regions as function of temperature for nanotitania, cobaltiferous titania and core-shell silica-titania photocatalysts.

Figure 6-15 Rate constants for the degradation of methylene blue using ST-2x, ST-3x and ST-4x photocatalysts calcined at 400°C, 500°C and 600°C.

Figure 6-16 The relationship between rate constants and specific surface areas of nanotitania [22] and core-shell ST-4x (400-600°C), and cobaltiferous titania (Co01, Co02 and Co05) [18] (Section 5.9.1).

6.7 Enhancement of Photocatalytic Activity

ST-2x, ST-3x and ST-4x calcined from 400°C to 600°C were chosen to investigate the photocatalytic activity of the titania shell with respect to thickness. PCO of MB obeys pseudo first order kinetics and titania is the only active phase. The photodegradation rate was considerably enhanced (2 – 2.5x) from ST-2x to ST-4x, with the latter calcined at 600°C showing a rate constant of 0.087 min^{-1} (Figure 6-15). Although the catalysts calcined at 400°C have higher surface areas (Table 6-2), their activity was not comparably higher than for materials treated at 500°C and 600°C, possibly as the titania is less crystalline.

The electronic band structure of titania will be modified by changes in Ti bonding. However, there are many contributing factors to the overall quantum yield and photocatalytic activity, including the phase assemblage and disposition of phases, surface chemistry and structure, and surface area [32]. The recognition that substantial amounts of amorphous gel and aperiodic titania co-exist with crystalline titania adds to the complexity of interpreting catalytic data. Although the specific surface area is often considered the primary determinant of performance, it is clear that the correlation is not direct (Figure 6-16). For example, titania powder and the core-shell material behave oppositely, with the latter showing superior activity at a lower specific surface area, when the rate constants of ST-4x calcined at 500°C and 600°C increase to 0.092 and 0.087 min^{-1} respectively (Figure 6-16). Coincidentally, the core-shell material yielded the highest coordination and σ^2 factors for Ti-O and Ti-Ti, but further work is required to establish if this is the key correlation for predicting enhanced activity, or the accompanying stability of small anatase crystals. While increasing X-ray amorphous content and σ^2 track each other within a given type of photocatalyst, they do not match across different types of material. Thus, nanotitania apparently shows a higher XRD amorphous content than the equivalent core-shell material calcined at the same temperature, but the latter yields higher Debye-Waller factors. This may be due to differences in crystallographic periodicity between the X-ray amorphous components, or more likely, indicate microabsorption is influencing the Rietveld analysis (Chapter 3). While it is generally supposed that

the introduction of transition metal defects in titania extends exciton lifetimes and photocatalytic activity, this was not confirmed in the present study.

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Chapter 7

Gold-Decorated Silica-Titania Pebble Catalysts

Decoration of silica-titania pebbles with gold nanocrystals (3 nm) yields a robust, low temperature catalyst for CO oxidation. By adjusting deposition-precipitation parameters including pH, aging time and calcination temperature a catalyst was obtained that achieved 100% CO conversion at $<90^{\circ}\text{C}$. High efficiency and selectivity requires that the gold be homogeneously dispersed and preferentially expose $\{111\}$ facets.

7.1 Advantages of Silica-Titania Co-catalysts

Monosized gold nanocrystals that are homogeneously dispersed over reducible (MnO_2 , $\alpha\text{-Fe}_2\text{O}_3$, Co_3O_4 , NiO , CuO and TiO_2) [1-2] and non-reducible (SiO_2 , Al_2O_3) [2-3] scaffolds are potential catalysts in electrochemistry [4-6], chemical sensing [4-5, 7], environmental protection [4-5, 8-10] and chemical synthesis [4-5, 11]. Such materials hold particular promise as CO oxidation promoters that co-circulate in fluidized bed catalytic cracking (FCC) units to enhance catalyst regeneration and reduce the environmental impact of flue gases. However, because the reaction is highly exothermic and afterburning in cyclones and flue lines can cause significant damage, CO oxidation at low temperatures ($< 100^\circ\text{C}$) is desirable. The seminal work of Haruta et al. [2] demonstrated that isolated colloidal gold particles decorating titania and alumina achieved 50% conversion to CO_2 and O_2 at temperatures as low as -25°C and 10°C , respectively, with CO turnover rate increasing dramatically when the metal crystals were ≤ 4 nm in diameter. A key innovation was deposition-precipitation (DP) synthesis using HAuCl_4 as a precursor to avoid agglomeration, that lead to strong adhesion of the gold crystals through $\{111\}$ facets, an orientation that favors CO absorption, migration and reaction with oxygen at the metal-oxide interface [2].

A range of parameters influence gold morphology and reactivity. Titania-supported gold nanoparticles (≤ 5 nm) with high dispersion have been synthesized by DP with the performance adjusted by heat-treatment conditions [12-13], chemical reduction [12-13], pH tuning and temperature control [14-15], variation of substrate surface area (10 to $305 \text{ m}^2/\text{g}$)^[15] and substitution of reagents (NaOH and urea) [16]. Soarces et al. [12] found DP superior to the incipient wetness (IW) method for depositing gold on titania, although the average size of the faceted icosahedral gold nanoparticles anomalously decreased from 7 nm (200°C) to 4 nm (400°C) after calcination. In general, a pH (6-7) near the isoelectric point (IEP) of a substrate leads to the formation of $[\text{AuCl}_x(\text{OH})_{4-x}]^-$ complexes that favor higher dispersion, smaller particle sizes, and strong interfacial connection [12]. Consequently, when Dimitratos et al. [13] prepared an active gold-on-titania catalyst by DP at very high pH (>9), with chemical reduction of the metal using

NaBH_4 coupled to liquid phase oxidation of glycerol, the gold nanoparticles (2-5 nm) were poorly dispersed due to electrostatic repulsion between the surface and gold hydroxide complex ($[\text{AuCl}(\text{OH})_3]^-$). By reducing the pH to 9, Moreau et al. [14] found that the performance of titania-supported catalysts improved as the gold nanoparticles were reduced to a mean size of ~ 2 nm [14-15]. However, the progressive decrease in the rate of CO conversion as the titania specific surface areas increased (10 to $305 \text{ m}^2/\text{g}$) remains poorly understood [15], but may be linked to interfacial changes between the metal and oxide support or alteration of gold crystal morphology. Thus, the general conditions favoring the synthesis of efficient catalysts are established, but it remains difficult to routinely obtain highly active products.

In a detailed study, Zanella et al. [16] examined the influence of two bases during DP synthesis, finding that urea promoted a higher gold loading (8 wt%) as compared to NaOH (3 wt%). The reduction from Au^{3+} to Au^0 was temperature dependent [$\text{NaOH}/100^\circ\text{C}$ and $\text{urea}/150^\circ\text{C}$] while for both materials, calcination at 200°C yielded crystal sizes from 2 - 2.3 nm and the highest activity for CO oxidation. This good performance was ascribed to $\{111\}$ gold faceting yielding large numbers of low coordination surface sites. When calcined at $> 200^\circ\text{C}$, the particles grew into truncated octahedra with more perfectly developed $\{111\}$ and $\{100\}$ facets that increase surface coordination and lowers catalytic activity. While the mechanistic aspects remain to be clarified, this behavior has been ascribed to a poor distribution of nanocrystals which reduces the number of interfacial sites [17] that decreases O_2 adsorption and CO catalytic oxidation [16]. In summary, activity and selectivity of CO oxidation are controlled by the oxide support, the metal-oxide boundary structure, and the size and shape of the gold particles, [18-20] with problematic metal dispersion of gold during DP resolved by adjusting the pH and aging time [3, 12-16].

The difficulty of reproducibly decorating nanotitania has prompted the investigation of alternative approaches employing hollow titania spheres [21] or supported titania [22-30] although these routes are usually synthetically complex and require the removal of polystyrene templates from the final product [21, 29-30]. In Chapter 6, it was demonstrated that nanosized titania (5 nm) supported on

silica spheres can be successfully fabricated using a simple sol-gel route without the need of pH adjustment, cationic polyelectrolytes, or surfactants [31]. It was also shown that slowing anatase growth during calcination enhances stability, increases specific surface area, and leads to improved photocatalytic activity [31-32]. Here, these developments are extended to the fabrication of low temperature CO oxidation catalysts using DP, where small gold crystals decorate silica-titania core-shell pebbles to deliver a robust co-catalyst of high surface area.

7.2 Gold Deposition-Precipitation (DP)

The pH of the gold stock solution was adjusted by adding 0.1 M NaOH dropwise to 20 ml of 6.35 mM aqueous HAuCl_4 ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.99%, Alfa Aesar). The calcined core-shell support was dispersed ultrasonically (15 mins) in water (1 ml), and then stirred vigorously with the gold stock at 80°C. The reaction pH and aging time were varied to optimize the dispersion of gold nanocrystals on the core-shell structure (Figure 7-1, Table 7-1). The gold seeded spheres were collected by centrifugation (2000 rpm) and washed 5 times using water. The powder was oven dried overnight at 100°C prior to heat treatment in air (200 - 400°C, 2 hrs, 1°C/min).

Figure 7-1 Optimized flowchart for the synthesis of catalysts composed of silica-titania core-shell structures decorated by nanocrystalline gold.

Table 7-1 The variation on the DP reaction pH, temperature and aging time of gold decoration on silica-titania pebbles.

Calcined pebbles (°C)	Reaction pH	Aging Time ^a (min)	Gold Size ^b (nm)
500	6.4	30	3
600	3	30	7
	5	30	7.5
		15	2.5
	6.4	30	3
		60	7.5
	7	30	5
	8	30	2

[a] With a fixed reaction temperature at 80°C.

[b] Determined by HRTEM.

7.3 Materials Characterization

Transmission electron microscopy (TEM) was used to collect bright field and high resolution images (HRTEM). The materials were ground gently and dispersed ultrasonically in water before depositing several drops of the suspension onto a holey carbon-coated copper grid.

Powder X-ray diffraction (XRD) patterns were collected in the manner detailed in Section 6.3. Diffracted intensity arising from amorphous silica spheres was refined at 20-23° by inserting a single Fundamental Parameters peak (FP) (Section 6.3) [31]. The absolute mass of silica [31], titania [32] and gold was determined by adding 20 wt% of Al₂O₃ (NIST SRM 676) [33] as an internal standard with the correction reported in Lim et al. [31]. To improve the refinement statistics and reduce microabsorption, each sample was homogenized (20 min) by manual grinding in an agate mortar before collecting XRD powder patterns [34]. The

atomic co-ordinates and thermal parameters of anatase [35] and corundum [36] were fixed at the reported values.

7.4 Catalytic Testing

A portion of the catalyst was pre-heated at 200°C for 1 h to remove impurities in a fixed-bed microreactor in which 50 mg catalyst was introduced for study of the core-shell support, while the dilutions by α -alumina (10 mg catalyst and 20 mg inert material) were applied to examine the influence of pH (3 to 8) and aging time (15 to 60 min) on performance. After cooling to room temperature, a reactant gas (1 vol% CO in air) was passed through the catalyst bed with a gas hourly space velocity (GHSV) of 15000 h⁻¹. The gas outlet was connected to an on-line gas chromatograph (GC) (Shimadzu-14B) equipped with thermal conductivity (TCD) and flame ionization (FID) detectors.

7.5 Structure of Core-Shell Support

Titania nanocrystals homogeneously coated the silica core at all calcination conditions (200 – 1000°C) irrespective of the dominant polymorph (anatase or rutile) or crystal size, with the development of larger crystals at higher temperatures leading to greater surface roughness. Quantitative XRD analysis showed the average titania crystallite size remains < 9 nm up to 1000°C as the silica core inhibits anatase growth prior to its reconstructive transformation to rutile (Figure 7-2) [31]. The pebbles heat-treated at 600°C gave the lowest relative amorphous content due to crystallization of the primary gel. The specific surface area (44.3 m²/g) was comparable to the pebbles calcined at 500°C (48.6 m²/g) but far greater than for free nanotitania powder (3.8 m²/g) (Table 6-2) [31].

7.6 Catalyst Optimization for CO Oxidation

7.6.1 Effect of Core-Shell Support

Gold loaded on pebbles calcined at 600°C at pH 6.4 with 30 min aging resulted in homogeneous nanocrystal (~ 3 nm) loadings (Figure 7-3a). While the morphology of the pebbles calcined at 500°C and 600°C was similar, the dispersion of the gold crystals is evidentially distinct (Figure 7-3a-b) and correlates with anatase crystallinity, since attachment is pseudo-topotaxial via the close packed Au {111} and anatase oxygen {112} layers [18]. Consequently, the 600°C pebbles with higher anatase crystallinity provide better developed {112} surfaces that promote higher gold loadings and stronger interfacial adhesion. As expected, bare pebbles are inactive towards CO catalytic oxidation at all temperatures, but complete CO conversion was possible at 35°C for the gold decorated 600°C pebble co-catalysts, which proved more efficient than the 500°C pebbles (78°C) (Figure 7-3c). Based on these preliminary results, subsequent optimization of the co-catalysts was conducted using the pebble supports fabricated at 600°C.

Figure 7-2 (a) The change of relative amorphous content (▲) and average crystallite size (■) of silica-titania pebbles as a function of temperature, and (b) the morphology of pebbles calcined at 600°C and coated with titania nanocrystals (~ 5 nm) but without gold decoration.

Figure 7-3 Bright field images of gold nanocrystals deposited on silica-titania pebbles calcined at (a) 600°C and (b) 500°C prepared at pH 6.4, 30 min aging and heat-treatment at 200°C. (c) CO conversion of bare silica-titania pebbles, pH 6.4 gold catalysts.

7.6.2 Effect of Synthetic pH

At pH 3-4 the neutral species ($\text{AuCl}_3 \cdot \text{H}_2\text{O}$) is dominant, and as the pH is raised, undergoes stepwise hydrolysis to $\text{AuCl}_2(\text{OH})_2^-$ (pH 5), $\text{AuCl}(\text{OH})_3^-$ (pH 6-7), and finally to $\text{Au}(\text{OH})_4^-$ (pH 10) [11]. Electrostatic attraction between the anionic species and the shell is favored at mid-pH values near the IEP (pH 6.2) of titania synthesized from an ethoxide precursor [37]. In acidic conditions, the gold nanocrystals (~ 7.5 nm) are poorly distributed over the titania shell as adsorption is unfavorable (pH 3) or takes place slowly (pH 5) (Figure 7-4a). By adjusting to pH 6.4 - 7, highly dispersed gold nanocrystals (3-5 nm) are obtained when the concentration of $\text{AuCl}_2(\text{OH})_2^-$ increases, leading to more rapid nucleation and growth (Figure 7-4b). At pH 8 where the prevalent species are $\text{AuCl}(\text{OH})_3^-$ and $\text{Au}(\text{OH})_4^-$, the gold nanocrystals are smaller (~ 2 nm) and dispersion remains high (Figure 7-4c). Under stronger basic conditions (pH > 8) metal deposition is hindered by electrostatic repulsion between the gold hydroxide complexes and the negatively charged titania surface.

Figure 7-4 Gold nanocrystals decorated on silica-titania pebbles (600°C) at pH (a) 5, (b) 7, (c) 8, and (d) the correlation of pH with CO conversion of supported gold catalysts.

Table 2 The calculated loading wt% and average crystallite size of gold supported on pH 6.4 (30 min) catalysts with calcination temperature.

Temperature (°C)	Loading Amount (wt%)	Average Crystallite Size (nm)
200	4.0	4.5
300	3.7	5.9
400	4.4	23.9

Because 100% CO conversion proved exceedingly rapid using the pure catalyst (35°C, 50 mg loading) (Figure 7-3c), dilution by α -alumina (66% by mass) was applied in subsequent experiments to better correlate activity and microstructure. For an optimal catalyst, the highest loadings and smallest gold crystals proved most active (pH 6.4, loading 4.0 wt%, Table 2) achieving 100% CO conversion at 90°C (Figure 7-4d). In contrast, complete oxidation required a higher temperature (105°C) for the pH 8 catalyst (2.5 wt%), while the pH 7 catalyst (126°C) was less effective as the gold was partially agglomerated (Figure 7-4b). The poorest performance was observed for the pH 5 pebbles which coincided with the largest sizes and inferior gold dispersion.

7.6.3 Effect of Gold Crystal Size

To further optimize the pH 6.4 catalysts, the DP aging time was varied from 15, 30 to 60 mins to control gold particle size. A shorter aging time (< 30 mins) produces gold (3 nm) of superior consistency (Figure 7-5a-b) and similar catalytic activities (90°C for 100% CO conversion) (Figure 7-5d). Where gold agglomeration (5 – 7 nm) was found after 60 min aging total conversion required 115°C (Figure 7-5c).

Figure 7-5 The crystal growth and distribution of gold loaded on pH 6.4 catalysts with aging times of (a) 15 min, (b) 30 min, (c) 60 min, and (d) their catalytic efficiencies of CO oxidation.

Figure 7-6 The distribution and size of gold nanocrystals on pH 6.4 catalysts after calcination at (a) 200°C, (b) 300°C, and (c) 400°C. (d) In XRD the strength of the {111} Au reflection is indicative of texture that arises from pseudotexture between the pebble anatase and gold crystals.

7.6.4 Effect of Calcination on Gold Nanocrystals

After heat-treatment at $< 200^{\circ}\text{C}$ the hemispherical gold single crystals (~ 3 nm) were homogeneously distributed over the pebbles calcined at 600°C (Figure 7-6a), but at higher temperatures faceting was evident with agglomerated sizes of ~ 6 nm (300°C) and ~ 20 nm (400°C) (Figure 7-6b-c). Quantitative X-ray phase analysis of the calcined catalysts confirmed gold loadings of 3.7 - 4.4 wt% and average crystallite sizes from 4.5 – 24 nm (Table 2). The oxide support is unchanged by treatment at 400°C with anatase the dominant dimorph in agreement with an earlier crystal chemical study of the non-decorated pebbles [31]. The anomalously high intensity of the gold $\{111\}$ Bragg reflections in the XRD pattern is indicative of texture that preferentially exposes these atomic planes (Figure 7-6d) [2, 18, 38]. This observation is consistent with lattice imaging (Figure 7-7) that directly reveals twinning [39] promoted by the strong interaction between the mismatched metal and anatase close-packed layers [18].

Figure 7-7 HRTEM image of a twinned gold crystal displaying $\{111\}$ faceting from a catalyst prepared at pH 6.4 catalyst and calcined at 400°C .

This chapter describes a simple DP method to homogeneously decorate silica-titania core-shell pebbles with gold nanocrystals (< 5 nm) with fabrication of these catalysts tuned for low temperature CO oxidation by appropriate selection of support, reaction pH, aging time and heat treatment. The optimal parameters for producing highly dispersed gold nanocrystals (3 nm) were (i) support pebbles calcined at 600°C , (ii) setting the DP pH at 6.4, (iii) restricting the aging time to 15 – 30 min, and (iv) avoiding excessive metal crystallization after drying by treating at 200°C (Figure 7-1). Nucleation and growth of gold was favored for $6.4 < \text{pH} < 8$ that was slightly above the IEP (pH 6.2) of sol-gel synthesized titania [37]. These catalysts were highly active towards CO oxidation before (100% conversion at 35°C) and after (90°C) dilution with alumina. The directly deposited gold crystals are hemispherical (~ 3 nm), but after mild heat treatment ($< 200^{\circ}\text{C}$) facets develop, and from $300 - 400^{\circ}\text{C}$ agglomerates (6 – 20 nm) appear. The preferential exposure of $\{111\}$ gold faces through interaction with the $\{112\}$ planes of anatase provides for robust interfacial connections and high concentrations of active low coordination sites.

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Chapter 8

Future Designs for Titania Catalysts

Recognizing titania phase complexity and the enhanced properties of the core-shell architectures leads directly to novel designs for better catalytic efficiency and selectivity. Magnetic core titania catalysts are proposed to resolve the problem of recovery and reuse, while the fabrication of metal and alloy decorated silica-titania pebbles can greatly extend the range of applications for these novel materials.

8.1 Principle Outcomes and Implications for Catalyst Design

These studies have led to a deeper understanding of the relationship between the titania dimorphs, specifically the role of an intervening amorphous phase during the anatase to rutile transformation. The implications of the presence of this ubiquitous encapsulating phase on catalytic activity remains to be fully explored. However, future studies should include the quantitative assessment of its content and correlate its abundance with physical properties (e.g. surface area) and functionality. Several studies have established that anatase crystal growth can be delayed through the introduction of “separation” phases such as alumina, and it seems likely that aperiodic material plays a similar role by enveloping crystalline polymorphs.

Recognition of phase complexity also impacts upon the synthesis of chemically modified titanias and the design of core-shell architectures. While variation in unit cell parameters is sometimes used to assess if band-gap modifying dopants have entered titania, the extent to which bulk non-stoichiometry (i.e. titanium vacancies) can modify the lattice metric is still not commonly recognized. Therefore, some care is needed when using diffraction methods to validate chemical insertions. In addition, the robustness of core-shell structures may benefit from the capacity of decorating metals to attach to titania substrates via an amorphous coating. While work in this area remains preliminary, it is clear that for CO oxidation catalysts, the temperature at which the titania support prepared is critical to optimize reaction rates, and is probably linked to the structure of the metal-oxide interface.

8.2 Magnetic Core Titania Catalysts

At the completion of waste water treatment, titania photocatalyst powders must be separated by filtration or centrifugation before the effluent is reused or discharged. Enhanced settling of the suspended titania in solid-liquid photocatalytic systems can be achieved by charge neutralization, coagulation and flocculation [1], however, such approaches may be uneconomic due to the large wastewater

volumes involved. As a result, the notion of immobilizing titania on a magnetic substrate / support to simplify recovery is attractive [2-8], especially when coupled with a fabrication process that generates large surface areas, a high concentration of active sites, and greater adsorptive capacity.

The feasibility of recovering suspended titania after heterogeneous photocatalytic reaction via magnetic separation has been established by Chen et al. [9-10] who reported the fabrication of a magnetic titania, $\text{TiO}_2/\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ composites. The introduction of a SiO_2 shell is essential to reduce the photodissolution effect of $\gamma\text{-Fe}_2\text{O}_3$ by inhibiting electronic interactions at the heterojunction with titania during illumination. It was found that $\text{TiO}_2/\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ structures gave superior UV degradation rates of orange II and fluorescein compared to $\text{TiO}_2/\gamma\text{-Fe}_2\text{O}_3$ core-shell structures, $\text{TiO}_2 + \gamma\text{-Fe}_2\text{O}_3$ mineral powders and $\gamma\text{-Fe}_2\text{O}_3$ particles [10]. Recently, magnetite core titania catalyst ($\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$) synthesis using a sol-gel technique had been reported by Beydoun and workers [11-13] following from the promising findings of Chen et al [9-10]. However, the fabricated magnetic cores (Fe_3O_4 nanoparticles) were in colloidal form with irregular morphology and the recovery and regeneration of photocatalytic activity has not been investigated thoroughly.

Based upon the present study, it is proposed that magnetic core catalysts $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ pebbles can be prepared and optimized in the same manner as the silica-titania core-shell composite described in Chapter 6. The preparation of these tri-stratal pebbles should be a relatively simple extension of the methods developed for bi-stratal materials, and possess the properties needed for environmental wastewater purification. Monodispersed Fe_3O_4 spheres with regular particle sizes of 7-13 nm can be obtained by a general liquid-solid-solution method [14]. The SiO_2 layer between the Fe_3O_4 kernel and titania shell will prevent the former from parasitically scavenging excitons during photooxidation which will detract from photocatalytic activity [69]. The titania coating will be the active catalytic phase. A similar sol-gel technique can be applied to coat the SiO_2 encapsulating the magnetic core [9-13] by titania following the methods described in this thesis.

8.3 Noble Metals/Metal Alloys Loaded Silica-Titania Catalysts

In Chapter 7, a silica-titania structure was successfully tailored for carbon monoxide oxidation by the introduction of very small gold nanocrystals (3 nm). The optimized core-shell co-catalysts exhibited promising catalytic CO conversion efficiency at relatively low temperature ($\leq 90^{\circ}\text{C}$). Similarly, other silica-titania supported catalysts can be fabricated to achieve high catalytic performance for environmental catalysis including:

- (i) Decoration by noble metals, such as Pt, Pd, Ru and Rh, for selective catalytic oxidation of carbon monoxide (CO), propane (C_3H_8), formic acid (HCO_2H), acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) and phenol ($\text{C}_6\text{H}_5\text{OH}$) [15-18].
- (ii) The loading of bimetallic alloys, including Sb/Pd, Ni/Fe, Co/Ni, Pt/Pd and Au/Co, for direct synthesis of aromatic and heteroaromatic acetate, Fisher-Tropsch synthesis, carbon dioxide (CO_2) reforming of methane, selective oxidation of SO_2 and propene epoxidation [19-23].

The novelty of these catalysts would arise not only with respect to the support architecture, but also by the development of a deposition-precipitation (DP) method (described in Section 7.2), rather than the commonly reported, incipient wetness co-impregnation method [15-17, 18-23].

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