Electrophoretic deposition of TiO₂ nano-particles : the peroxo-titanium route to fabricating photocatalytic films

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ELECTROPHORETIC DEPOSITION OF TiO_2 NANO-PARTICLES: THE PEROXO-TITANIUM ROUTE TO FABRICATING PHOTOCATALYTIC FILMS

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ABBREVIATIONS

AFM	Atomic force microscopy
APCVD	Atmospheric pressure chemical vapour deposition
BE	Binding Energy (eV)
CE	Counter electrode
CIF	Crystallographic information file
DLVO	Dergajuin-Landau-Verway-Overbeek
E₀	Electric field strength (V cm ⁻¹)
EDL	Electrical double layer
EPD	Electrophoretic deposition
F	Photon flux (photons cm ⁻² s ⁻¹)
FQE	Formal quantum efficiency (molecules photon ⁻¹)
FWHM	Full width half modulation
G-C	Gouy Chapman
I	Light intensity (W cm ⁻²)
J	Current density (A cm ⁻²)
MR-	Micro- reflectance- Fourier transform infrared spectroscopy
PTC	Peroxo-titanium complexe/s
PXRD	Powder X-ray diffraction
R_a	Average roughness (nm)
RE	Reference electrode
RF	Heating under reflux
R_q	Root-mean-square roughness (nm)
R_t	Total roughness (nm)
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
U	Particle velocity (m s ⁻¹)
UV	Ultraviolet
VASE	Variable angle spectroscopic ellipsometry
V_e	Electromobility (m V ⁻¹ s ⁻¹)
VOC	Volatile organic compounds
WCA	Water contact angle (°)
WE	Working electrode
XPS	X-ray photon spectroscopy
z₋	Negative ion charge
z₊	Positive ion charge

LIST OF SYMBOLS

ζ	Zeta potential (V)
μ	Viscosity ($\text{kg m}^{-1} \text{s}^{-2}$)
λ	Wavelength (nm)
ϵ	Dielectric constant of the medium: $\epsilon_0 \times \epsilon_r (\text{C}^2 \text{J}^{-1} \text{m}^{-1})$
ϵ_0	Permittivity of free space (Const.) : $8.854 \times 10^{-12} \text{C}^2 \text{J}^{-1} \text{m}^{-1}$
ϵ_r	Relative permittivity of the medium ($\text{C}^2 \text{J}^{-1} \text{m}^{-1}$)
ψ	Surface potential (V)
δ	Electric double layer thickness (nm)
η	Particle electromobility ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$)
ϕ	Interaction energy (J)

ABSTRACT

TiO₂ materials are inorganic semi-conductors that experience electron- hole separation when irradiated with UV light ($\lambda < 380\text{nm}$) possessing energy greater than its band gap. This photon- induced charge separation is widely considered to react with ambient oxygen and water to produce reactive oxygen species (ROS) such as $\cdot\text{OH}$, O_2^- , $\cdot\text{O}$, $^1\text{O}_2$ and H_2O_2 . ROS produced on photo-activated TiO₂ films undergo reactions with organic compounds to produce harmless by-products. Concomitant to these photo-sensitized reactions is the UV-induced super-hydrophilicity of TiO₂ surfaces. As such, the photocatalytic and hydrophilic properties of TiO₂ films have been utilized in commercial products such as self-cleaning coatings, solar conversion cells and water/air purification reactors.

There are several established techniques to produce TiO₂ thin films including sol-gel dip coating, atmospheric chemical vapour deposition (APCVD) and electrophoretic deposition. In terms of cost and energy efficiency, low temperature aqueous electrophoretic deposition provides an attractive alternative to the other techniques. Conventional electrophoretic deposition (EPD) processes utilize acidic and/or organic suspensions. These acidic and organic EPD suspensions pose environmental problems such as the evolution of volatile organic compounds (VOCs) during EPD and the need for acidic waste disposal after EPD.

In the present work, the electrophoretic deposition of TiO₂ films was achieved within a neutral, aqueous and low temperature environment. By utilizing a stable peroxo-titanium suspension containing anatase particles during the EPD process, no high temperature post annealing was required to convert amorphous films to photocatalytic crystalline TiO₂ films. The properties of the electrophoretically deposited TiO₂ films were analyzed through photocatalysis and surface wettability tests. The quantum efficiency of the deposited films was determined through FTIR spectroscopy and photochemical calculations. Surface wettability tests involving the Sessile method of water contact measurements determined that the electrodeposited films exhibited UV-induced hydrophilicity. The mechanism/s motivating super- hydrophilicity was investigated through X-ray photon and FTIR spectroscopy.

Investigations in the EPD process showed that colloid stability was critical in maintaining deposited film uniformity. The colloidal stability of anatase particles within EPD suspensions was attributed to the electrostatic stabilization of anatase particles with negative peroxo-titanium ions. Using EPD fabrication techniques, O₂ evolution at the depositing electrode during water electrolysis was used to alter the nanostructure of electrodeposits. The

photocatalytic rate constants of deposited films were found to increase by ~70% as deposited grain sizes increased from 35 to 50nm; similar rate constant increases of ~75% were observed when film R_a values increased by several nanometers. The use of the EPD process was demonstrated to produce photoactive TiO_2 films. Potential control during deposition could be utilized to vary the fabricated film morphology, and hence directly influence film photoactivity. During TiO_2 photocatalysis, the hydrophilicity of TiO_2 films was observed. Based on XPS, FTIR and water contact angle measurements, the hydrophilic nature of UV irradiated TiO_2 surfaces was attributed to the increased hydroxylation and degradation of hydrophobic organic monolayers on the film. Preliminary investigations on the bioreactivity of UV irradiated TiO_2 films towards the *Escherichia coli DH5a* strain suggested that EPD fabricated films could be utilized as photocatalytic substrates for biological reactors.

1. Introduction and Objective

Heterogenous photocatalytic reactions and their coupling applications have gained much interest academically and industrially since photoelectrochemistry research started in the early 1900s. The use of the semiconductor material TiO_2 in the water-splitting experiment first conducted by Fujishima and Honda in 1969 introduced a multitude of industry possibilities. Today, TiO_2 photocatalysis technology is used in self-cleaning surfaces in hospital indoor tiles and external building scaffoldings,[1] air[2] and water purification,[3] anti-bacterial surfaces for biomedical facilities,[4] UV sensitized cancer cell killing[5] and biomedical implant anti-inflammatory coatings[6]. Presently, much research on TiO_2 photocatalysis has been concentrated on the thin film application of TiO_2 materials for photocatalytic applications. Active research areas in TiO_2 film fabrication include optimizing the strength and adhesion of TiO_2 particles to film supports, improving TiO_2 photocatalytic efficiency, and developing deposition systems that optimize coating properties such as TiO_2 film uniformity and coverage.

These problems are presently being researched by a large number of global industrial and research institutes signaling a great potential for TiO_2 thin film self-cleaning technology. In 2005, “Innovations Report”, an industrial forum funded by Siemens, introduced an industrial project termed the “Development and evaluation of coatings and surface conditions on steel for antibacterial and easy-to-clean properties, DECOBIOF” to be run by a research team constituting personnel from CORUS UK Limited (UK), the Max Planck Institute (Germany), OCAS-Arce-lor N.V. (Belgium), SIMR (Sweden), ACERINOX (Spain) and the Centro Sviluppo Materiali (Italy).[7] Other research and commercial institutes have joined the race to develop viable TiO_2 in terms of function and strength, and these include the Laboratory for Environmental Research, Nova Gorica Polytechnic, Slovenia[8] (Sept 2004), Tampere University of Technology, Finland[9] (in collaboration with Finnish companies, ABR Innova Oy and Beneq Oy, May 2006) and the Institute for Nanoscale Technology in Sydney, Australia (June 2006)[10] to list a few. Apart from current ongoing research, the boom in TiO_2 thin film photocatalysis has spurred many commercial products that exhibit self-cleaning such as SunCleanTM (Self-cleaning glass windows by company PPG)[11]

Pilkington ActivTM (Self- cleaning glass substrates by company Pilkington)[12] and, concrete and cement coatings with self cleaning TiO₂ (by construction company, Skanska),[13] to name a few. Although TiO₂ coated glass are already being sold as commercial products, the study of photocatalytic TiO₂ on stainless substrates have largely been confined to laboratory research without the production of a commercial product.

In this project, the objective is to develop an energy efficient and environmentally friendly electrodeposition technique to fabricate TiO₂ films on stainless steel substrates for photocatalytic applications. Stainless steel is the substrate of choice due to its high mechanical strength, anti corrosion properties and wide application realm. Apart from the wide use of stainless steel materials in heavy industries, stainless steel is also utilized for building scaffolding, indoor and biomedical facilities. The fabrication of photocatalytic TiO₂ films on stainless steel supports produces self cleaning surfaces that can minimize the buildup of dirt and bacteria in indoor and outdoor living spaces. The development of such technology is in line with the global push in research for green technology that can alleviate the burden of increasing pollution within cities.

This report presents the developmental work done in optimizing the EPD process for uniform TiO₂ film fabrication and the subsequent characterization of the deposited film properties. In the following second and third chapter of the present work, the theoretical background in the EPD technique and TiO₂ photocatalysis was respectively discussed. The subsequent fourth chapter presents the experimental work done in optimizing the electrophoretic deposition of photocatalytic TiO₂ films. Following which, the fifth chapter presents the use of the developed EPD technique to vary TiO₂ film morphology; the morphological effects on TiO₂ film photocatalytic efficiency was analyzed through AFM measurements in this chapter. In the subsequent sixth chapter, the UV light-induced hydrophilicity of the electrodeposited TiO₂ films was analyzed through water contact angle measurements, X-ray photon spectroscopy and FTIR spectroscopy. In the proceeding chapter seven, the anti-bacterial properties of the electrodeposited films were analyzed using a biological probe (*Escherichia coli*) to determine the bactericidal function of the electrodeposited films. In conclusion, the eighth chapter summarized the various capabilities of TiO₂ films fabricated through

this newly developed electrophoretic deposition process and the future outlook of this project was discussed.

2. Theroretical Background on Electrophoretic Deposition and TiO₂ Photocatalysis

The theoretical background pertaining to the mechanism of electrophoretic deposition and TiO₂ photocatalysis is discussed in this chapter. This chapter is separated into 2 major sections; the first section (section 2.1) introduces the theory relating to electrophoretic deposition while the second section (section 2.2) covers topics relating to the science of TiO₂ photocatalysis.

2.1 An Introduction to Electrophoretic Deposition

Electrophoretic deposition is a deposition technique where ceramic deposits/ green bodies are formed directly from stable colloidal suspensions under a constant applied electric field. The mechanism of EPD observed by Ulberg *et al.*[13] was divided into 2 major processes: electrophoresis and electrocoagulation. Electrophoresis is defined as the motion of particles towards an oppositely charged electrode under an applied electric field. During electrophoresis, the electric field directly controls the particle motion via the particle surface charge. On the other hand, electro-coagulation refers to the coagulation of charged particles near an oppositely charged electrode; this step is a necessary and intermediate step before actual deposition can occur. The mechanism in which electro-coagulation occurs is not well- understood and several theories have been proposed to predict this phenomenon, these include: particle charge neutralization, pH and ionic concentration changes near the electrode, and particle electric double layer relaxation. In the section 2.1.1, particle electrophoresis is discussed in relation to the electric field induced particle movement that arises due to the formation of charges on the particle surface. In the following section 2.1.2, the formation of this charge is discussed in relation to other forces acting on the particle such as electrostatic attractive forces. The concept of colloid stability is discussed in the DLVO (Derjaguin-Landau-Verway-Overbeek) theory. In addition, the electro-coagulation models developed are discussed alongside the various electrophoretic deposition strategies currently utilized.

2.1.1 Electrophoresis: Electrokinetic parameters

Particle transport via electrophoresis occurs when an electric field (applied current or voltage) is exerted on a charged particle. In a single particle system surrounded by air, the electrokinetic behaviour of the particle is determined by its surface potential (Ψ_s). This parameter still exists when the particle is submerged in a suspension, although it is no longer deterministic of the electrokinetic behaviour of the particle within the suspension as shown in Fig 2.1.

Considering a diphasic solution containing non-permeable solid particles within a liquid solvent, the movement of the particle within the solution is now determined by its electric double layer and more specifically, its zeta potential. The formation of an electric double layer around submerged particles has been attributed to the following processes:[14]

1. Surface group ionization and dissociation: The particle surface ions can dissociate within a solvent to change the ionic charge around the particle (i.e. $[\text{particle-OH}] \rightarrow [\text{particle}]^+ + \text{OH}^-$).
2. Isomorphic substitution: The particle surface ions may be substituted by a lower valence ion within the solution to change the overall charge of the particle (i.e. $[\text{particle-Ti}^{4+}]^x + [\text{Al}^{3+} \text{ solution}]^{-x} \rightarrow [\text{particle-Al}^{3+}]^{x-1} + [\text{Ti}^{4+} \text{ solution}]^{1-x}$).
3. Preferred ionic adsorption: Solution ions preferentially adsorb onto charged particles with opposite charge. This type of adsorption normally occurs when ionic surfactants are externally added to particulate suspensions (i.e. $[\text{Particle-NH}_3\text{Cl}]^x + [\text{surfactant solution}] \rightarrow [\text{Particle-NH}_3]^{x+1} + [\text{Cl}^-, \text{NH}_3^+ + \text{surfactant solution}]$).

Figure 2.1 Formation of electric double layer surrounding particles submerged in solvents.

The adsorption of ionic layers through the above-mentioned mechanisms is known formally as the formation of the electric double layer. The concept of an electric double layer was first theorized by Hemholtz to contain a layer of affixed counter-ions (ions of opposite charge to the charge particle/ surface) and an adjacent diffuse layer.[15] Within this diffuse layer, electroneutrality is maintained. The theory of such a diffuse double layer was also independently developed and presented as the Gouy-Chapman (G-C) diffuse double layer model.[16,17] In the G-C model, the diffuse double layer does not experience charge neutrality and the ions in the solutions are regarded as point charges within a homogenous dielectric medium. Although the G-C model has been found to provide close quantitative predictions of the electrokinetic behavior of the charged surface for low surfaces potentials ($\Psi_s \sim 25\text{mV}$), there are several assumptions that limit its practical use. The G-C model considers solution ions as point charges with negligible solvation spheres and hence ionic diameter. The practical implication of this assumption would be the infinite physical approach of ions towards the charged surface. As such, estimations based on the G-C model have generally produced electric double layer thicknesses that are generally smaller than those experimentally measured.

Figure 2.2 Stern model of the electric double layer.[18]

In 1924, Stern[18] suggested an electric double layer model that unified the concept of a molecular capacitor and an adjacent diffuse layer containing ions with a finite size. The structure of the Stern electric double layer model is shown schematically in Fig. 2.2. In Fig. 2.2, the stern layer consists of a layer of stationary counter-ions and the thickness of this layer is defined as the radius of the counter-ion and its solvation sphere. The definition of a stationary counter-ion layer electrostatically bound near the charged surface is similar to the concept of a molecular capacitor first presented by Helmholtz. In the Stern model, the potential at this layer is known as the Stern potential (Ψ_δ) and is considered to be equivalent to the IHP potential (Ψ_1) defined in the Helmholtz model. The adjacent diffuse layer consists of a relatively larger concentration of mobile counter-ions than co-ions. This potential drop within this diffuse layer is considered to be similar to that defined in the G-C model. The total thickness of the EDL (δ) is defined as the combined length of the dense layer and diffuse layer of ions surrounding the charged surface.

A new electrokinetic parameter known as the electrokinetic or zeta (ζ) potential is introduced in the Stern model. This ζ potential is considered to be the potential that resides on the hydrodynamic plane of shear; this is an imaginary plane defined such that ions within this boundary move together with the charged entity and ions that exist outside this boundary are considered to shear away as the charged entity moves. Henceforth, it is thus implied that during electrophoresis, the movement of the particle 'seen' by the liquid is dominated by the ζ potential rather than the surface charge of the particle per se. However, the ζ potential of a particle cannot be easily measured experimentally. Instead, the ζ potential is calculated from various theoretical models using the measured particle electromobility. Particle electromobility within a suspension is defined as the particle velocity per unit of applied electric field. During optimized electrophoretic deposition, the film formation is directly controllable by the applied electric field and hence, singularly dependent on particle electromobility. This direct field effect on the deposition process would not be possible if particle sedimentation occurs. Particle sedimentation is an indication of suspension stability and this is directly associated to the electrostatic, London van der Waals and gravitational body forces. In the following chapter, the importance of particle electromobility in electrophoretic deposition is discussed. The relevance of the

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electrostatic repulsion and hence colloid stability due to particle ζ potential is also analyzed.

2.1.2 Electrophoresis: Particle electromobility and colloid stability

In the earlier part of this chapter, the origin of surface charge and predominantly, zeta potential on charged surfaces/ particles was introduced. An association map of the discussed parameters is schematically shown in Fig. 2.3. The terms in grey were discussed in the previous section. In this section, the theoretical models developed to convert particle electromobility into particle ζ potential are discussed. Additionally, the connection between particle ζ potential and suspension stability is analyzed within the construct of the DLVO theory.

Figure 2.3 Overview of parameters that directly affect the EPD process.

2.1.2.1 Particle electromobility conversion to ζ potential

The zeta potential of a particle is theoretically defined as the potential at the “boundary” of the hydrodynamic plane of shear. During electrophoresis, particle transport occurs and ions within the hydrodynamic boundary of shear move along with the particle while ions exterior of this boundary shear away. Experimentally, this plane is difficult to define and techniques such as laser Doppler electrophoresis are utilized to determine this quantity indirectly. The laser tracks particle motion by correlating

Doppler shifts when a known alternating electric field is applied. The experimentally obtained variable is known as the particle electromobility. The particle electromobility is the velocity of a charged particle for every unit of electric field applied. The SI units for this variable is $\text{m s}^{-1} \text{V}^{-1}$. Theoretically, the electromobility variable is derived from the Poisson- Boltzman calculations of charge distribution. In order to understand the physics behind the observed phenomenon of electromobility, several theoretical models that correlate particle surface charge to particle electromobility have been derived.

The connection between particle velocity to ζ potential during electrophoresis was first developed by Smoluchowski[19]. The following expression for particle velocity under an applied electric field was derived:

$$U = \frac{\varepsilon \zeta}{\mu} E_0 \quad (\text{E 2.1})$$

where U (m/s) is the particle velocity due to the applied electric field, E_0 (V/m) and ε ($\text{C}^2 \text{J}^{-1} \text{m}^{-1}$), μ (Pa s), and ζ (V) refer to the suspension dielectric constant, viscosity and zeta potential respectively.

The Smoluchowski expression in (E 2.1) is valid for particles that have considerably thin homogeneous electric double layers across the particle radius, i.e. $\frac{a}{\delta} \gg 1$, where a and δ are the particle radius and particle electric double layer thickness respectively. Additionally, the surface potential uniformity across the radius of the particle assumes that the particle material is non-conducting. In the practical context, a particle with a considerably small electric double layer would result during cases where the surface potential is considerably low or when the ionic concentration of the suspension is extremely high. As such, the limiting condition of $\frac{a}{\delta} \gg 1$ is restrictive for particles submerged in low ionic suspensions that have large electric double layers. Thus, a model depicting particle electrophoresis within the range of $\frac{a}{\delta} \ll 1$ was developed by Debye-Hückel.[20]

The Debye-Hückel approximation is valid for cases whereby the electric double layer thickness is sufficiently larger than the particle radius, i.e., $\frac{a}{\delta} \ll 1$. The expression is also derived based on the interaction of hydrodynamic and electrophoretic forces. However, in the Debye-Hückel approximation, the electric double layer is thick, implying that the curvature of the particle and thus, fluid flow across the particle occurs radially. As such, unlike the Smoluchowski expression, the Debye-Hückel expression does not approximate fluid flow across the particle radius to flow across a horizontal plate. In Fig 2.4, the body forces acting on a single spherical particle during electrophoresis are schematically shown.

Figure 2.4 Body forces acting on a negatively charged single sphere under a constant electric field.

The Debye-Hückel expression for particle electromobility is thus derived as equation (E 2.2).

$$\eta = \frac{U}{E_0} = \frac{2\zeta\epsilon}{3\mu} \quad (\text{E 2.2})$$

The Debye-Hückel expression differs from the Smoluchowski expression by a factor of $2/3$. Later analysis by Henry[21] defined this factor as $f(a/\delta)$ and solved the above expressions for the limiting case of $1 \ll a/\delta \ll 1$. It would be prudent to note however, that both the Smoluchowski and Debye-Hückel expressions make underlying assumptions that might not prove to be valid in practical circumstances. Firstly, the electric double layer relaxation around the particle is not considered. During electrophoresis, the ionic concentration around the particle does not remain symmetrically distributed as the particle moves. The electric double layer relaxes, and

results in an uneven charge distribution such that there is a significant difference in surface charge density between the leading and trailing edge of the particle motion. As such, a correction factor is generally applied to the electromobility or ζ potential term for specific predictions of particle movement during electrophoresis.

Another assumption made in the development of the Debye-Hückel and Smoluchowski model is the non-conductance of the particle experiencing electrophoresis. This consideration would imply that the applied electric field bends around the particle and its electric double layer; the particle and its electric double layer does not modify the direction or magnitude of the externally applied electric field. In circumstances when porous particles are used, this would be an important implication. Clearly, these assumptions would not be valid within a practical context when predicting absolute values of particle electromobility. However, in the case where the particle electromobility is directly measured and the zeta potential needs to be defined to determine the relative stability of the particles via the DLVO theory, the theoretical construct of either model would be adequate given that the model used for electromobility conversion to zeta potential is consistent. In the following section, the effect of zeta potential on the electro-osmotic repulsion between particles within our TiO₂ suspensions is discussed. The experimentally obtained electromobility values were converted into zeta potential values using the Smoluchowski relation (E 2.1); these zeta potential values were approximated as the particle surface potential and subsequently used to calculate the electro-osmotic repulsion forces. The resultant effect of the electro-osmotic repulsion and London van der Waals attraction forces on colloid stability was calculated and analyzed via the DLVO theory.

2.1.2.2 Colloid Stability: DLVO theory

During EPD, the presence of coagulated particles can result in poor particle packing within the deposited films. Additionally, in the cases where gravitational potential energy (sedimentation) exceeds the applied electric potential energy, deposition of particles on the electrode is unlikely to occur. The stability of a colloidal suspension is predominantly determined by its propensity to flocculate and/ or coagulate. An unstable colloid will experience rapid flocculation and as a consequence, particle sedimentation occurs rapidly. Considering the above definition of colloidal

stability, the term ‘rapid’ appears contentious: how is rapid or even slow flocculation defined? In the practical context, a suspension can be considered stable during EPD if flocculation and sedimentation does not occur during the deposition duration. Theoretically, the stability discussed in the present chapter is transient and can more accurately be determined as meta-stability. However, instead of discussing colloidal stability as a function of time (sedimentation), the concept can be analyzed more appropriately by the determination and comparison of energy quantities. In a colloidal suspension containing charged particles that predominantly experience electro-osmotic and London van der Waal interaction energies, the DLVO theory describes the likelihood of particle coagulation and hence, provides a uniform platform to compare the colloidal stability of different suspensions.

2.1.2.2.1 Electro-osmotic repulsive energy, ϕ_r

In the earlier section, the Debye length, κ , was introduced when the Debye-Hückel model was discussed. The inverse Debye length, κ^{-1} , determines the electric double layer thickness, δ . The κ^{-1} variable defines the particle to particle electro-osmotic repulsion as two equally charged particles approach each other. As two particles approach each other, the interaction between the suspension free ions and the particles’ electric double layer results in ionic diffusion. The ionic diffusion results in an electro-osmotic flow and hence pressure between the two particles and their respective electric double layers. The electro-osmotic pressure is the repulsive energy present between two approaching particles. Therefore, the κ^{-1} values of the two approaching particles directly affect the electro-osmotic repulsive energy between two particles. The inverse Debye length can be calculated from the Poisson Boltzmann distribution and is defined in (E 2.3) for symmetric ionic suspensions.

$$\kappa^{-1} = \left(\frac{\epsilon k_B T}{2e^2 z^2 n_\infty} \right) \quad (\text{E 2.3})$$

Where ϵ is the dielectric constant of the suspension, k_B is the Boltzmann constant ($1.3806503 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$), T is the temperature in Kelvins, e is the electron

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charge (1.602×10^{-19} C), z is the solution ion charge ($z=1$ for H^+ and $z=-1$ for OH^-) and n_∞ is the ionic number concentration.

The ionic number concentration can be calculated from the suspension ionic molarity and Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$):

$$n_\infty = \left(M \frac{\text{mol}}{L} \right) \left(1000 \frac{L}{m^3} \right) \left(N_A \frac{1}{\text{mol}} \right) \quad (\text{E 2.4})$$

In diluted colloidal aqueous suspensions, the major ionic species are considered to be H^+ and OH^- . The concentration of either ion, since $[H^+] = [OH^-]$ can be derived from direct pH measurement of the suspension. The suspension pH is known as the “power of hydrogen” and is directly associated with the H^+ concentration, $[H^+]$ by (E 2.5):

$$\text{pH} = -\log_{10}[H^+] \quad (\text{E 2.5})$$

The $[H^+]$ quantity is the suspension ionic molarity, M , in (E 2.5) for aqueous based colloidal suspensions. As such, for an aqueous based suspension with known pH values, the ionic concentration, n_∞ can be calculated. The known ionic concentration can then be used to solve for the inverse Debye length, κ^{-1} , in (E 2.3).

The inverse Debye length, κ^{-1} is a variable in the Derjaguin approximation for particle to particle repulsive interaction energy, ϕ_r . [22,23] The interaction energy, ϕ_r is defined by the Derjaguin approximation given in (E 2.6).

$$\phi_r = \varepsilon \left(\frac{k_B T}{e} \right)^2 G_D \left[\mp (\psi_1 + \psi_2) \ln(1 - e^{-2\kappa h}) \right] + 2\psi_1 \psi_2 \ln \left(\frac{1 + e^{-\kappa h}}{1 - e^{-\kappa h}} \right) \quad (\text{E 2.6})$$

For equally charged spheres, $\psi = \psi_1 = \psi_2$. The Derjaguin electrostatic repulsion can be simplified to (E 2.7).

$$\phi_r = 2\varepsilon G_D \left(\frac{k_B T}{e} \right)^2 \psi^2 \left[\mp \ln(1 - e^{-2\kappa h}) + \ln \left(\frac{1 + e^{-\kappa h}}{1 - e^{-\kappa h}} \right) \right] \quad (\text{E 2.7})$$

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The variable G_D introduced earlier in (E 2.6) and (E 2.7) is known as the Derjaguin shape factor.[22,23] The shape factor of 2 spherical particles with radius' of a_1 and a_2 is:

$$G_D = \frac{a_1 a_2}{a_1 + a_2} \quad (\text{E 2.8})$$

For equal spherical particles, the shape factor is $0.5a$, where $a=a_1=a_2$ is the radius of the two approaching particles.

2.1.2.2.2 London van der Waals attractive energy, ϕ_a

In the DLVO theory, the electrostatic London van der Waals (LVDW) attraction energy, ϕ_a counters the electro-osmotic repulsive energy, ϕ_r . The LVDW interaction energy between 2 spherical particles is defined in equation (E 2.9).[22,23]

$$\phi_a = -G_D \left(\frac{A}{6h} \right) \quad (\text{E 2.9})$$

where A is the Hamaker's constant for the particle material in vacuum, G_D is the Derjaguin shape factor of the interacting particles and h is the interparticle distance.

The Hamaker's constant for different materials in a vacuum environment is commonly found in the literature.[24] In the practical context, for discussions pertaining to colloidal suspensions, particle to particle interaction occurs within a solution. As such, the Hamaker's constant can be determined for a diphasic system as:[25]

$$A_{212} = \left(A_{11}^{1/2} - A_{22}^{1/2} \right)^2 \quad (\text{E 2.10})$$

The subscript in this 'combined' Hamaker's constant is derived for the intervening medium (suspension) (1) and two approaching particles of the same material (2). A_{11} and A_{22} are the respective Hamaker's constant for the suspension and the particle material.

2.1.2.2.3 Total interaction energy, ϕ_t

The two previous sections defined the repulsive and attractive interaction energy particles experience when they approach each other. Utilizing the DLVO theory, the total interaction energy between two approaching particles can be derived by the summation of the electro-osmotic repulsive energy and the LVDW attractive energy:[22,23]

$$\phi_t = \phi_r + \phi_a \quad (\text{E 2.11})$$

The DLVO total interaction energy can be plotted for any 2 approaching particles once parameters defining the repulsive and attractive energies are known. The magnitude of repulsive and attractive energy increase as they approach closer. The generalized DLVO profiles of ϕ_t , ϕ_r and ϕ_a are plotted in Fig. 2.5.[22,23]

Figure 2.5 Generalized DLVO total interaction energy.

Considering the DLVO profile in Fig. 2.5, it can be observed that the final DLVO profile is heavily dependant on the individual repulsive and attraction energy profiles. As discussed in the earlier sections, these profiles are essentially defined by colloidal suspension characteristics such as suspension ionic concentration, particle size and geometry, and surface potential. The DLVO total interaction energy shown in Fig. 2.5 has several features such as two energy barriers (E_{b1} , E_{b2}) and two energy wells. E_{b2} is the energy barrier that must be overcome before reversible coagulation can occur between two particles. The approach between the two particles is considered to be reversible because the following secondary minimum energy well is shallow. To escape the shallow energy well, external agitation of the colloidal suspension can provide the required energy impetus for particle separation. As the particles approach closer, their electric double layers overlap and the electro-osmotic repulsive energy dominate. The next energy barrier, E_{b1} has to be overcome before irreversible particle coagulation can occur. The following deep energy well dominates until the particle surfaces meet infinitely close. At this point, the repulsive energy must dominate since it is not physically possible for the two particles to approach pass each particles' surface. However, the classical DLVO theory illustrated in Fig 2.5 does not explain particle to particle interaction as they approach infinitely closer to each other.

2.1.2.2.4 Assumptions and limitations of the DLVO theory

Considering the earlier sections on the separate components of the DLVO theory, several assumptions were made. The fundamental assumption of the DLVO theory is that the interaction between two colloidal entities is solely attributed to electro-osmotic repulsive energy and LDVW attractive energy. In practical circumstances, other forces such as steric repulsive energy may be present in the colloidal system. Ligands chemically adsorbed onto the surfaces of particles would provide additional repulsion between two particles.

Analyzing the individual components of the DLVO theory, one may observe certain assumptions regarding the calculation of the electro-osmotic repulsion energy. During the determination of the Debye length of colloidal particles, the Poisson-Boltzmann distribution is utilized. The Poisson-Boltzmann distribution assumes that the ions are point charges without finite physical dimensions. This assumption would not apply when two particles approach within a few nanometers of each other.[26] Additionally, in the DeJaguin approximation, the geometry of the two approaching particles is assumed to be independent of the particle surface roughness. The distribution of ions around particles with high roughness values would not be as uniform as assumed in the DLVO theory. The non-heterogeneity of charges around particles results in the DLVO theory overestimating the magnitude and range of the total interaction energy between approaching particles.

Despite the limitations of the DLVO theory, the theory provides remarkably accurate qualitative information on colloidal stability in complex colloidal systems.[2,14,26] In practical applications, the DLVO theory can be used to qualitatively compare the colloidal stability of particulate suspensions with negligible steric energy interactions.

2.1.2.2.5 Case study: DLVO prediction of TiO_2 colloid stability

In the various pots of TiO_2 solutions that were synthesized through the peroxo-titanium route (see chapter 4.2 and 4.3 for details), the zeta potentials and particle sizes were measured (see chapter 4.3). Briefly, the TiO_2 colloids of varying stability were synthesized by refluxing amorphous peroxo-titanium solutions for 2, 4 and 8 hours.

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The measured and calculated variables are summarized in Table 2.1. The calculated variables summarized in Table 2.1 were derived by substituting the measured variables into equations (E2.1), (E2.3), (E2.4), (E2.5), (E2.8), (E2.1) and (E2.10). The measured variables were subsequently used to calculate the electro-osmotic repulsive energy, ϕ_r , and the London van der Waals attractive energy, ϕ_a , through equation (E2.7) and (E2.9) respectively, as a function of inter-particle distance, h . The total interaction energy, ϕ_t , could then be obtained through (E2.11) and is plotted in Fig. 2.6.

Table 2.1 Measured and calculated variables required for DLVO analysis.

Measured variables	TiO ₂ Colloids		
	RF 2	RF 4	RF 8
pH	7.3 ± 0.3	8.0 ± 0.4	7.8 ± 0.1
Electromobility, × 10 ⁻¹⁰ (m V ⁻¹ s ⁻¹)	-5.89 ± 0.39	-5.47 ± 0.55	-2.13 ± 0.06
Aggregate particle radius, a × 10 ⁻⁹ (m)*	10.52 ± 0.32	12.73 ± 0.75	14.11 ± 1.05, 127.50 ± 0.95
Solution conductivity × 10 ⁻³ (S cm ⁻¹)	0.45 ± 0.01	0.31 ± 0.01	0.35 ± 0.01
Calculated variables			
Ionic number concentration, n _∞ × 10 ⁻⁸	5.01	1.00	1.58
EDL thickness, κ × 10 ⁻⁶ (m)	1.36	3.04	2.41
Debye length, κ ⁻¹ × 10 ⁵ (m ⁻¹)	7.36	3.29	4.14
Zeta potential, ζ × 10 ⁻³ (V)	-75.16 ± 9.72	-68.89 ± 6.97	-26.76 ± 0.72
Hamaker's constant, A ₂₁₂ × 10 ⁻²⁰		9.98	
Derjagun shape factor, G _D × 10 ⁻⁹ (m)	5.26	6.36	7.05, 63.75
Physical constants[#]			
Dielectric constant, ε		8.8854 × 10 ⁻⁸	
Boltzman constant, k (J K ⁻¹)		1.380 650 × 10 ⁻²³	
Electron charge, e (C)		1.602 176 × 10 ⁻¹⁹	

* Aggregate particle sizes of colloidal particles were measured in solution through the dynamic light scattering technique (see chapter 4.2 for details).

[#] Values of physical constants are valid for an ambient temperature of 298K.

From Fig. 2.6, it can be observed that for RF2 and RF4 colloidal particles, an energy barrier exists as the inter-particle distance, h , decreases to approximately 30nm. However, no such energy barrier was observed for RF8 colloids containing particle sizes of 14.1nm and 127.5nm. Particles within the RF8 colloids were found to experience negative interaction energy (overall attractive energy) at interparticle

distances of less than $\sim 180\text{nm}$; conversely, RF2 and RF4 colloidal particles had to approach each other within 15nm or less before they experience an overall attractive energy.

Figure 2.6 (a)DLVO interaction energy of synthesized TiO_2 nanoparticulate solutions and **(b)**photo of the various TiO_2 nanoparticulate solutions. (RF 2, 4 and 8 refer to the duration of reflux during the synthesis of the solution- reader is referred to chapter 4.2 and 4.3 for details).

From the present DLVO calculations, RF8 colloids were found to be the least stable among the three colloids. Experimentally, we observed that longer heat treatment resulted in an increase in particle sizes and a decrease in colloid transparency. By observation of the various colloids, it was found that particles within RF2 and RF4 colloids did not experience significant sedimentation even after 2 to 3 months, while RF8 colloids were found to experience particle aggregation and sedimentation within a matter of 3 to 5 days. From literature, various experiments conducted on colloids have found a good correlation between colloidal stability and an electromobility with a critical ζ potential of $25\text{-}30\text{mV}$. [27] In our experiments, a similar correlation was observed; the stable RF2 and RF4 colloids had a ζ potential value of ~ 75 and 68mV respectively while the flocculating RF8 colloids had a ζ potential value of $\sim 27\text{mV}$.

2.1.2.3 Electrophoretic particle deposition

The electrophoretic deposition of films from colloidal suspensions requires the movement of charged particles near the depositing electrode and the subsequent deposition of the particles on the depositing electrode. Although the electrokinetic behavior of colloidal particles is well established, the mechanism in which deposition occurs on the electrode is not well understood. The exact deposition mechanisms of particles remain controversial and seem to vary for different colloidal systems. The following sections discuss the various mechanisms of particle deposition as particle accumulation, electrochemical coagulation and charge neutralization occurring at the depositing electrode.

2.1.2.3.1 Deposition by Particle Accumulation

In 1939, Hamaker and Verway[28] observed that colloidally stable suspensions slowly formed mechanically strong sediments that did not easily disperse upon external agitation. On the other hand, they also observed that unstable and flocculated suspensions resulted in weak and low density sediments that easily dispersed with little external agitation. The 2 accompanying observations led Hamaker and Verway to suggest that electrophoretic deposition required a stable suspension. The primary function of the applied electric field was to draw the particles near the depositing electrode and did not play a dominant part in the subsequent electro-coagulation mechanism. It was thus suggested that particle accumulation on the electrode occurred due to the pressure building near the electrode as more particles were attracted to the same location. It was also observed that in some cases, deposited layers exhibited characteristics of a viscous fluid (solid-gel like). These observations showed that the density and uniformity of deposits compacted on the depositing electrode had a direct causal link to the colloid stability and hence, the surface potential of the depositing particles.

Later experiments conducted by Sarkar and Nicholson[29] also observed the development of a viscous layer during EPD of unstable suspensions. They suggested that the deposit viscous behavior was not a result of energistic interactions between the

concentrated deposit and less concentrated suspension, but rather a direct consequence of zeta potential reduction near the depositing electrode. Sarkar demonstrated this through the deposition of particles via a dialysis membrane that allowed the transition of ions but not particles.[30] He found that regardless of the location of the membrane, deposits were formed on the membrane. This observation supports Hamaker's and Verway's pressure building mechanism where particles brought within the vicinity of any surface are pressed by other approaching particles brought near to the surface by the externally applied electric field, hence forming a deposit by a local increase in pressure. However, regarding the formation of a viscous deposit through the equilibration of potential energy near the electrode, Sarkar found that this was not so since depositing occurred on the membrane at any location between the cathode and anode. The use of a dialysis membrane that filters ions in this experiment also excludes the possibility of ions resulting in electrochemical precipitation that could aid the formation of deposits; the most probable cause for deposition is zeta potential reduction near the membrane. Subsequent experiments by Giersig *et al.* on the deposition of gold colloids under low voltages of 10- 100mV at short durations of a few seconds proved that pressure buildup near the depositing electrode could not be the sole mechanism resulting in deposition of particles onto the electrode.[31] Depositions carried out at low voltage for short durations could not have allowed the buildup of particles and pressure near the electrode. The existence of a thin gold monolayer resulting from the above EPD parameters suggested that pressure buildup near the electrode occurs after a certain time had passed, and continues after an initial intermediate unknown mechanism. The discrepancies between the proposed mechanism of Hamaker *et al.* and other groups resulted in the formulation of an alternative mechanism by Sarkar *et al.*[29] and the development of alternative models of deposition occurring during EPD.

2.1.2.3.2 Deposition via Electrochemical Coagulation

The mechanism of electrochemical coagulation arises from the difference in suspension chemical concentration near the electrode compared to in the bulk suspension. Koelmans and Overbeek[27] observed that during electrophoresis, a fluid layer appeared adjacent to the oppositely charged electrode; the fluid layer however, did not make contact with the electrode until the repulsion between the double layer of

the incoming particle flux and the electrode had been overcome. Therefore, an adhering deposit could only be formed after a critical time of electrophoresis had elapsed. More specifically, this critical time was directly associated to the transport of ions via diffusion, thereby changing the electrolyte concentration at the depositing electrode.[27]

Cathodic reactions resulting in the production of OH⁻ near depositing electrodes were later determined by Zhitomirsky.[32] Zhitomirsky[33] also proposed the electrochemical route of forming titania deposits via the hydrolysis of a titanium precursor in a methyl alcohol- water mixture, the proposed chemical reactions are as follows:

The generation of OH⁻ species near the depositing electrode is postulated as:

The decomposition of the electrosynthesized peroxotitanium hydrate deposit by subsequent sintering produces:

From E2.14 above, it becomes apparent that Zhitomirsky's proposed electrosynthesis of titanium peroxo hydrate requires a subsequent sintering step for crystallization into TiO₂ which may result in the formation of cracking and mechanical detachment of deposits.

Apart from the electrochemical coagulation mechanisms observed by Zhitomirsky, Sarkar *et al.* proposed another electrochemical process that occurs when no noticeable increase in chemical concentration is observed near the depositing electrode. Sarkar *et al.* postulated that fluid dynamics and the applied electric field resulted in the distortion of the double layer surrounding particles thus causing a non-uniform

distribution of zeta potential around the particle. The deposition process proposed to occur near the depositing electrode using a model suspension of Al_2O_3 particles in ethanol is schematically shown in Fig. 2.7. The mechanism of deposition shown in Fig. 2.7, was proposed based on observations made during the electrophoretic deposition of positively charged Al_2O_3 particles. Consider an overall positive lyosphere system $[(\text{M-OH}_2)^+ \cdot \text{X}^-]$ that moves towards the cathode under an externally applied field. The adsorbed counter-ions that travel with the particle under an applied electric field reorganize as the approaching particle reaches the cathode, this causes the double layer envelope to thin near the depositing edge and expand at the trailing end. As deposition occurs, the positive ions are also attracted to the depositing electrode, while the positive ions near the trailing end of the lyosphere become attracted to negative ions within the lyosphere and shear off from the lyosphere envelope. As the particle is deposited onto the electrode, the lyosphere reduces in size and the thinning of another approaching particle allows for electrocoagulation to occur.

Figure 2.7 Deposition Mechanism proposed in ref[29].

The proposed deposition mechanism occurring for the Al₂O₃ system proposed by Sarkar *et al.* was subsequently countered by an alternative mechanism observed during EPD from the same system. De and Nicholson found that electrochemical reduction of H⁺ occurred at the cathode, contrary to Sarkar's postulation that electrochemical reactions did not occur in the Al₂O₃ system.[30] It was proposed that apart from the singular thinning of the particle lyosphere occurring near the depositing electrode, it was the simultaneous electrochemical reduction of H⁺ at the electrode that resulted in the change in local pH near the electrode. The local increase in pH towards the isoelectric point (the pH value where Al₂O₃ particles have near zero zeta potentials) resulted in the subsequent deposition. The discharge of H⁺ near the depositing electrode occurs as follows:

The charge transfer occurring at the depositing electrode consumes H⁺ thus causing a local reduction in H⁺ concentration. The resultant concentration gradient variation with distance and time was solved by De *et al.* using the classical diffusion equation and the solution obtained was:

$$C = C_{bulk} - \frac{\lambda}{D_{eff}^{0.5}} \left[2 \left(\frac{1}{\pi} \right)^{0.5} \exp \left(\frac{-x^2}{4D_{eff}t} \right) - \frac{x}{D_{eff}^{0.5}} \left\{ 1 - \operatorname{erf} \left(\frac{x^2}{4D_{eff}t} \right)^{0.5} \right\} \right] \quad (\text{E 2.16})$$

Figure 2.8 (a) H⁺ concentration gradient, (b)pH gradient, both with respect to distance to depositing electrode and as a function of deposition time.[30]

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The solution above was used to predict the concentration of H⁺ near the depositing electrode and is plotted in Fig. 2.8(a-b). Fig. 2.8(a) shows the co-ion H⁺ concentration increase as the deposition time is increased. A concentration gradient with respect to an increase in distance to the depositing electrode can be observed. Fig. 2.8(b) shows the change in pH with respect to the distance between the depositing electrode and the bulk suspension, as the deposition time was increased. From Fig. 2.8(b), it can be observed that as steady state is reached by fluid diffusion and charge transfer of H⁺ ions, the pH on the depositing electrode reaches a value of 7. At pH 7, the Al₂O₃ particles' zeta potential approaches near zero (the isoelectric point) and flocculation of Al₂O₃ particles results in the formation of a deposit.

2.1.2.3.3 Deposition via Charge Neutralization

Other studies conducted on suspensions differing from those reviewed in the former sections were found to undergo a different deposition mechanism. Grillion *et al.* proposed that deposition during EPD occurred because particles experienced charge neutralization as they touched the depositing electrode, thus losing their propensity for motion.[34] Such a proposed mechanism was found to be dominant for single/monolayer deposition from dilute suspensions during short durations but not in cases where deposition time is long (deposits formed are thick) and where electrochemical variations near the depositing electrode such as a concentration gradient or pH gradient occurred.

2.1.2.3.4 Electrophoretic deposition strategies

There are generally 2 broad TiO₂ electrodeposition strategies: 1)electrochemical gelation[32,33,35-40] and 2)direct particle deposition.[41-48] In the electrochemical gelation process,[32,33,35-40] the synthesis of an amorphous peroxo-titanium solution is first achieved through the hydrolysis of titanium alkoxides (Ti-OR) or the partial peroxide (H₂O₂) dissolution of TiO₂ powders in acidic organic solvents. The peroxo-titanium solution is subsequently used as the electrochemical/ electrophoretic bath to form a peroxo-titanium hydrate film. A crystalline TiO₂ film is then formed by sintering the peroxo-titanium hydrate at temperatures above 300°C. While the technique has been reported to produce thick TiO₂ films, problems related to the

uniformity and homogeneity of the film usually arise due to the high sintering temperatures required after deposition. [20, 21] Furthermore, the peroxo-titanium solutions used during electrophoretic deposition are usually acidic and have a pH range of 1.5 to 3.1.[32,33, 35-40] In general, more recent studies on the electrolytic/electrophoretic deposition of TiO_2 films have involved various permutations of the forementioned technique; these permutations include the variation of deposition substrate materials [35-37] and the patterning of deposited film morphology through templating [38-40]. The templating method has produced TiO_2 films with differing morphology such as nanorods and nanotubules (see Fig. 2.9).

Figure 2.9 (a) TiO_2 nanorods achieved by electrodeposition through an anodic alumina membrane (AAM) [38] and (b) TiO_2 nanotubule film achieved through electrodeposition on a ZnO template.[39]

Alternatively, other studies have used the direct particle deposition strategy to avoid the high temperature sintering step required in the electrochemical gelation strategy. [41-48] While crystalline TiO_2 particles could be used to directly deposit crystalline TiO_2 films with photocatalytic functions, the electrophoretic baths used are usually fully or partially organic and environmentally unfriendly. The need for organic solvents is associated to the nature of TiO_2 particles (ranging from several μm in diameter) in solutions; TiO_2 particles have been shown to disperse well in ethanol[41,42] and isopropanol[48] solvents. Recently, the shift towards environmentally friendly film fabrication techniques has increased research interest in the semi-aqueous route of electrophoretically depositing TiO_2 films. [43,44] These studies [43,44] report the stabilization of TiO_2 particles through the addition of additives such as polyethylenimine[43] and polyvinyl butyral.[44] Indeed, the use of

organic compounds or solvents are generally prevalent in synthesized electrophoretic baths.[41-48] Recent developments in this direct particle deposition strategy have involved permutations of external deposition factors such as the application of a magnetic field during deposition[49] and the compaction of deposited particles during electrophoretic deposition.[50] Perhaps one interesting study in this area of work is a new colloidal stabilization technique using nanoparticle halos; the stabilization of negligibly charged micron sized particles in deionized water was achieved by adding a critical volume of highly charged nanoparticles.[51] The study is unique as the stabilization is not electrostatically dependent or fully steric. In conventional electrostatic stabilization strategies, the stabilization of particles is attributed to the formation of charges around particles. Alternatively, in conventional steric stabilization strategies, additives such as surfactants (containing charged or neutral ligands) are adsorbed onto particle surfaces; these ligands act as coils adsorbed onto the particle surface, sterically repeling otherwise flocculating particles. In ref [51], stabilization is not accrued to the particle by the adsorption of ligands, but rather, the presence of a critical volume of highly charged nanoparticles; this stabilization was achieved without any adsorption of the nanoparticles onto the microspheres. The observations of this stabilization technique are shown in Fig. 2.10. Such a technique is potentially viable for stabilizing micron-sized TiO_2 particles within a solute matrix of TiO_2 nanoparticles, thereby creating interesting deposited film morphologies, with variable photocatalytic activity towards organic compounds (since differing particle sizes have been shown to affect photocatalytic activity of TiO_2 materials[52,53]).

Figure 2.10 (a) Volume fraction, Φ , plots for microspheres and highly charged nanoparticles ($a_{\text{micro}} = 0.285\mu\text{m}$; $a_{\text{nano}} = 3\text{ nm}$) at $\text{pH} = 1.5$. (a is the particle diameter) (b) Optical images and accompanying schematic illustrations of the phases in regions: (i) gel containing large aggregates, (ii) fluid with stabilized microspheres, and (iii) gel of smaller aggregates. Optical micrographs

(scale bar = 5 mm) correspond to samples prepared from dilute mixtures of larger microspheres ($a_{\text{micro}} = 0.001$; $a_{\text{micro}} = 0.590$ mm) and nanoparticles. The accompanying illustrations highlight the proposed distribution of microspheres (in blue) and nanoparticles (in red) in solution. [51]

2.1.2.4 Summary

An important implication of the forementioned studies in sections 2.1 and 2.2 is that colloidal stability is directly associated to the electrophoretic deposition process. From a review of the various electrodeposition strategies used to deposit TiO_2 films, it becomes apparent that regardless of the techniques used, organic and usually acidic solvents are widely used to maintain colloidal stability during deposition.[35-48] Furthermore, efforts in developing a semi-aqueous deposition technique have involved the use of organic additives or stabilizers.[43,44] While these techniques[39-48] have been found to produce photocatalytic and thick TiO_2 films, there are major drawbacks such as the emission of VOCs (volatile organic compounds) during high voltage electrophoretic deposition and the presence of organic compounds within the deposited films. Organic content within TiO_2 films can be detrimental to film photoactivity. Similarly, permutations of essentially similar electrolytic/electrophoretic deposition routes have focused on external deposition parameters to alter film structures/ morphology for the optimization of deposited TiO_2 films photoactivity. Alternatively, the development of new peroxo-titanium synthesis methods (to produce stable, neutral and entirely aqueous TiO_2 colloids) that contrast starkly from the conventional electrophoretic deposition strategies could be attempted.

2.2 An Introduction to Titanium dioxide photocatalysis

Semiconductor photocatalysis is an intense area of interest in photoelectrochemistry. This research area is focused on semiconductor sensitized photocatalysis, in which the semiconductor materials act as a photo sensitizing material that promotes a photochemical reaction as a result of the initial absorbed radiation. Among the many semiconductor materials that have been studied for photocatalytic properties (n-SrTiO₃, n-MoSe₂, p- GaAs), only the TiO₂ semiconductor is capable of both photo induced oxidation and superhydrophilicity. However, the presence of superhydrophilicity is noncommittal to photo oxidation and both properties are usually present in varying degrees depending on the synthesis method of the catalyst. The following sections summarize the semiconductor characteristics of the TiO₂ material, along with reported works on the photoinduced functions and mechanisms occurring during TiO₂ photocatalysis.

2.2.1 Basic principles of TiO₂ semiconductor photocatalysis

TiO₂ materials belong to a group of metallic compounds known as semiconductors. The Ti element has a valance charge of 4+ and its metal oxide is known as a group (IV) semiconductor. Semiconductor materials exhibit different electronic and atomic properties from insulators or pure conductors due to their electronic band structure. The electronic properties of a material are defined by the band theory that essentially describes the allowed electronic energy levels that exists for different materials. The difference in band structure for insulators, conductors and semi-conductors are schematically shown in Fig. 2.11. It can be observed from the schematic diagram that the semiconductor band structure is somewhat a 'hybrid' of that for conductor and insulator materials. In insulators, the energy gap between the conduction and valance band is wide; an infinitely large input energy is required to allow the movement of charge between the bands that is required for conductivity. Conversely, in conductor materials, the valance and conduction band consist of multiple levels that overlap each other thus facilitating the transfer of charge between the two bands. Alternatively, in semiconductor materials, the conduction and valance band is separated by a small and finite Fermi energy (E_f) and band gap energy (E_{bg}). Conductivity (or electron mobility) within the semiconductor material occurs when an energy input that is greater than the band gap energy is provided. TiO₂ materials are n-type

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semiconductors that result in electron (e⁻) movement and hole (h⁺) formation within the lattice when UV light (<380nm) with photon energy greater than E_{bg}=hν=3.2eV is illuminated on TiO₂ materials (see E2.17).

Figure 2.11 Difference in band structure of insulators, conductors and semiconductors.

During UV initiated electron-hole separation, the electrons and holes generated within the TiO₂ semiconductor lattice migrate towards the surface of the TiO₂ particle and experiences electron/ hole driven processes that are presented in (E2.18) to (E2.24) and Fig. 2.12 (A and B represent adsorbed organic compounds that are reduced and oxidized respectively). [54] The nomenclature for the symbols in (E2.18 to E2.24) and Fig 2.12 are defined in Table 2.2.

The photochemical reactions that occur on TiO_2 semiconductor surfaces are known to have redox abilities towards biological[55-61] and organic compounds under aerated conditions.[62-71] The generalized electrochemical pathways that occur during TiO_2 semiconductor photocatalysis are summarized in Fig. 2.12.

Table 2.2 Nomenclature for symbols in (E2.18) to (E2.24) and Fig. 2.12

Parameters	Definition
h_{vb}^+	Valance band positive "hole"
h_s^+	Surface positive "hole"
e_{cb}^-	Conduction band negative electron
e_s^-	Surface negative electron
A (A^-)	Adsorbed organic compounds that are reduced
B (B^+)	Adsorbed organic compounds that are oxidized
h	Plank's constant= $6.262 \times 10^{-34} \text{ J}\cdot\text{s} = 4.136 \times 10^{-15} \text{ eV}\cdot\text{s}$
v	Frequency of radiation (s^{-1})

Figure 2.12 Major electron- hole reactions occurring on a TiO_2 particle under UV illumination with photon energy $\geq E_{bg}$.

2.2.2 TiO_2 material properties

Titanium dioxide is usually found bound to other elements and are found in minerals such as Rutile, Anatase, Ilmenite, Brookite, Leucosen, Perovskite and Sphene. Each of these minerals contain different percentages of TiO_2 with Rutile containing the highest percentage (93- 96% TiO_2). Apart from the various polymorphs of TiO_2 found naturally (anatase, brookite, rutile, etc.), synthetic high pressure methods have produced 2 new polymorphs from rutile: TiO_2 (II)- having a PbO_2 crystal structure[72] and TiO_2H - having the Hollandite structure. Application driven

research on the comparative photocatalytic activity and stability of the various polymorphs have found anatase TiO₂ to be photocatalytically most active and rutile to be most stable in room temperatures.[73-75] The mechanism of the anatase to rutile conversion via increased pressure or temperature methods has been researched in many papers concerning applications of TiO₂ as a photocatalyst, catalyst, additive or ceramic membrane material.[76-78]

Initial studies on the band gap energy of the anatase and rutile TiO₂ polymorphs suggested that the anatase phase of TiO₂ would result in higher photocatalytic activity as compared to the rutile phase due to its larger band gap energy (anatase: 3.0eV, rutile:3.2eV). It was earlier postulated that the larger band gap in anatase TiO₂ would deter recombination of the electron and holes formed during photocatalytic reactions, thus promoting the self-cleaning interaction between the free radicals and organic waste. Later studies subsequently disproved this,[79] dissociating band gap energy from the photocatalytic effect of the various polymorphs of TiO₂. It has been suggested in various papers [78,79] that alternative intermediate reactions between the radicals in anatase promote the recombination of electron hole-pairs, although direct proof of the validity of these intermediate reactions have been elusive even though the presence of intermediate reactions have been identified via the detection of by-products.

The wealth of studies related to the photoinduced reactivity of TiO₂ materials have largely been attributed to the wide industrial application of TiO₂. The recent trend towards nanotechnology has also opened new opportunities in surface science studies of TiO₂ surfaces and nanoparticles. Since the discovery of the photocatalytic properties of TiO₂, several defining mechanistic studies have been conducted to directly show the behavior of TiO₂ surfaces during UV irradiation; these studies focused on explaining the science behind the photocatalytic and superhydrophilic functions of TiO₂ coatings. The following section reviews the literature on TiO₂ photochemical reactions and applied research.

2.2.3 Early work on TiO_2 photocatalysis

The photo-oxidative property of TiO_2 was first discovered by Fujishima and Honda[80] when initial research on TiO_2 (a group IV metal) as a semiconductor for photochemical solar conversion cells was conducted. The concept of TiO_2 UV light induced water splitting was physically observed in a photochemical cell containing an n-type single crystal TiO_2 semiconductor electrode and a platinum black counter electrode in an electrolyte suspension. Without the application of an external voltage and upon UV light activation, the circuit was found to generate its own short-circuit current. This occurred alongside the production of oxygen and hydrogen at the TiO_2 and platinum black electrode interfaces respectively. The gas generation during UV-light activation showed that water could be decomposed into its singular components without the application of an external potential. The experiment resulted in the postulation of key reactions involved in TiO_2 photo-oxidation of water. These have since become widely accepted in the field of photocatalysis.

The experiment setup used to directly observe the photo-oxidation of water is shown in Fig. 2.13. Upon UV light irradiation of the TiO_2 electrode, electron-hole separation occurred and the detection of a voltage was directly associated to the photogenerated electron charge carriers. The production of electron hole carriers resulted in the photo-oxidation of water and hence, the production of oxygen and hydrogen by-products. Drawing a parallel to the photosynthesis of plants with the photo-oxidative properties of TiO_2 , this experiment by Fujishima and Honda was first presented in 1969 in *Kogyo Kagaku Zasshi*[80] (in Japanese) and subsequently in *Nature*[81] in 1972.

Among the developments in research on TiO_2 photocatalysis is the continual work involved in increasing the efficiency of TiO_2 photocatalyst and promoting TiO_2 photocatalysis reactions towards the visible light spectrum. The efficiency of TiO_2 in the visible light spectrum is important as solar energy constitutes largely of visible light wavelengths rather than UV light wavelengths. The enabling of photocatalysis under visible light facilitates the use of TiO_2 photocatalysis in indoor applications.

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Figure 2.13 (a) Photo-oxidation of H₂O on a TiO₂ electrode demonstrated through (b) the experiment setup proposed by Fujishima and Honda. The components listed as 1- 6 are as follows: 1) single crystal n-type TiO₂ electrode, 2) platinum black counter electrode, 3) ionic conducting membrane, 4) gas collector buret, 5) load resistance and 6) voltmeter.[80,81]

To understand the photocatalytic properties of TiO₂, the mechanism/s involved in water photolysis was studied in photoelectrochemistry research through the 1970s and continues to be of research interest. The photochemistry resulting in the reactions for water photolysis (Fig 2.13) is represented schematically in Fig 2.14. It can be observed from the standard electrode potential scale that the standard electrode potential required for electrolysis and hydrogen evolution resides within the band gap energy of TiO₂ semiconductors, thus making it possible for water photolysis at an input energy of $h\nu \geq 3.0\text{eV}$ (UVA and UVB light wavelength).

Figure 2.14 Photochemical mechanism of water photolysis on UV light illuminated TiO₂ electrodes.

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The photo-induced properties of TiO₂ were initially proposed for the efficient production of energy from photochemical solar conversion cells in 1972 and the optimization of solar power conversion from TiO₂ semiconductors was subsequently intensely researched in the 1970s. The first efforts in applying TiO₂ photocatalysis for environmental purposes were initiated by Frank and Bard.[62] In 1977, the Frank and Bard experiment[62] highlighted the use of TiO₂ aqueous electrolyte suspension for the degradation of cyanide in water. After the introduction of the pollutant degradation function of TiO₂ powders by Bard *et al.* in 1977, the focus on TiO₂ photocatalysis rapidly shifted from hydrogen production (through water photolysis) to the photo-oxidation and degradation of pollutants in TiO₂ powder systems. These systems could be utilized in water and air purification applications. Environmental applications of TiO₂ materials moved research interest to the development of TiO₂ films on supports in the late 1980s.

To explain the photocatalytic mechanism/s of UV light activated TiO₂ photocatalysis, research interest in the TiO₂ polymorphs (anatase, rutile and brookite) increased in the 1990s. Initial research by Ohtani *et al.* compared the photocatalytic efficiency of the different TiO₂ polymorphs in the photo-decomposition of 2-propanol.[83] The results from the study showed that the Anatase polymorph was most stable and photoactive. It was proposed that this was a consequence of the large band gap energy of the anatase polymorph obstructing random electron- hole recombination. Shang *et al.* later studied the electronic structure of the 3 polymorphs and confirmed this by showing that anatase had the largest direct band gap energy of 3.22eV.[84]

The Ohtani study defined the subsequent photocatalytic studies on TiO₂ and photocatalysis research was mostly focused on the Anatase polymorph thereafter. Although various studies have shown that Anatase is indeed the most photoactive of the 3 polymorphs, the proposed connection of photoactivity and large direct band gap energy still remains contentious. In addition, the photochemical process by which TiO₂ surfaces oxidize organic species was also debated. Several studies on the oxidization capabilities of TiO₂, proposed that the OH radical was responsible for the breakdown of organic material into CO₂ and H₂O. Alternatively, other studies proposed that the oxidant was in fact the superoxide, O²⁻ that was being produced as the OH radicals attached themselves to the organic pollutant.[85,86] The specific photochemical

degradation of various organic pollutants on TiO₂ surfaces is further discussed in the later section 2.2.3.1.

Towards the end of the 1990s, the focus on photocatalytic TiO₂ for environmental applications moved towards the use of TiO₂ for antibacterial and deodorization purposes such as the coating of hospital tiles and indoor walls. In 1995, the accidental discovery of UV light induced superhydrophilicity was demonstrated by Fujishima *et al.* and expedited the industrial application of TiO₂ thin films.[87] The specific mechanisms resulting in hydrophilicity and the accompanying applications of UV assisted superhydrophilic TiO₂ surfaces is discussed in-depth in the later section 2.2.3.3. In 1995, the novel use of TiO₂ photocatalysis for biomedical applications was also developed; by using an endoscopic TiO₂ delivery system, TiO₂ was transported into a tumor and resulted in the reduction of tumor size under UV light activation.[61] The early part of the 1990s involved much research on the discovery of other semiconductor materials that have similar photo-oxidation and water splitting properties as TiO₂, namely, WO₃, ZnO, CdO and In₂O₃. These materials have been shown to achieve high solar conversion efficiencies, although none have exhibited both water splitting and photo-oxidation functions as well as the TiO₂. Much of the work concerning these other semiconductors has been summarized in literature.[88]

The later part of the 1990s promoted continual research interest in the use of TiO₂ for industrial water and environmental purification systems but with the development of TiO₂ thin film strategies for stronger and more durable photocatalytic coatings. Towards the end of the 1990s, research involving the improvement of TiO₂ photocatalysis was undertaken after the general mechanisms of TiO₂ was determined through laser flash photolysis experiments.[89]

Improvements in TiO₂ photocatalysis, upon understanding the basic mechanisms occurring during UV irradiation of TiO₂ surfaces, were later conducted through novel strategies involving: Variations of TiO₂ structure or morphology, doping of the TiO₂ lattice, sensitization of TiO₂ particulate surfaces and development of composite TiO₂ semiconductors. These strategies along with their respective references are reviewed in the later section 2.2.3.1. Research on the photocatalytic printing technology of TiO₂-polymer composites and the development of novel nanostructured thin films for

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microelectronics and gas sensor applications were developed and first reported in the beginning of 2000.[93]

Table 2.3 Selected TiO₂ Developmental Studies from 1972 to 2006

Year	TiO ₂ Development	Reference
1969-1972	UV activated photolysis of water on n-TiO ₂ electrode (Fujishima <i>et al.</i>)	[81, 82]
1977	First proposed environmental application of TiO ₂ photo-oxidation, Degradation of Cyanide in TiO ₂ slurry by reactions: $CN^- \rightarrow OCN^-$, $CrO_4^{2-} \rightarrow Cr^{3+}$ (Bard <i>et al.</i>)	[62]
1983	Degradation of trichloroethylene and chloromethane in aqueous TiO ₂ suspensions (Pruden <i>et al.</i> [11] ; Hsiao <i>et al.</i> [12] respectively, 1983)	[64,65]
1984	Photo-decomposition of Dibromoethane, Chloroacetic acids and Trichlorophenoxyacetic acids. (Nguyen <i>et al.</i> [54] ; Ollis <i>et al.</i> [55] ; Barbeni <i>et al.</i> [56], 1984)	[66-68]
1987	Degradation of Benzoic acid (Mathews)	[69]
1988	Degradation of Benzoic and Salicylic acid (Mathews)	[70]
1992	Selective killing of T-24 cancer cell by UV light irradiated TiO ₂ particles (Cai <i>et al.</i>)	[61]
1993	Comparison of Photocatalytic properties of TiO ₂ polymorphs (Ohtani <i>et al.</i>)	[83]
1994	Doping of TiO ₂ with Fe ³⁺ , Mo ⁵⁺ , Ru ³⁺ , Os ⁴⁺ , Re ⁵⁺ , V ⁴⁺ & Rh ³⁺ metal ions to improve photocatalytic efficiency (Choi <i>et al.</i>)	[71]
1995	Study of Electronic and Optical properties of TiO ₂ polymorphs (Ching <i>et al.</i>)	[84]
1995	Photo-induced Hydrophilicity of TiO ₂ coated surfaces (Discovery by TOTO Inc, Fujishima <i>et al.</i>)	[77]
1995	Determination of photochemical reactions during degradation of organic compounds by laser flash photolysis experiments (Hoffmann <i>et al.</i>)	[89]
1999	Study on bacteria killing mechanisms of TiO ₂ – reactions in aqueous slurries (Maness <i>et al.</i>)	[90]
2001	Remote oxidation of Methyl Blue organics through the migration of gaseous reactive species from UV irradiated TiO ₂ films- decay kinetics of O ₂ ^{-•} species (Tatsuma <i>et al.</i>)	[91]
2006	Selective patterning of TiO ₂ nanostructures via UV irradiation (Kida <i>et al.</i>)	[92]

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Table 2.3 lists the development of TiO₂ photocatalysis from the 1970s to 2000s. The table lists the discoveries relevant to the studies conducted in this project and is not exhaustive as many important findings related to the materials and application research aspects of TiO₂ have been discovered since Fujishima and Bard studies in 1972 and 1977 respectively.

2.2.3.1 Photocatalytic Degradation of Organic Compounds

The photocatalytic degradation of organic pollutants (cyanide and sulfite) on UV-activated TiO₂ powders or surfaces was first suggested by Bard *et al.*[62] Subsequent studies on the degradation of other organic pollutants was intensively carried out by Ollis *et al.*[64,66,67] In 1995, the photocatalytic studies on TiO₂ powders and films moved from empirical to mechanistic studies to determine the processes occurring during the photocatalytic degradation of organic substances. The first mechanistic study was conducted by Hoffmann *et al.*[89] in the form of laser flash photolysis experiments where the mechanism of UV assisted photodegradation of organic pollutants was proposed. The probable reactions that determine the rate of photo-oxidation of these substances on TiO₂ surfaces are shown in the following Table 2.4.

Table 2.4 Primary processes and their corresponding characteristic time in TiO₂ photodegradation of organic pollutants.[89]

Photo-induced reactions	Characteristic Time
Charge carrier generation: $\text{TiO}_2 + h\nu \rightarrow h^+ + e^-$	Femtosecond (very fast)
Charge Carrier Trapping: $h^+ + >\text{Ti}^{\text{IV}}\text{OH} \rightarrow \{>\text{Ti}^{\text{IV}}\text{OH}^{++}\}$ $e^- + >\text{Ti}^{\text{IV}}\text{OH} \leftarrow \rightarrow \{>\text{Ti}^{\text{IV}}\text{OH}\}$ $e^- + >\text{Ti}^{\text{IV}} \rightarrow >\text{Ti}^{\text{III}}$	10ns (fast) 100ps (shallow trap, dynamic equilibrium) 10ns (deep trap)
Charge Carrier Recombination: $e^- + \{>\text{Ti}^{\text{IV}}\text{OH}^{++}\} \rightarrow \cdot\{>\text{Ti}^{\text{IV}}\text{OH}\}$ $h^+ + >\text{Ti}^{\text{III}}\text{OH} \rightarrow >\text{Ti}^{\text{IV}}\text{OH}$	100ns (slow) 10ns (fast)
Interfacial charge transfer: $\{>\text{Ti}^{\text{IV}}\text{OH}^{++}\} + \text{organic pollutant} \rightarrow \text{Ti}^{\text{IV}}\text{OH} + \text{oxidized pollutant}$ $\{\text{Ti}^{\text{III}}\text{OH}\} + \text{O}_2 \rightarrow \text{Ti}^{\text{IV}}\text{OH} + \text{O}_2^{\cdot-}$	100ns (slow) ms (very slow)

The study[89] showed that TiO₂ surface hydroxyl groups play an important part in the photo assisted degradation of organic compounds. The processes proposed suggest that hydroxyl groups participate directly with photogenerated holes. These photogenerated holes approach the catalyst surface to form highly reactive $\cdot\text{OH}$ surface radicals. The adsorbed hydroxyl groups not only act as surface hole traps but are also considered as adsorption sites for organic compounds. Thus it was deduced

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that peroxo titanium complexes consisting of hydroxyl groups adsorbed on TiO₂ particles and within TiO₂ slurries might greatly aid the photocatalytic degradation of organic pollutants.

Apart from mechanistic studies, empirical studies on the photo assisted degradation of toxic substances on TiO₂ surfaces were analyzed by various research groups.[62,94-103] The bulk of the substances studied and their corresponding proposed reactions are summarized in Table 2.5.

Table 2.5 TiO₂ photosystems for the degradation of organic pollutants.[88]

Degradation Reaction: $A + B \rightarrow A^- + B^+$	Reference
$O_2 + 2NO_2^- \rightarrow 2NO_3^-$	[94]
$O_2 + 2SO_3^{2-} \rightarrow 2SO_4^{2-}$	[62]
$2O_2 + H_2O + S_2O_3^{2-} \rightarrow 2SO_4^{2-} + 2H^+$	[95]
$O_2 + 2CN^- \rightarrow 2OCN^-$	[96]
$5O_2 + 4H^+ + 4CN^- \rightarrow 2H_2O + 4CO_2 + 2N_2$	[97]
$M^{n+} + (n/2) H_2O \rightarrow M^0 + nH^+ + (n/2)O_2$	[62,98]
$M^{n+} + (n/6)CH_3OH + (n/6)H_2O \rightarrow M^0 + nH^+ + (n/6)CO_2$	
(Ag> Pd> Au> Pt >>Rh> Ir >> Cu=Ni=Fe=0 using the following metal salts respectively: AgNO ₃ , PdCl ₂ , AuCl ₃ , H ₂ IrCl ₆ , Cu(NO ₃) ₂ , Ni(NO ₃) ₂ and Fe(NO ₃) ₃	[98,99]
$M^{2+} + (1/2)O_2 + H_2O \rightarrow MO_2 + 2H^+$ ($M^{2+} \equiv Mn^{2+}$ and Pb^{2+} (requires platinized TiO ₂))	[100,101]
$2BrO_3^- \rightarrow 2Br^- + 3O_2$ (works best with Pt/TiO ₂)	[102]
$5O_2 + 6NH_3 \rightarrow 2N_2 + N_2O + 9H_2O$	[103]

The large number of studies conducted on the photocatalytic degradation of various organic compounds necessitates the selection of a standard TiO₂ photocatalyst. A standard TiO₂ photocatalyst provides a uniform platform to compare the photocatalytic degradation of different organic compounds studied by different researchers. The common TiO₂ photocatalyst studied in most of the literature listed above is the Degussa P25 TiO₂ particulate photocatalyst. The Degussa P25 photocatalyst is synthesized through the flame hydrolysis of Titanium tetrachloride (TiCl₄) in the presence of hydrogen and water. The produced powder photocatalyst is 99.5% pure, consisting of ~70% anatase and ~30% rutile phase. It is of cubic particulate form with rounded edges. The P25 powders have a surface area of $50 \pm 15 \text{ m}^2\text{g}^{-1}$ and have an average diameter of 21nm, although the particles do not exist singularly but in aggregates of sizes of approximately 0.1µm in diameter.[104]

Studying the extensive database of organic compounds that can be degraded during TiO₂ photocatalyst, one may observe that TiO₂ photocatalyst exhibit varying degrees of photoactivity for similar organic compounds under identical experiment conditions.[105,106] These differences have been found to be largely attributed to TiO₂ photocatalyst treatment conditions resulting in differences in TiO₂ particle primary and aggregate sizes, morphology, crystallinity, the ratio of active surface sites to photocatalyst surface area and the degree of hydroxylation on TiO₂ surfaces.

2.2.3.2 TiO₂ photoactivity tests

The large number of photoactivity studies on TiO₂ surfaces have given rise to a slew of methods for measuring the photoactivity of TiO₂ surfaces towards organic compounds. Several prominent methods such as the stearic acid test, the dye (methyl blue or orange) test, the gaseous formaldehyde or volatile organic compound (VOC) count test and the E.coli/ bacteria count test have been utilized to determine the efficiency of TiO₂ surfaces in breaking down organic and biological substances. These tests are usually classified into 3 major areas: tests for self cleaning and stain resistant TiO₂ surfaces, tests for antibacterial properties of TiO₂ surfaces and tests for air purification systems containing TiO₂ laden surfaces or filters. The focus of this review is in the testing of self cleaning surfaces and shall thus be focused on the stearic acid test and dye test.

One the most widely used techniques for determining the efficiency of TiO₂ surfaces in breaking down organic substances is the stearic acid test. Stearic acid is an organic compound that is used to represent a standard organic pollutant during photoactivity studies of TiO₂ surfaces. The stearic acid is generally spin or dip coated on TiO₂ surfaces and the decomposition of the compound is observed through spectroscopic techniques such as ellipsometry,[107] FTIR spectroscopy[108] or AFM thickness and morphology[107,109] analysis. The degradation of stearic acid is known to occur as follows:

In the studies referenced above[107-109] and others referenced in the individual studies, the TiO₂ coated substrates under analysis are coated with a thin film of stearic

acid and exposed to UV radiation. An example of the stearic acid test studied in ref [109] is shown in Fig. 2.15.

The FTIR plot (Fig. 2.15(a)) adapted from ref[109] shows the peak absorbance due to the presence of stearic acid on the TiO_2 films. The peak at wavenumber 2957.5cm^{-1} is attributed to the C-H asymmetrical in- plane stretching due to the CH_3 group and the bands at 2922.8cm^{-1} and 2853.4cm^{-1} is caused by the C-H stretching of the CH_2 group. The plot shows the peak areas decreasing as the TiO_2 film is irradiated for 0, 3, 7, 15, 25, 40, 60, 90, and 120 mins of irradiation. The inset absorbance plot shows the decrease in peak area as UV irradiation time is increased. The AFM micrographs shown in Fig 2.15(b) is the stearic acid surface morphology before UV irradiation and Fig. 2.15(c) is the stearic acid surface after UV irradiation, showing an increase in roughness in the stearic acid layer on top of the TiO_2 film as it was being decomposed. These tests have been shown to be viable for directly quantifying the photocatalytic function of TiO_2 films.[107-109]

Figure 2.15 (a) FTIR spectrum of photodecomposition of Stearic acid on UV irradiated TiO_2 surfaces, (inset) Absorbance area plot of FTIR plot as UV irradiation time is increased, (b-c) AFM micrograph of TiO_2 surface before and after UV irradiation.[109]

Apart from the formerly mentioned stearic acid test for self cleaning surfaces, the dye test is another popular technique used to directly show the decomposition of organic compounds on TiO_2 coated surfaces. Dyes such as methyl blue[110] and orange[111] are generally coated on TiO_2 films and the decrease in colour co-ordinates

(x,y or L,a,b) are inspected through a colour spectrophotometer, and subsequently calculated into colour intensity to quantitatively calculate the change in dye colour intensity. It should be noted that for methyl blue dye test however, the dye degrades and evaporates under ordinary room conditions after a few days. In these cases, the degradation kinetics of the dye on TiO₂ photocatalysts has to be put into perspective by comparing the degradation kinetics of the dye on a control sample that has no TiO₂ material.

In summary, the two most common methods utilized to quantify the efficiency of TiO₂ photoactivity function is the stearic acid test and dye test. The tests listed here are however, not exhaustive since the testing of photo-oxidation function of TiO₂ films is generally application based where research groups focused on self cleaning surfaces for building surfaces may concentrate on specific organic pollutants, not necessarily stearic acid or organic dyes. From literature review, it is apparent that lab controlled experiments on TiO₂ photocatalytic function produce fairly different results depending on the experiment protocol used during photoactivity tests. In photoactivity studies conducted in the following chapters, the stearic acid test is utilized due to the stability of the solid contaminant in room conditions and the sensitivity of the micro- FTIR detection technique.[112]

2.2.3.3 UV Induced Superhydrophilicity of TiO₂ surfaces

In 1995, the UV light induced superhydrophilicity of TiO₂ surfaces was discovered by chance by Fujishima and Honda during a project collaboration with TOTO Inc.[87] The wettability of TiO₂ surfaces are usually termed as either super-hydrophobic, hydrophobic, Super-hydrophilic or Hydrophilic depending on the water contact angle (WCA) measured. The WCA of surfaces are measured as the angle between the solid surface and the tangent line of the liquid bead surface adjoining to the solid surface. As a general guideline, TiO₂ surfaces are considered to be hydrophilic when the WCA is <20° and are considered super-hydrophilic when the WCA is <10°.

Initial studies on UV assisted TiO₂ hydrophilic surfaces first suggested that the behavior of such surfaces was directly attributed to a clean surface resulting from the photo-oxidation of adsorbed dirt on the surfaces. This simple explanation of the presence of TiO₂ surface hydrophilicity was later proved to only partially explain the hydrophilicity of TiO₂ surfaces and mechanistic studies that followed, showed that it was the metastable structural changes in TiO₂ surfaces during UV irradiation that were observed to result in such surface behavior.[113,115] The proposed mechanisms underlying UV-induced hydrophilic transformation of TiO₂ surfaces is summarized in Fig. 2.16.

Comparison studies designed to verify the hypothesis of a clean surface resulting in surface hydrophilicity (arising from TiO₂ photo-oxidation) were hence conducted. In ref[114], several experiments were conducted: Firstly, oleic acid was applied to TiO₂ surfaces and irradiated with UV light. The contact angle changes of stained TiO₂ surfaces were subsequently measured as a function of UV irradiation. The amount of oleic acid present on the TiO₂ surfaces was also measured through XPS measurements as a function of UV exposure time. Experiment results showed that despite the presence of oleic acid, the WCA of stained TiO₂ still reached near 0° after UV exposure of 60mins. The second experiment conducted involved comparisons between the WCA of stained TiO₂ and that of mechanically cleaned TiO₂ surfaces. It was found that without UV irradiation of the surface, the WCA of mechanically cleaned TiO₂ surfaces only reached a WCA of 20°. Thus these experiments conducted showed that

the chemical and physical state of the TiO₂ surfaces change as they are exposed to UV irradiation regardless of whether the surface are “clean” or “unclean”.

Figure 2.16 (a-d) FFM images on TiO₂ surface with UV irradiation show oxygen vacancies within the lattice structure, (b to d) are progressive magnifications of (a) and (e) depicts the proposed mechanism behind UV assisted TiO₂ hydrophilicity.[115]

Recently, a study[117] showed that during UV irradiation, hydrophilic conversion on a TiO₂ surface occurred almost immediately after the surface adsorbed hexane (an organic contaminant) was degraded by TiO₂ photocatalysis. To date, this seems to be the most comprehensive study of UV-induced hydrophilicity on TiO₂ surfaces as real time water contact angle measurements were conducted during UV irradiation in a controlled ultra high vacuum environment. (see Fig. 2.17) In ref[117], small amounts of hexane (120, 360ppm) were pre-adsorbed onto a TiO₂ single crystal (110) film. Upon UV irradiation for 154 seconds, the hexane monolayer was observed through Auger electron spectroscopy to be completely catalyzed, and the simultaneous measurement of water contact angles showed the sudden onset of surface wetting during the 155th second. Based on these observations, the authors[117] proposed that

the change in TiO_2 surface wettability during UV irradiation was entirely reliant on a microscopically clean surface.

Figure 2.17 (a) Ultra high vacuum apparatus used during in-situ water contact angle measurements and (b-d) immediate hydrophilic response of UV irradiated TiO_2 single crystal film after surface adsorbed hexane is catalyzed.[117]

However, a point of contention in this study[117] is the lack of explanation on the adsorption and photo-oxidation process of hexane gas onto the TiO_2 surfaces. During the degradation of hexane, it was unknown if the complete degradation of hexane was solely responsible. A photo-oxidized by-product produced during the degradation of hexane could equally have been responsible for the UV-induced surface hydrophilicity. Additionally, the change in “flatness” (structure/ morphology) of the film surface devoid of organics could be the actual reason for UV-induced surface hydrophilicity. Although the presence of a clean TiO_2 surface has been directly associated to surface hydrophilicity[117], the question of necessity still remains. Is hydrophilicity present only on clean TiO_2 surfaces and are clean TiO_2 surfaces necessarily hydrophilic? The speculative nature of models regarding UV-induced hydrophilicity of TiO_2 surfaces warrants further study.

3. Experimental Apparatus, Setup and Sample Details

3.1 Electrophoretic cell and electrode pre-treatment

Electrophoretic depositions (EPD) were performed in an open cylindrical 3-electrode cell with 120cm^3 capacity and a thermal blanket that maintained the deposition bath temperature at $10\text{--}15^\circ\text{C}$. The depositing and counter electrodes were 2 stainless steel electrodes with an effective planar area of 6cm^2 and thickness of 1mm. Prior to deposition, the stainless steel electrodes were degreased using an NaOH ethanol solution (0.60M) and rinsed with a copious amount of DI water. During EPD, an Ag/AgCl reference electrode was connected to the two electrodes and a Solartron SI 1287 potentiostat/ galvanostat supplied the required d.c voltage. Deposition was carried out under constant applied potentials of 1.2V, 1.5V and 2.0V. A standard deposition time of 75 seconds was used during all EPD experiments. After deposition, a dip coater retrieved the electrodes at a constant draw rate of $42\mu\text{m s}^{-1}$. The deposited films were then dried in air for 2 hours.

Figure 3.1 EPD bath apparatus and setup

3.2 EPD bath reagents

The starting materials for the Titanium dioxide (TiO_2) suspensions were Titanium tetrachloride (TiCl_4 , 36 wt%) and ammonia (NH_4OH , 3.2%) from Merck, and

hydrogen peroxide (H_2O_2 , 30%) from AnalaR®. Photocatalytic experiments were conducted using stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$, 98.9%) from Merck, dissolved in methanol (CH_3OH , 99.8%) from Sigma Aldrich. These chemicals were used without further purification. Distilled (DI) water used in all experiments had a conductivity of lower than $0.25\mu\text{S}$ at 25°C .

3.3 Electrophoretic suspension preparation

The TiO_2 suspensions were synthesized through three consecutive processes: (1) the precipitation of a titanate hydrate, (2) the synthesis of an amorphous peroxo-titanium suspension and (3) the TiO_2 anatase particle growth from the peroxo-titanium solution. During step (1), TiCl_4 (36 ml, 0.01M) was added dropwise to a mixture of ice-cooled DI water (1L) and NH_4OH (0.1M). The solution was left to settle (~6 hours) until a white precipitate was formed. The precipitate was then flushed with DI water until no NH_4^+ and Cl^- ions were detected. The precipitate was subsequently vacuum compacted into a semi-dried titanate hydrate. In step (2), the titanate hydrate (14.5g, ~5wt% amorphous TiO_2) was stirred in a solution containing H_2O_2 (12.2ml) and NH_4OH (0.54ml, 0.3M) at 10°C . After 1 hour, the hydrate was entirely dissolved and a completely transparent deep red peroxo-titanium solution with $\text{pH} \leq 3$ was formed. At this stage, the solution was immediately diluted with DI water to a concentration of 12.5v/v%. In step (3), the peroxo-titanium suspension was heated under reflux at 100°C for 2, 4 and 8hrs to form colloidal suspensions containing TiO_2 nanoparticles. The suspensions were labeled S2, S4 and S8 corresponding to the heat reflux durations of 2, 4 and 8 hours respectively. The heat refluxed suspensions were homogenized by agitation from a high shear mixer at 2000rpm for 3 minutes. The homogenized suspensions were used for all the electrophoretic experiments.

3.4 Electrophoretic suspension characterization

The aggregate particle sizes within the TiO_2 suspensions were measured at a temperature of 15°C using a Zetasizer Nano ZS dynamic light scattering (DLS) equipment from Malvern Instruments. The average DLS particle sizes reported were obtained from 30 measurement runs. Primary particle sizes and shapes were measured using a Jeol 2010 transmission electron microscope (TEM) with a point-to-point

resolution of 0.19nm. The average primary particle sizes reported were calculated by sampling 50 particles from 3 different TEM micrographs for each suspension. All errors associated with the reported particle sizes are the calculated standard deviations of the sample pool (n=50).

Electrokinetic measurements of particle electromobility were performed using the Zetasizer Nano ZS by applying a voltage of 25V·cm⁻¹ across a capillary electrode cell. Particle zeta (ζ) potentials were calculated from the measured particle electromobility values by applying the Helmholtz- Smoluchowski expression in equation (4.1):[14]

$$\eta = \frac{\epsilon_0 \epsilon_r \zeta}{\mu} \quad (\text{E 4.1})$$

where η , μ , ϵ_0 and ϵ_r are the particle electromobility (m² V⁻¹ s⁻¹), solvent viscosity (0.893X10⁻³ Pa s), the permittivity of free space (8.854 X 10⁻¹² C² J⁻¹ m⁻¹) and the relative permittivity of the medium (80.10 C² J⁻¹ m⁻¹, assuming no significant difference from that of water).

3.5 Film characterization

The microstructure of TiO₂ films was analyzed using an atomic force microscope (AFM, Nanoscope III) from Digital Instruments. Phase analysis of TiO₂ deposits were conducted using X-ray diffraction (XRD) patterns of powders obtained from dried TiO₂ electrodeposits. The electrodeposits were dried in air for 8 hours and subsequently dried at 60°C for 30 minutes to form powder samples. Power XRD spectra were measured with a Philips PW 1877 diffractometer (Voltage=30kV, Current=20mA), using monochromatic Cu-K_α radiation (λ= 1.5044Å) The spectra were collected within the 2θ range of 20° to 60°, with a step size of 0.03°. The measured XRD spectra were indexed using the JCPDS reference database.[149] The films' thickness were estimated by AFM phase analysis of the cross-sectional areas of the films. The thickness measurements were then verified by variable angle spectroscopic ellipsometry (VASE) from J.A. Woollam. During VASE measurements, the film thicknesses were obtained using a Cauchy-substrate film model.

Photoactivity of the TiO₂ films was analyzed using stearic acid as an organic contaminant. 0.2ml of stearic acid that had been dissolved in methanol (100ml, 20mM) was spin coated at 2500rpm onto the TiO₂ films. Spin coating of the stearic acid layers was repeated for 5 times; after each layer was coated, the layer was dried at 80°C for 5 minutes before the next layer was coated. After 5 layers of stearic acid were coated, degradation of the organic film was performed using a UV lamp (ENF-280C/FE) of centre wavelength 254nm from Spectroline. The incident light intensity on the TiO₂ films was measured from a wavelength range of 240nm to 280nm by a Solatell Solacheck system and found to be $85\mu\text{W cm}^{-2}$. This light intensity corresponds to a photon flux of 1.087×10^{14} photons s⁻¹ as determined from ferrioxalate actinometry.[150]

The UV light assisted degradation of the stearic acid layer on the TiO₂ films was observed using microscopic reflectance Fourier transform infrared spectroscopy (MR-FTIR) from Biorad. The background spectra were first obtained by focusing a beam of 1μm diameter on a flat gold mirror. The MR-FTIR sample scans were subsequently collected from 64 scans and the integrated area under the spectra was analysed using the Win-IR software (ver 4.0) from Biorad.

3.6 Film water contact angle measurements

Water contact angle (WCA) experiments were conducted using a commercial water contact machine, VCA Optima XE. The equipment had a measurement error of $\pm 2^\circ$. The contact angles of water droplets at a minimum of 5 separate locations on the deposited film were measured as a function of UV pre-irradiation time. All WCA images were captured within 1 second upon water droplet contact on the films. The WCA measurements were performed in room temperature and ambient air conditions (Relative humidity 60%). Analysis of the angle of water droplet contact was performed using a dedicated VCA software that mathematically calculated the angle between the water droplet meniscus and the film horizon. As the system requires operator input to determine the shape of the droplet meniscus, the operator error per WCA measurement was $\pm 1^\circ$. It should be noted that this error increases exponentially when the water contact angle drops below 10° due to the difficulty of fitting the meniscus shape to the water droplet at low water contact angles.

3.7 XPS and FTIR spectroscopic film analysis

The UV light driven hydrophilic response on the TiO₂ films was observed using microscopic Fourier transform infrared spectroscopy (FTIR) from Biorad. Micro-FTIR spectroscopy analysis was carried out under in-situ UV light irradiation of wavelength 254nm and intensity 85μW/cm² under a Nitrogen purge environment. The background spectra were first obtained by focusing a beam of 1μm diameter on a flat gold reference mirror and subsequent sample scans were obtained by focusing the beam onto the TiO₂ films. A total of 64 scans were collected during each sample measurement.

Surface analysis of the TiO₂ films under different experiment conditions were conducted using X-Ray Photospectroscopy, XPS (Kratos Axis Ultra) with a monochromatic Al Kα source of excitation 1486.71eV. Charge referencing was done by assigning the C(1s) peak of adventitious hydrocarbons to a binding energy of 285eV. XPS measurements of TiO₂ pre-illuminated surfaces were carried within 2 to 4 hours after UV irradiation in the XPS pre-vacuum chamber of 10⁻⁷ Torr pressure. The measurement delay was inevitable as several hours were required to pump down the XPS vacuum chamber to ultra high vacuum (UHV) conditions of 10⁻⁹ Torr (required for X-ray photon detection). The XPS spectra for the samples under analysis were collected at a takeoff angle of 45°. Data processing of the XPS spectra were carried out using the Vision Processing 2.1.3 software and a Shirley type background selection subtraction method was used for all the spectrums. Quantitative analysis of the relative peak areas under the deconvoluted component peaks was calculated using a mixture of Gaussian- Lorentz functions.

4. Anodic electrophoretic fabrication of TiO₂ photocatalytic films

Chapter Summary

The anodic electrophoretic deposition of TiO₂ anatase nanoparticles was studied. The formation of anatase particles from amorphous peroxo-titanium suspensions was achieved by heating the amorphous suspension under reflux at 100°C for 2, 4 and 8 hours. The electrokinetic properties of the anatase particles such as ζ potential and, primary and aggregate particle size were analyzed using laser Doppler electrophoresis measurements, dynamic light scattering measurements (DLS) and high resolution transmission electron microscopy (HR-TEM) respectively. The electrodeposited films were uniform and contained spheroid anatase grains with diameters ranging from 28nm to 65nm. All the particulate films exhibited photoactivity that resulted in the degradation of an organic stearic acid layer. A maximum quantum efficiency value of 89.751×10^{-5} molecules photon⁻¹ was achieved for electrodeposited films with the highest anatase content.

4.1 Introduction

In recent years, Titanium dioxide (TiO₂) photocatalytic materials have generated considerable scientific interest in applications as diverse as self-cleaning surfaces,[45,118-125] electrochromic devices,[118,126-129] and solar energy conversion cells.[130-132] There are several established techniques to produce TiO₂ thin films for these applications. These include sol-gel dip coating,[121,124,125,133-135] atmospheric chemical vapour deposition (APCVD),[112,119,123,136] atomic layer deposition[137-140] and electrophoretic deposition.[43,44,47,49,130,135,141-144] With respect to cost and energy efficiency, electrophoretic deposition provides an attractive alternative to the other techniques. However, conventional electrophoretic deposition (EPD) processes often utilize acidic and/or organic suspensions for the fabrication of uniform TiO₂ films. These acidic and organic EPD suspensions pose environmental problems such as the evolution of volatile organic compounds (VOCs) during EPD and the disposal of acidic waste after EPD. EPD of TiO₂ films from

aqueous and neutral peroxo-titanium suspensions would overcome these environmental issues.

Electrodeposition methods such as electrophoretic[141] and electrolytic deposition [33,132,141,145-148] from peroxo-titanium suspensions often form amorphous peroxo-titanium hydrate gel films as an intermediate step. The peroxo-titanium hydrate film is precipitated when cationic peroxo-titanium complexes are charged neutralized by OH^- species present at the cathode. These OH^- species are formed when water within the aqueous peroxo-titanium suspensions are electrolytically decomposed into OH^- ions and H_2 molecular gas at the cathode. Crystalline TiO_2 films are subsequently produced from the amorphous peroxo-titanium hydrate film by heating at above 300°C . [33,135,145-148] Although electrodeposition of photocatalytic TiO_2 films have been achieved through this peroxo-titanium mediated route, several drawbacks still exist. The above process requires high temperature post annealing to convert amorphous films to photocatalytic crystalline TiO_2 films. The high temperature post heating limits the deposition of TiO_2 films onto heat-sensitive substrates. Alternatively, EPD from peroxo-titanium suspensions containing crystalline TiO_2 particles has been performed to eliminate the need for high temperature heating.[141] However, the process was carried out in an acidic environment ($\text{pH}<3$) to prevent rapid polynuclearization of the peroxo-titanium complexes and the resulting TiO_2 particle sedimentation at higher pH values.

As such, other strategies for the electrophoretic deposition of TiO_2 films have also been attempted by using surfactant stabilized TiO_2 particle suspensions.[43,44,45,47,49,144] TiO_2 nano-particulate[43,45,47] or nano-tubular[44] powders can be dissolved in organic EPD suspensions containing stabilizers such as polyethylenimine,[43] polyvinyl butyral[44] and polyvinylpyrrolidinone.[144] Major drawbacks of this technique include the emission of VOCs during high voltage electrophoretic deposition and the presence of organic compounds within the deposited films. Organic content within TiO_2 films can be detrimental to film photoactivity. Therefore, in order to optimize film photoactivity, post annealing at temperatures greater than 300°C would still be required to decompose any remaining organic compounds.

In this chapter, an environmentally friendly route of electrodepositing TiO₂ thin films from neutral, aqueous and stable peroxo-titanium suspensions was developed. Temperatures of 100°C and below were used during TiO₂ nanoparticle synthesis and film deposition. The effect of heat treatment on particle formation within the peroxo-titanium suspensions was investigated. The morphology and phase of the deposited TiO₂ films were also determined. These film properties were analyzed alongside the film photocatalytic activity against an organic stearic acid layer.

4.2 Experimental

The experimental techniques used are summarized in Chapter 3. In this section, briefly, the TiO₂ suspensions are subjected to the experiment parameters summarized in Table 4.1

Table 4.1 Experiment parameters of EPD suspensions treatment

Sample Name	Reflux Duration (hrs)	Deposition voltages (V)
S2	2	
S4	4	1.2, 1.5, 2.0
S8	8	

The EPD apparatus used is schematically shown in Fig. 3.1 (Chapter 3). Characterization of TiO₂ particles in suspension were conducted via transmission electron microscopy, dynamic light scattering and zeta potential measurements. During electrophoretic deposition, the electrochemical process was monitored via electrical and impedance measurements. Following deposition, the morphology and phase of the TiO₂ films were analyzed through atomic force microscopy and X-ray diffraction respectively. The photochemical characteristics of the deposited films were observed through Fourier transform infra-red detection of the progressive degradation of the stearic acid organic probe.

4.3 Results and discussion

4.3.1 Morphology and electrokinetic properties of TiO₂ suspensions

The TiO₂ suspensions: S2, S4 and S8 that were used during electrophoretic deposition had neutral pH values within pH 7-8. In peroxo- titanium suspensions of

pH >3, the colour-forming peroxo-titanium species present are expected to be anionic and dinuclear, $\text{Ti}_2\text{O}_5(\text{OH})_x^{(2-x)}$, where $x > 2$. [151,152] Based on other previous findings, [153] these anionic species prevented particle flocculation and hence stabilized peroxo-titanium modified TiO₂ suspensions through strong ionic repulsion. The decrease in peroxo-titanium species within TiO₂ suspensions as heat treatment continued was observed from the progressive reduction of the colour-forming species as illustrated in Fig. 4.1. [141,151] The presence and subsequent decrease in anionic peroxo species in heat treated TiO₂ suspensions was further evidenced by electromobility measurements shown in Table 4.1. The negative electromobility and hence, negative ζ values of TiO₂ particles within the suspensions suggests the occurrence the surface adsorption of anionic peroxo-titanium species on TiO₂ particles formed from heat treated suspensions. It can be observed from Table 4.1 that an increase in heat treatment duration causes a reduction in the ζ potential of TiO₂ particles within suspensions. The concomitant increases in aggregate particle sizes as shown in Fig. 4.2 indicates a direct correlation between particle dispersion and zeta potential. The increase in particle flocculation and hence the presence of large aggregates within S8 suspensions suggest that the anionic peroxo-titanium species act as stabilizing agents. Although the increase in particle flocculation could be attributed to increasing primary particle sizes, TEM images of TiO₂ particles (shown in Fig. 4.3) did not measure drastic increases in average primary particle sizes.

Figure 4.1 The decomposition of peroxo-titanium colour forming species after (a)0, (b)2, (c)4 and (d)8 hours of heat treatment.

TEM images shown in Fig. 4.3 illustrate the changes in particle shape and size as heat treatment proceeded. The average primary particle dimensions were observed to increase within the same order of magnitude. It is unlikely that this increase in primary

particle sizes solely led to the formation of larger aggregates. In the present experiments, it was deduced that the anionic peroxy-titanium species play a key role in stabilizing TiO₂ particles within neutral or slightly alkaline suspensions.

Table 4.2 pH, electrokinetic and average particle size measurements of anionic TiO₂ suspensions after heating under reflux. Measurements taken at a temperature of 288K.

Samples	pH	Electromobility $\times 10^{-10}$ ($\text{m V}^{-1} \text{ s}^{-1}$)	ζ potential $\times 10^{-3}$ (V)	DLS aggregate particle diameter ^a (nm)	TEM primary particle dimensions (nm)
S2	7.3	-5.89 ± 0.39	-75.16 ± 9.72	21.04 ± 0.64	11 ± 9 (Diameter)
S4	8.0	-5.47 ± 0.55	-68.89 ± 6.97	25.45 ± 1.50	15 ± 8 (Diameter)
S8	7.8	-2.13 ± 0.06	-26.76 ± 0.72	$28.21 \pm 2.10, 255 \pm 1.90$	20 ± 6 by 7 ± 2 (Rod shaped)

Figure 4.2 Particle size distribution within heat refluxed suspensions. Error bars represent $\pm$ standard deviation ($n=10$).

Figure 4.3 TEM micrographs of TiO₂ nanoparticles synthesized within peroxy-titanium suspensions: (a) S2, (b) S4 and (c) S8. Insets are select area diffraction patterns of their respective micrographs.

During EPD film fabrication, particle dispersion is crucial as sedimenting particles experience electrical double layer relaxation and a sedimentation potential.[14] This

sedimentation potential can be considered to affect the direction and magnitude of the applied electric field during electrophoresis.[14] Likewise, the aggregation of primary particles within EPD baths directly affects the packing density of deposited films. As such, the minimization of particle sedimentation (stable colloidal suspensions) is a prerequisite for electrophoretic deposition that can be directly controlled by the externally applied voltage.

4.3.2 Electrophoretic deposition

Electrophoretic deposition of TiO_2 films from the heat treated suspensions were studied by varying the applied voltage over a fixed deposition duration. Electrophoretic deposition from S2, S4 and S8 suspensions were found to produce uniform films at short deposition durations of less than 3 minutes. However, longer deposition durations produced thicker films that had lower particle packing densities and more cracks after drying. As such, an optimized deposition duration of 75 seconds was chosen to deposit thin films under applied voltages of 1.2, 1.5 and 2.0V for all the heat treated suspensions. The applied voltages were kept below 2.0V to avoid gas evolution that occurs during water electrolysis at higher voltages.

The current density behaviour during EPD from S8 suspensions is shown in Fig. 4.4. S2 and S4 suspensions exhibited similar current density trends during EPD. From Fig. 4.4, it can be observed that the starting current density decreased rapidly within the first 5 seconds of deposition. This immediate decrease in current density is likely to be caused by the initial deposition of a thin layer of particles on the electrode.[29,154] The rate of current density decrease slowed as a thicker film formed on the electrode, adding increased electrical resistance to the EPD system as deposition proceeded.[29,141,154] In addition to this process, the reduction of current density during EPD can also be associated with the depletion of current carrying conductive species such as peroxo-titanium anions and TiO_2 particles.[155] Alternatively, Hamaker *et al.*[156] has attributed the drop in current during electrophoretic deposition from aqueous suspensions, to the evolution of gas at the electrodes. However, in the present experiments, at applied voltages of 2V or less, no significant gas evolution was observed during deposition. It is thus suggested that the contribution of gas evolution to current drop is minimal although this is difficult to

ascertain quantitatively during the process of electrophoresis. The anodic deposition of TiO_2 particles from S8 suspensions resulted in film thickness increases from $70 \pm 10.5\text{nm}$ to $120 \pm 18\text{nm}$ as the applied voltage was increased from 1.2V to 2V. During EPD from all the suspensions, the film thicknesses were found to increase as the applied voltage was increased. At the maximum applied voltage of 2V, S2 and S4 suspensions produced maximum film thicknesses that were less than 100nm. S8 suspensions produced the thickest films as compared to the S2 and S4 suspensions during EPD at 2V. This can be attributed to the larger particle aggregates found in S8 suspensions as compared to S2 and S4 suspensions (see Fig. 4.2 and 4.3).

Figure 4.4 Current density decrease during EPD from S8 suspensions at different applied voltages.

At EPD voltages of 2V or lesser, the anodic deposition of uniform TiO_2 films is considered to occur via two processes: the electrophoresis of TiO_2 particles and the electro-coagulation of peroxo-titanium species along with TiO_2 particles at the anode. The charge neutralisation of TiO_2 particles at the depositing electrode has been attributed to the local pH changes due to base (OH^-) generation at the electrode during water electrolysis.[33,141,142,155] Zhitomirsky *et al.*[33] suggested that peroxo-titanium complex species could electrodeposit on cathodes because of the generation of OH^- resulting in the coagulation of charge neutral titanium hydrate ($2\text{TiO}_3(\text{H}_2\text{O})_x$) films. Peiro *et al.*[141] combined anatase TiO_2 particles within a peroxo-titanium suspension and suggested that cationic TiO_2 particles would only electrodeposit to

form adherent films in the presence of an amorphous TiO₂ polymeric matrix formed via the mechanism suggested by Zhitomirsky *et al.* In the Zhitomirsky deposition model, the peroxo-titanium complex electrochemically deposits onto the electrode due to the production of OH⁻ at the cathode thus making deposition possible only at the electrode.

The acidic suspensions used in the Zhitomirsky series of experiments were considered to contain peroxo-titanium cation complexes that were observed to slowly condense into the peroxotitanium hydrate (TiO₃·H₂O):[151]

During EPD, Zhitomirsky suggested that at voltages higher than 1.23V, the water electrolysis resulted in the formation of OH⁻ species at the depositing cathode. The OH⁻ was considered to charge neutralize and electrocoagulate the approaching cationic peroxo-titanium species at the cathode, thus accelerating the formation of the peroxotitanium hydrate:[146]

where n, m and k are relative moieties of their respective compounds depending on the number of water molecules available for reaction.

The fabrication of TiO₂ films is obtainable from the titanium hydrate film upon decomposition of the unstable peroxo-titanium complex, 2TiO₃(H₂O)_x, where x denotes the number of water molecules attached to the oxygen groups:

The chemical mechanism described in (E 4.2) would imply that deposition could only specifically occur at the electrode where OH⁻ species were available. Similarly, this would also suggest that an applied voltage greater than the water electrolysis

voltage was necessary to induce particle deposition at the electrode. In the present experiments, deposition was achieved at the anode (H^+ ions) instead of the cathode, thus ruling out the need for OH^- species to be present during deposition. Likewise, water electrolysis did not particularly aid the deposition of TiO_2 particles in the present series of experiments. At a low applied voltage of 1.2V, the amount of OH^- formed from water electrolysis is considerable low. If hydroxide formation was required for uniform TiO_2 particle deposition, the films deposited at an applied voltage of 1.2V would be incomplete and less uniform than those deposited at higher voltages of 1.5V and 2.0V. This was not observed in the AFM images shown in Fig. 4.5. Instead, deposition at 1.2V produced uniform and densely packed TiO_2 films (Fig. 4.5(a)) that did not differ significantly from films deposited at 1.5V (Fig. 4.5(b)) and 2.0V (Fig. 4.5(c)). Furthermore, the electrophoretically deposited films had a yellow tinge, suggesting that TiO_2 particles were co-depositing with peroxo-titanium ligands; this suggests that a considerably small amount of peroxo-titanium species had condensed into the white titanium hydrate due to electrode reactions.

Figure 4.5 AFM ($1\mu\text{m} \times 1\mu\text{m}$) micrographs of films electrodeposited from a S2 suspension at (a) 1.2V, (b) 1.5V and (c) 2.0V.

Apart from the deposition mechanisms proposed by Zhitomirsky *et al*, the mechanism behind electrophoretic particle deposition has also been attributed to electrokinetic factors such as particle electrical double layer distortion and the buildup

of hydrodynamic pressure[29] at the vicinity of the depositing electrode. The exact mechanism of particle coagulation and deposition on the electrode after electrophoresis, however, remains contentious. In the present case, it is unlikely that H^+ generation at the cathode predominantly resulted in the deposition of uniform TiO_2 films. Thus, based on our observations, a combination of particle electrical double layer distortion and hydrodynamic pressure buildup is a more likely mechanism occurring near the anode.[29] As negatively charged TiO_2 particles move towards and near the anode, the particle electrical double layer, consisting of surface adsorbed peroxo-titanium anions and H^+ cations distorts. The peroxo-titanium anions rearrange within the double layer and concentrate within the leading edge of the particle. At this stage, the zeta potential is considered to increase in negativity at the leading flow edge. Simultaneously, the H^+ cations that are repulsed by the positive charge at the anode move towards the trailing edge of the particle. The next incoming particle moves towards the depositing particle as it is attracted by the accumulated positive charge at the trailing edge of the initial depositing particle. The continual flux of incoming particles is likely to create hydrodynamic pressure on the particles nearest to the anode, causing them to “press” and coagulate onto the anode. The process continues and a nanoparticulate film such as those observed in Fig. 4.5 was proposed to eventually form.

4.3.3 Film phase and morphology

During the EPD process, the presence of crystalline anatase TiO_2 particles within the EPD suspensions meant that no post annealing of the film was required. The crystallinity of TiO_2 electrodeposits obtained from EPD was analyzed using measured TEM diffraction patterns and XRD patterns. Analysis of TEM diffraction patterns (see inset in Fig 4.3(a-c)) illustrate the improvement in diffraction ring resolution. The sharper and thinner diffraction rings indicate, qualitatively, the improvement in particle crystallinity as heat treatment proceeded.

Figure 4.6 Powder XRD spectra of dried electrodeposits from (a) S8, (b) S4 and (c) S2 films.

Alternatively, comparing the XRD spectra in Fig. 4.6, it can be observed that electrodeposits obtained from S8 suspensions had the largest anatase content (PDF 21-1272).[149] From Fig. 4.6(a), it can be observed that an additional peak around $2\theta=30^\circ$ forms after 8 hours of reflux treatment. This peak is attributed to the brookite phase (PDF 29-1360),[149] this phase has been reported to form from the anatase phase at calcination temperatures of 100-350°C for TiO_2 powders that were obtained from TiCl_4 precursors and synthesized through hydrolysis and condensation- similar to the present synthesis method.[157] Additionally, comparing Fig. 4.6(a) to 4.6(c), it can be observed that the anatase peaks[149] narrow; the decrease in XRD peak breadth can be associated to increases in particle sizes.[158] The longer heat treatment of suspensions

resulted in the production of larger particles and hence, electrodeposits with larger grain sizes.

Figure 4.7 AFM height mode micrographs of electrodeposited TiO_2 films from (a,b) S2, (c,d) S4 and (e,f) S8 suspensions. (a,c,e) are low magnification ($1\mu\text{m} \times 1\mu\text{m}$) micrographs; (b,d,f) are high magnification ($350\text{nm} \times 350\text{nm}$) micrographs.

The observed increase in grain size during anatase phase transformation is in agreement with previous studies on nanocrystalline TiO_2 particles.[159] The anatase grain growth is considered to occur through the growth of individual anatase crystals within agglomerates; as heat treatment proceeds, these anatase crystals grow through coalescence and finally form a single anatase grain.[159] The increase in anatase crystal size and hence TiO_2 film grain size was also observed from AFM images shown in Fig. 4.7. The average film grain width was found to increase progressively from *ca.* 28nm (Fig. 4.7a,b) to 50nm (Fig. 4.7c,d) and finally 65nm (Fig. 4.7e,f) for S2, S4 and S8 films respectively. These films were deposited from S2, S4 and S8

suspensions at a fixed voltage of 2V to eliminate, if any, grain size effects attributed by the deposition process. As such, XRD and AFM data showed that the deposition of nanocrystalline TiO₂ particles could be achieved by suspension heat treatment. Interestingly, these observations would imply that the suspension particle size could directly control the morphology of electrodeposited TiO₂ films. This information is useful in controlling the nanoscale morphology of electrophoretically deposited TiO₂ films to achieve optimized photoactivity.

4.3.4 Photoactivity of TiO₂ films

The photocatalytic activity of TiO₂ films is commonly assessed by the rate of photocatalytic degradation of an organic contaminant.[107,109, 112,119,120,136,160,161] In-situ FTIR techniques have previously been used to determine the rate of photocatalytic degradation of stearic acid on TiO₂ films.[112,119,120,136,160] During the photocatalytic degradation of stearic acid, equation 4.1 is known to occur in ambient room conditions:[109]

The destruction of the stearic acid layer was monitored using FTIR absorbance spectroscopy by observing the peaks at 2957.5cm⁻¹, 2922.8cm⁻¹ and 2853.4cm⁻¹. The 2957.5cm⁻¹ peak is attributed to the asymmetric in-plane C-H stretching mode of the CH₃ group, and the 2922.8cm⁻¹ and 2853.4cm⁻¹ peaks represent the asymmetric and symmetric stretching modes of the CH₂ group respectively.[119,120] The FTIR absorbance peaks attributed to the stearic acid layer were observed to decrease in intensity as UV light exposure increased (see Fig. 4.8).

The integrated area of the stearic acid FTIR absorbance peaks is considered to be directly proportional to the degradation rate of stearic acid molecules on the TiO₂ film.[107,109] A generic stearic acid layer with an integrated absorbance area of 1cm⁻¹ corresponds to *ca.* 3.17 × 10¹⁵ molecules cm⁻² of stearic acid.[112,119,120] Fig. 4.9 plots the decrease in the number of stearic acid molecules as a function of UV irradiation time for all the TiO₂ films deposited at an applied voltage of 2V. The rate of stearic acid decrease was observed to be of zero order. Both zero and first order

kinetics have been previously observed for the photocatalytic breakdown of stearic acid layers on TiO_2 films.[119,120] Zero order kinetics have been attributed to the complete saturation of TiO_2 film sites by stearic acid molecules.[112,120]

Figure 4.8 Real time FTIR spectra of the stearic acid layer on electrodeposited TiO_2 films obtained from S4 suspensions. The change in absorbance within the spectral range of 3000cm^{-1} to 2800cm^{-1} is plotted as a function of UV exposure time.

Figure 4.9 Total integrated absorbance area change within the spectral range of 3000cm^{-1} to 2700cm^{-1} as function of UV irradiation time for an uncoated substrate, S2, S4 and S8

electrodeposited TiO₂ films. The number of stearic acid molecules was directly calculated from the absorbance peak area.

The rate of photocatalytic degradation of stearic acid is heavily dependent upon the UV light photon flux applied. For easy comparison, this rate can be decoupled from the irradiated UV light photon flux into a quantity that is termed as the quantum efficiency. The quantum efficiency of the various TiO₂ films can be calculated from equation 4.1.[163] An example calculation of the quantum efficiency values from FTIR obtained data can be found in **Appendix A**.

$$\delta = \frac{\text{rate of light reaction (molecules s}^{-1}\text{)}}{\text{incident light intensity (photons s}^{-1}\text{)}} \quad (\text{E 4.5})$$

Table 4.3 Photodegradation data on TiO₂ films

Films	Rate of photodegradation ^a (10 ¹³ molecules cm ⁻² min ⁻¹)	Quantum Efficiency (10 ⁻⁵ molecules photon ⁻¹)
S8	0.587 ± 0.001	89.751 ± 2.257
S4	0.311 ± 0.003	47.568 ± 0.441
S2	0.309 ± 0.008	47.185 ± 1.171
Control	0.059 ± 0.005	9.1057 ± 0.770
P25 Degussa ^b	1.670	256.000
P25 Degussa ^c	1.760	270.000
Activ TM ^b	0.065	10.000

^a Quantum efficiency values obtained/ corrected for a photon flux of 6.52 × 10¹⁵ photons cm⁻² min⁻¹ (85μW cm⁻²).

^b Photodegradation data for spin coated P25 Degussa films (thickness: ca. 90nm) and commercial APCVD TiO₂ ActivTM films (thickness: ca. 15nm).[112]

^c Photodegradation data for spin coated P25 Degussa films (thickness: ca. 1.3μm).[120]

In Table 4.2, a summary of the calculated quantum efficiencies for the electrodeposited films is presented. Interestingly, the quantum efficiency of the electrodeposited films was found to improve as particle crystallinity increased. This would suggest that the anatase content within the particles and hence the electrodeposited films directly affect film crystallinity. This correlation between particle anatase content and particle photoactivity is in agreement with photoactivity studies carried out on anatase nanocrystallites.[78,164] However, it is difficult to conclude the directness or magnitude of this correlation due to confounding factors such as particle size and shape, and particle packing within the films.

Commercial products such as P25 Degussa and Pilkington ActivTM films are commonly used for comparison with TiO₂ films produced by other deposition techniques. The values of quantum efficiencies of these products obtained in similar stearic acid photoactivity tests[112,120] are compared to the quantum efficiency values obtained for electrodeposited TiO₂ films in the present study. Commercial TiO₂ films such as P25 Degussa films are considered to be the benchmark standard in TiO₂ photocatalytic performance. However, these films have been found to be mechanically unstable and exhibit poor adhesion to their coupled substrates.[112,120] As such, other deposition techniques such as APCVD (ActivTM films) have been attempted to produce thin TiO₂ films with comparable photocatalytic efficiencies. Comparing the quantum efficiencies of our electrodeposited films (in particular S8 films) to the various commercial products, the electrodeposited films were found to have comparable photocatalytic performance, albeit poorer performance than P25 Degussa films. This is not surprising since the P25 Degussa films are likely to be thicker (1.3µm) and more crystalline than the present films given the high temperatures utilized during P25 powder synthesis; P25 Degussa films have been found to consist of ~80% anatase and ~20% rutile phase, with little amorphous material.[136] Nonetheless, comparing the photocatalytic efficiency of the electrodeposited films to that of control samples, the photocatalytic effect of the electrodeposited TiO₂ films is appreciable (*ca.* 5-10 times improvement in photocatalytic efficiency). Moreover, in the present case, the EPD fabrication technique enabled the formation of photocatalytic thin films through environmentally friendly and low temperature processes.

4.4 Conclusions

The low voltage EPD synthesis of uniform TiO₂ thin films from entirely aqueous and neutral peroxo-titanium modified suspensions was demonstrated. Stabilization of anatase TiO₂ particles within peroxo-titanium suspensions was attributed to surface adsorbed peroxo-titanium species. AFM analyses coupled with powder XRD spectra provide direct evidence that nanoparticulate anatase films were formed via this environmentally friendly EPD technique. The size of grains deposited could be easily controlled by varying the size of particles within the EPD suspension. The growth of a

uniform TiO₂ film during low voltage EPD was analyzed as a direct consequence of the particles' electrical double layer distortion and increased hydrodynamic pressure near the anode. The observations suggest that amorphous peroxo-titanium species are deposited alongside anatase TiO₂ particles during EPD. Due to the anatase content within the EPD suspensions, all the deposited films were photoactive against stearic acid. An important advantage of the TiO₂ thin films developed via this EPD fabrication method is their controllable and reproducible nanostructure, and their environmentally friendly and low temperature fabrication. The EPD method described here would make it feasible to implement large scale production of photocatalytic TiO₂ films without accruing large quantities of organic and acidic by-products. Additionally, the ease of control of electrodeposited film morphology by either varying EPD suspension particle sizes or deposition voltages opens up an exciting route to manufacturing controllable nano-scale structures on heat sensitive substrates.

5. The influence of surface topography on the photocatalytic activity of EPD TiO₂ films

Chapter Summary

In this chapter, the effect of film crystallinity and morphology on film photocatalysis was individually investigated. The applied voltage during EPD was increased from 1.2V to 2.0V in an effort to vary deposited film morphology. At applied voltages of greater than the water electrolysis threshold voltage ($\sim 1.23\text{V}$), the aqueous peroxo-titanium suspension experienced electrolysis resulting in H₂ gas evolution at the depositing electrode. H₂ evolution at the depositing electrode caused the mechanical interference/ detachment of depositing particles during the EPD process. Depositions carried out within similar suspensions at varied applied voltages produced films with similar crystallinity and varied roughness values. FTIR and AFM analysis of the TiO₂ film photoreaction against a stearic acid layer showed that large film roughness values directly improved photocatalytic efficiency. The increases in particle size and consequently, film crystallinity, were also found to improve the TiO₂ film photocatalytic performance.

5.1 Introduction

Nanocrystalline TiO₂ films are attractive photocatalytic materials due to their photo-oxidising abilities. The photocatalyst reacts with ambient oxygen and water to produce reactive oxygen species when irradiated with a wavelength shorter than 380nm. These reactive species react and oxidise organic compounds into non-toxic products like carbon dioxide, water and mineral compounds.[88,165] Commercially, TiO₂ photocatalytic technology has been utilized in applications such as self-cleaning surfaces, water/air-purification devices and dye-sensitized solar cells.

Despite various efforts in fabricating and optimizing TiO₂ materials for commercial photocatalytic technologies, the correlation between photocatalytic efficiency and film physical morphology such as grain/crystal size, surface roughness and packing density, is not well understood. For photocatalytic reactions, the Langmuir-Hinshelwood kinetic models that take into account surface preadsorption and

hence surface area have been shown to predict practical photocatalytic rate kinetics for the degradation of gases on TiO₂ particles.[166,167] TiO₂ particles within the sub-micron sizes have been shown to exhibit improved photocatalysis as surface area effects become prominent.[168] The large surface areas of sub-micron particles are considered to improve the preadsorption of organic contaminants and allow a larger accessibility of electrons and holes to the pollutant, thus speeding up photocatalysis.[168] However, conclusive evidence of this interpretation is elusive,[169] and the isolated effect of surface area on TiO₂ photocatalysis remains unclear.

Alternatively, the size of TiO₂ particles and crystallites has been found to influence photocatalysis on a fundamental quantum level. At smaller size ranges (5nm or less), photocatalytic efficiency has been theorized to increase due to quantization effects. Quantization effects are considered to increase the effective band gap, thus hindering electron-hole recombination.[170] However, several experiment reports have claimed otherwise, citing an improvement in photocatalysis as particle sizes increased.[159,171] The counter size effect has been attributed to the higher packing density of nanoscale particles per unit area; the larger amount of particles per unit area suggest that more electron-hole recombination sites exists per unit area as compared to larger sub-micron particles.[119,171] Although several explanations have been suggested for the correlation between morphology. and TiO₂ photocatalysis, the bulk of such studies have been confined to TiO₂ particles [168,159,170,171] The difficulty in controlling film morphology within the sub-micron range and, other confounding factors such as film crystallinity and film grain size, have restricted deterministic studies on the isolated film morphology effects on TiO₂ film photocatalysis. From a practical viewpoint, a fundamental understanding of factors that affect TiO₂ film photocatalyst will aid the development and optimization of existing TiO₂ photocatalytic materials.

In this chapter, electrophoretic deposition of TiO₂ films was employed to investigate the effect of TiO₂ film roughness on TiO₂ photocatalytic activity. TiO₂ film roughness was varied by employing different deposition parameters. The isolated surface morphology effect on TiO₂ surface photocatalysis was determined through FTIR analysis of stearic acid degradation as a function of UV light irradiation time.

The effect of crystal size, phase and crystallinity on film photocatalytic activity was also systematically studied.

5.2 Experimental

In this series of EPD experiments, the Solartron potentiostat and impedance analyzer was used to control the deposition voltage from 1.2 to 2.0V with an accuracy of $\pm 2\text{mV}$. Characterization of EPD TiO₂ nanoparticles in suspension were achieved through TEM and DLS. TiO₂ film morphology and phase was analyzed through AFM and XRD measurements respectively. The correlation between TiO₂ film photocatalytic activity and surface morphology was deduced through the FTIR detection of stearic acid molecular degradation during photocatalysis. Comparison of photocatalytic rates was established based on modeling experimental degradation rates to zero order linear rate degradation. The sample details for films used during photocatalytic experiments are summarized in Table 5.1.

Table 5.1 Experiment parameters of EPD suspensions treatment

Sample Name	Reflux Duration (hrs)	Deposition voltages (V)
S2	2	
S4	4	1.2, 1.5, 2.0
S8	8	

5.3 Results

5.3.1 Nanoparticulate TiO₂ colloidal EPD solutions

TiO₂ films were formed by electrophoretic deposition of nanoparticulate TiO₂ colloidal suspensions. From TEM analysis, it was observed that the size of TiO₂ particles increased as heat treatment duration was extended. In addition, after 8 hours of heat treatment, the particle shapes transformed from spherical to spheroid particles. A comparison of the particle sizes obtained through TEM and DLS is presented in Table 5.2.

The increase in aggregate particle sizes within the S8 solutions suggests that longer durations of heat treatment promotes the coagulation of smaller particles and reduces the suspension stability. In summary, it was found that primary particle sizes increased

with heat treatment. The increase in suspension heat treatment was also found to suppress the zeta potential of particles, hence promoting particle coagulation that resulted in the presence of large TiO₂ aggregates in S8 suspensions. The effect of suspension aggregate size on EPD film morphology is discussed in the following section.

Table 5.2 Comparison of TiO₂ particle sizes obtained through TEM and PALS measurements.

EPD suspensions	Primary particle size-TEM Micrographs (nm)	Aggregate particle size- DLS (nm)*
S2	11 ± 9 (Spherical diameter)	21.0 ± 0.6
S4	15 ± 8 (Spherical diameter)	20.5 ± 1.5
S8	20 ± 6 by 7 ± 2 (Spheriod ⁺)	28.2 ± 2.1, 255.00 ± 1.9

* PALS calculated diameter for the velocity of a spherical aggregate

⁺ Spheriod dimensions are given as the longer axis length and the shorter axis length.

5.3.2 Effect of EPD suspension heat treatment on film crystallinity, grain size and roughness

The effect of suspension calcination duration on the deposited grain sizes produced in the TiO₂ films is presented in Table 5.3. During the electrophoretic deposition process, the particles within the EPD suspension bath are directly deposited onto the anode. Considering this process, when the applied deposition voltage is adequately low to prevent the EPD suspension from heating, the deposited grain sizes are directly and solely related to the particle sizes within the EPD suspensions. Indeed, AFM measurements of films deposited from the same suspension, at different deposition voltages, did not register significant changes in deposited grain sizes ($\Delta < 5\%$). Hence, the variables in Table 5.3 are considered to be independent of the applied deposition voltage.

Table 5.3 TiO₂ phase and grain size variations for S2, S4 and S8 films

Film	EPD voltage (V)	Crystallite size ⁺ (nm)		Average grain size (nm)	Phase ⁺ (%)		
		A	B		Amp	A	B
S2	1.2, 1.5, 2.0	5.3	-	35.89 ± 6.26	41	59	-
S4	1.2, 1.5, 2.0	8.3	8.9	38.22 ± 5.72	32	63	5
S8	1.2, 1.5, 2.0	9.6	10.3	49.56 ± 5.17	5	74	21

⁺ Amorphous (Amp), Anatase(A) and brookite(B) material within the electrodeposited TiO₂ films.

Figure 5.1 XRD profiles of (a)S2, (b)S4 and (c)S8 films with Rietveld refined profiles (smooth lines) obtained by the Bruker Topas software. The goodness of fit of the Rietveld refinement is (a) 2.08, (b) 1.55 and (c) 1.72.

The measured XRD profile and the Rietveld refined profiles for the characteristic anatase (101) peak are shown in Fig. 5.1. It can be observed from Fig. 5.1 that the anatase (101) peak increases in intensity and narrows as heat treatment proceeds from 2 hours (S2 films) to 8 hours (S8 films). The narrowing of the anatase peak is generally associated with an increase in anatase crystal sizes. In Table 5.2, it can be observed that an improvement in the anatase crystallinity invariably led to an increase in the crystallite size and hence, the deposited grain sizes. Additionally, the increase in EPD suspension sintering durations led to the growth of brookite crystals in the case of films deposited from S4 and S8 suspensions. These results are in agreement with calcination experiments on TiO_2 particles synthesized from TiCl_4 precursors; the formation of the brookite phase is commonly observed during low temperature ($\geq 200^\circ\text{C}$) anatase formation from TiCl_4 precursor solutions.[157] Porter *et al.*

suggested a model for the phase transformation of nanocrystalline titania aggregates;[168] as the titania sample was calcinated, anatase crystals were initially formed through the coalescence of aggregate amorphous particles, followed by the formation of the metastable brookite phase and the later transformation to the most stable rutile phase upon crystal coarsening. Therefore, in the present case, it is not surprising that a phase transformation from anatase (S2, S4 films) to anatase and brookite (S8 films) was observed as calcination time increased.

5.3.3 Effect of EPD applied voltage on film morphology

Changes in EPD applied deposition voltages consequently led to variations in the deposited film morphology. EPD from aqueous suspensions experience water electrolysis at potentials of greater than 1.23V at standard conditions. The significance of this effect at overpotentials is the electrochemical reactions taking place at the cathode (5.2) and anode (5.3) during deposition:

Figure 5.2 AFM micrographs of films deposited from an S2 suspension under an applied voltage of (a)1.2, (b)1.5 and (c)2.0V. Scan area of 1μm by 1μm.

In the present case, the negatively charged TiO₂ particles deposit at the anode and experience disruption to their flow in the vicinity of the anode due to O₂ evolution (see equation 5.3). O₂ evolution consequently leads to the formation of pores within the depositing TiO₂ layers as the molecular O₂ escapes through the forming deposit, thus adversely affecting film morphology. At overpotentials of 1.5 and 2.0V, the

electrophoretically deposited films were found to have greater film roughness values than films deposited at 1.2V. The AFM roughness values obtained by AFM 3-dimensional measurements of all the TiO₂ films deposited at voltages of 1.2, 1.5 and 2.0V is shown in Table 5.4. As observed in Fig. 5.2, the packing density of particles in films obtained at voltages higher than 1.2V was also observed to decrease, indicating turbulence near the depositing electrode due to O₂ evolution.

Table 5.4 Roughness measurements of deposited TiO₂ films

Film	EPD voltage (V)	Film R _a (Å)	Film R _q (Å)	Film R _t (Å)
S2	1.2	29.06 ± 0.43	36.60 ± 0.48	270.46 ± 12.80
	1.5	30.33 ± 1.01	38.44 ± 1.23	293.03 ± 10.39
	2.0	35.98 ± 0.83	45.44 ± 1.01	355.09 ± 10.39
S4	1.2	30.88 ± 0.83	38.94 ± 1.04	296.32 ± 7.59
	1.5	30.38 ± 1.51	38.28 ± 1.51	294.97 ± 7.87
	2.0	35.76 ± 1.33	45.36 ± 1.80	344.39 ± 13.25
S8	1.2	54.84 ± 1.35	68.34 ± 1.77	458.05 ± 8.17
	1.5	54.98 ± 5.27	68.36 ± 5.27	472.53 ± 35.67
	2.0	55.18 ± 3.20	69.08 ± 4.20	451.52 ± 21.65

Figure 5.3 Bearing ratio plot of S8 films deposited at various voltages. Inset schematically shows the effect of bulk TiO₂ film porosity on the bearing ratio plot.

The effect of deposition voltage on film bulk porosity can be associated to the calculated bearing ratio (BR) curves of the AFM micrographs. The bulk porosity of

the film is determined by considering the AFM surface in question to consist of material and air. In the case where the BR is 100%, a film that is entirely constituted of material exists. In the case where the BR is 0%, no film material exists.[172] It should be noted that the bearing ratio investigation of film porosity is a bulk technique that does not give information about the pore structure within the film. Additionally, the use of this technique is limited by the maximum pore depth that the AFM tip can penetrate. The former and latter limitations of the bearing ratio analysis however, are moot when comparing the relative degree of bulk porosity between samples measured consistently with the same AFM tip. The BR curve for S8 films deposited at 1.2, 1.5 and 2.0V is illustrated in Fig. 5.3.

Considering a 0% BR as the air interface of the material and a 100% BR as a complete film, the S8 films deposited at 2V consisted of deeper pores in bulk as compared to films deposited at 1.2 and 1.5V. The gentle gradient from air (BR=0%) to a complete TiO₂ film (BR=100%) suggest the presence of pinnacled TiO₂ islands within the deposited films. The increase in pore depth at high deposition voltages was observed regardless of the suspensions used, thus providing further evidence that gas evolution at the depositing electrode could be effectively utilized to vary film morphology (porosity and roughness) on a nanoscale. This electrophoretic technique was found to directly control film morphology on a nanoparticulate system by variations in deposition voltages.

5.3.4 Photocatalysis rate kinetics- Effect of TiO₂ film crystallinity and grain size

Photocatalytic degradation of stearic acid (C₁₇H₃₅COOH) layer was monitored using ATR-FTIR absorbance spectroscopy. The complete mineralization of stearic acid is known to occur via the following reaction:

The oxidative breakdown of stearic acid leading to complete stearic acid mineralization occurs via the formation of oxidative fragments and the direct mineralization of these fragments:[173]

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(1) Formation of oxidative fragments:

(2) Direct mineralization of oxidative fragments:

(3) Decarboxylation process leading to mineralization:

During photocatalysis, oxygen attack occurs at different locations along the stearic acid chain and causes preferential cleavage to the C-C backbone (equation 5.5 to 5.10). The degradation process results in the decrease in absorbance of several peaks detected from the FTIR spectra of the stearic acid layer; the peak at 2957.5 cm⁻¹ is attributed to the asymmetric in-plane C-H stretching mode of the CH₃ group, and the peaks at 2922.8 cm⁻¹ and 2853.4 cm⁻¹ represent the asymmetric and symmetric stretching modes of the CH₂ group respectively.[109,119] The integrated area of the stearic acid FTIR absorbance peaks is considered to be directly proportional to the degradation rate of stearic acid molecules on the TiO₂ film.[109,119] A generic stearic acid layer with an integrated absorbance area of 1 cm⁻¹ corresponds to *ca.* 3.17 × 10¹⁵ molecules cm⁻² of stearic acid.[109,119] The successive FTIR measurements illustrated in Fig. 5.4 reveals that the initial degradation rate kinetics for all the electrodeposited TiO₂ films were zero order (linearity correlation coefficients for line fits were calculated to be between 0.95 and 0.99):

$$[C_{17}H_{35}COOH]_0 - [C_{17}H_{35}COOH]_t = k_{obs}t \quad (E\ 5.10)$$

where [C₁₇H₃₅COOH]₀ and [C₁₇H₃₅COOH]_t is the stearic acid concentration before and after UV illumination, k_{obs} is the observed zero order rate constant and t is the time elapsed after UV irradiation.

In Fig. 5.5, it can be observed that the S8 film with the largest grain size of 50.3nm was the most photoactive among the studied samples, with a initial degradation rate

constant of $k_{\text{obs}} = 8.60261 \times 10^{10} \text{ molecules cm}^{-2} \text{ s}^{-1}$. The negative sign is omitted in the photochemical calculations since it is understood that a reduction in stearic acid occurs during photocatalysis. The comparison of grain and crystal size versus the measured k_{obs} during stearic acid degradation is illustrated in Fig. 5.5.

Figure 5.4 Degradation of stearic acid (in terms of number of molecules) as a function of UV irradiation time.

Figure 5.5 Plot of zero order rate constants, k_{obs} , against the average grain size within TiO_2 films. Inset shows plot of k_{obs} against the anatase crystal size determined by the Rietveld refinement of XRD data.

A brief consideration shows that the larger the grains/ crystals deposited, the greater the k_{obs} for stearic acid degradation on TiO₂ films. This trend (in Fig. 5.5) is in agreement with photochemical experiments on different TiO₂ colloid sizes for heterogeneous photocatalysis.[164,174] In subnanosecond relaxation dynamics in TiO₂ colloidal sols (of diameter 2.0 to 26.8nm) previously studied,[174] smaller particles(2nm) were observed to experience a greater fraction of electrons(e^-) and holes(h^+) that recombined as compared to larger particles(13.3, 26.7nm).

The recombination process is detrimental to the photochemical reaction as e^- and h^+ excitons are not available for reaction with surface adsorbed water and oxygen to produce reactive species for the breakdown of pollutants. The faster e^-/h^+ recombination in smaller particles in ref[174] was attributed to the lower photon adsorption per unit particle volume and the proximity of e^-/h^+ excitons on the particle surface, promoting charge carrier recombination. This recombination effect is predominant in ultrafine semiconductor particles,[159] and photocatalytic rates have been found to decrease as particle/ grain size increase.[88]

Figure 5.6 Plot of zero order rate constants, k_{obs} , against the relative anatase phase concentration(%). Inset shows plot of k_{obs} against the relative amorphous phase concentration (%).

Exclusively considering the film grain size effect on photocatalysis, however, would not suffice without critical examination of the film crystal phase. The increase in film grain sizes invariably resulted in changes in film phase and crystallinity in the present experiments. Accordingly, the change in degradation rate constants due to grain crystallinity is analyzed in Fig. 5.6. It can be observed that an increase in crystallinity and anatase content resulted in an increase in stearic acid degradation rate constants. The photocatalysis rate enhancement due to phase and grain modifications suggest that grain crystallinity and structure within the deposited films were both factors that contributed significantly to the photocatalysis process. Photocatalysis rate constants were found to improve as the amorphous content of the films decreased to ~5% and as film grain sizes increased to ~50nm. Concurrent studies of electron paramagnetic resonance (EPR) and XRD analysis of amorphous, semi-crystalline (anatase) and single crystal (anatase) TiO₂ films have found that crystal structure has a direct impact on the photochemical behavior of the TiO₂ semiconductor.[83, 164, 174] The number of lattice defect sites in TiO₂ semiconductors is proportional to the geminate rate of e^- and h^+ recombination. Amorphous TiO₂ contain many defects such as dangling bonds, impurities and microvoids; these defect sites leads to additional electronic states within the band gap and hence behave as recombination centres for e^- and h^+ . In terms of photocatalytic function, the lower concentration of the amorphous phase in S8 samples reduces the probability of lattice e^- and h^+ recombination, thus allowing e^- migration towards the particle surface to take part in redox reactions with adsorbed organic compounds.

5.3.5 Photocatalysis rate kinetics- Effect of TiO₂ film morphology

The rate of TiO₂ catalytic reactions that are initiated by photon absorption is determined by the competition between charge carrier recombination and the accessibility of electron and hole excitons to the pollutant adsorbed on the film or particle surface. Correspondingly, the film roughness was expected to have a pronounced effect on photocatalysis rate kinetics since it is a crucial factor in determining the accessibility of e^-/h^+ excitons to the adsorbed stearic acid layer.

Fig. 5.7 illustrates the effect of film average roughness (R_a) and total roughness (R_t) on the k_{obs} in photocatalysis experiments. It can be observed from Fig. 5.7 that an

increase in film roughness (R_a and R_t) resulted in significant improvements in film photocatalysis rate kinetics of approximately 45%. The increase in average film roughness is considered to improve the trapping excitons within the interface between the TiO_2 film and stearic acid layer. The similar trend in the graph pertaining to the variable R_t (that relates to the peak to valley depths across the film surface) suggests that the larger valleys within the TiO_2 films resulted in an increase in the vertical surface contact areas between the stearic acid and the photocatalysis. It is proposed that due to the larger contact areas between the stearic acid molecules and TiO_2 active species, the accessibility of e^-/h^+ excitons per stearic acid molecule increased, thus resulting in higher photocatalytic rates for films with large R_t values.

Figure 5.7 Plot of zero order rate constant, k_{obs} , against the average film roughness, R_a . Inset shows plot of k_{obs} against the total film roughness, R_t .

Presently, to the best of our knowledge, no AFM studies correlating the effect of nanoscale changes in film roughness and TiO_2 bulk photocatalysis has been reported. However, comparing the photophysical changes in rate kinetics due to film roughness values, to previous studies on TiO_2 mesoporous film bulk photocatalysis, the general observation is that the improvement in surface catalysis due to film morphology is limited to the extent of permeation of reactant molecules and the accessibility of catalytic active species to these molecules.[175-177] In the present study, AFM analysis of films deposited at 2.0V from S8 EPD suspensions exhibited an average

inter-grain distance of ~15nm; considering that the molecular length of a single stearic acid molecule is 2.6~5.0nm,[178] the perpendicular and parallel permeativity of stearic acid molecules within the film structure would have improved as compared to an entirely flat catalytic surface. Conversely, AFM analysis of TiO₂ films deposited at 1.2V from S2 EPD suspensions, measured dense packing orders (~1.0nm average inter-grain separation); considering parallel permeativity, the adsorption of stearic acid molecules would have been much lesser than S8 films, thus explaining the lower catalytic rates during stearic acid degradation on more uniform and flat films.

5.4 Conclusions

The manipulation of TiO₂ film physical properties such as film crystallinity/grain structure and roughness was achieved by employing electrophoretic deposition of TiO₂ films at voltages above water electrolysis overpotentials. The films produced from electrophoretic deposition were photoactive towards the degradation of a generic stearic acid layer. Analysis of catalytic rates demonstrated that films which consisted of larger grains (~50nm) were more photoactive (~45%) than films containing smaller grains of ~30nm. The synergistic effect of an increase in both crystal size and film crystallinity also resulted in enhanced catalytic rates. The improvement in catalytic rates due to surface morphology was considered to be a consequence of the increased molecular permeativity of stearic acid molecules on rougher film structures. The observations made in this chapter open up a promising area in the use of electrophoretic deposition to engineer film morphology for enhanced photoactivity without the use of polymeric templates and high sintering temperatures. It is noted, however, that the current synthesis method of TiO₂ nanoparticles is based on thermal growth mechanism. As such, an increase in particle sizes occurs concurrently with the progressive crystallization of the particles. It is considered that a probable method of studying this phenomenon fundamentally would be to grow TiO₂ particles to fixed sizes with variable crystallinity via templates.

6. Analysis of superhydrophilicity in electrophoretically deposited TiO₂ films

Chapter summary

Electrophoretically deposited TiO₂ films were observed from water contact measurements to exhibit UV-induced surface hydrophilicity. The films exhibited an improvement in UV-induced hydrophilicity response as film crystallinity increased; findings from the earlier chapter indicated that an improvement in photocatalytic degradation resulted as film crystallinity improved. This trend suggested that the hydrophilic conversion of TiO₂ films could be related to the photocatalytic oxidation of surface adsorbed hydrocarbon species (present in ppm quantities in the environment) resulting in a clean wettable surface. XPS investigations of TiO₂ films suggested that water adsorption increased significantly after UV irradiation. FTIR spectra showed a similar increase in surface adsorbed water and a concomitant reduction in adsorbed CH₃ species. In order to elucidate the interactions between adsorbed hydrocarbon layers and water, water contact angle measurements were performed during the UV-assisted degradation of a stearic acid layer. Based on the different phases in hydrophilic conversion during catalytic degradation, a model of the TiO₂ film hydrophilic conversion was postulated.

6.1 Introduction

Apart from the photo-oxidizing abilities of TiO₂ materials, the mechanism of UV-induced hydrophilic conversion in TiO₂ films have previously been observed and investigated through various spectroscopic and analytical methods.[113,117,179-182] The most direct and common method of observing changes in surface wetting is water contact angle measurements. The UV-induced hydrophilicity of TiO₂ films have been more recently studied to determine the mechanisms leading to changes in TiO₂ surface energy and hence, wettability. A fundamental understanding of TiO₂ UV-induced superhydrophilicity would allow the design and optimization of other metal oxide materials with controllable wetting characteristics (using TiO₂ as a model surface).

Although many mechanisms have been proposed for the hydrophilic conversion on UV irradiated TiO₂ surfaces,[117,179-182] the majority of the literature can be classified into three models: -(1)UV induced TiO₂ lattice defects,[113,179-181] (2)UV induced dangling Ti-OH bonds,[117,182] and (3)photo-oxidation of hydrophobic layers on TiO₂ surfaces.[183] Model (1) was first discussed by Fujishima *et al.* to explain the wetting transformations of TiO₂ surfaces. Based on X-ray photon spectroscopy, FTIR, frictional force microscopy and water contact angle measurements, Fujishima *et al.* postulated that UV irradiation resulted in structural changes in the TiO₂ surface; UV irradiation generates oxygen vacancies within the TiO₂ lattice where water dissociation was postulated to occur. The TiO₂ surface was considered to comprise of microscopic hydrophilic and hydrophobic domains. During UV irradiation, the TiO₂ surface was proposed to revert to primarily hydrophilic domains, thus resulting in the macroscopic wetting of the surface. The microscopic hydrophilic sites were attributed to the defect formation of oxygen vacancies and Ti³⁺ sites during UV irradiation. Although the authors conceded that photo-oxidation of adsorbed hydrocarbons had occurred on TiO₂ surfaces during hydrophilic conversion, it was proposed that the photo-oxidation occurred independent of the hydrophilic conversion based on other studies of SrTiO₃ materials.[52] Regardless of the high photocatalytic activity of SrTiO₃, surface wetting of SrTiO₃ materials remained unchanged during UV irradiation, suggesting that surface “cleaniness” was not a pre-requisite for surface hydrophilicity.

Alternatively, model (2) was later suggested to occur during TiO₂ UV-induced hydrophilic conversion by Gao *et al.*[183] In this model, hydroxyl groups were presumed to be adsorbed onto TiO₂ surfaces prior to UV irradiation. UV irradiation was considered to increase Ti-OH surface adsorption on TiO₂ in the presence of ambient water, and induce the rupture of Ti-OH bonds to result in unstable Ti-O-dangling bonds that act as water adsorption sites. The bulk formation of these dangling bonds was proposed as a possible reason for photoinduced hydrophilicity on TiO₂ surfaces. This mechanism, however, has been quantitatively investigated by FTIR spectroscopy under high vacuum conditions[117] and the findings have suggested that this model does not occur. Observations of FTIR peaks within the spectral range of 3000 to 3800cm⁻¹ (assigned to adsorbed OH and H₂O) did not register significant changes after in-situ UV irradiation of TiO₂ surfaces with a photon flux of 1.76×10^{21}

photons cm⁻² ($\lambda=375\text{nm}$). Due to the ambiguity of the nature of hydrophilic conversion on TiO₂ surfaces, later investigations[117,183] were carried out to determine the in-situ changes in TiO₂ water contact angles during UV irradiation. One later study[117] showed that during UV irradiation, hydrophilic conversion occurred almost immediately after the surface adsorbed hexane (an organic contaminant) was degraded by TiO₂ photocatalysis. To date, this is considered to be the most comprehensive study of UV-induced hydrophilicity on TiO₂ surfaces as real time water contact angle measurements were conducted during UV irradiation in a controlled ultra high vacuum environment. However, a point of contention in this study[117] is the lack of explanation on the adsorption and photo-oxidation process of hexane gas onto the TiO₂ surfaces. During the degradation of hexane, it was unknown if the complete degradation of hexane was solely responsible. A photo-oxidized by-product produced during the degradation of hexane could equally have been responsible for the UV- induced surface hydrophilicity. Additionally, the change in “flatness” (structure/ morphology) of the film surface devoid of organics could be the actual reason for UV-induced surface hydrophilicity. Although the presence of a clean TiO₂ surface has been directly associated to surface hydrophilicity,[117,182] the question of necessity still remains. Is hydrophilicity present only on clean TiO₂ surfaces and are clean TiO₂ surfaces necessarily hydrophilic? The speculative nature of models regarding UV-induced hydrophilicity of TiO₂ surfaces warrants further study.

In this chapter, the UV-induced hydrophilic conversion of electroporetically deposited TiO₂ films was investigated. The mechanisms of hydrophilic conversion of these films were analyzed through XPS, FTIR and water contact angle measurements in the presence and absence of organic contaminants on the TiO₂ films. The use of homogenous photocatalysis (solid phase stearic acid layer degrading on solid phase TiO₂ films) to determine the interactions between organic contaminants and surface hydrophilicity excludes the need for gas adsorption analysis during wettability studies. Based on results from this study, a possible mechanism was suggested for the UV-induced hydrophilicity of electrodeposited TiO₂ films.

6.2 Experimental

The TiO₂ films (that consisted of particles refluxed for 2 (S2), 4(S4) and 8(S8) hrs) were electrophoretically deposited under a constant voltage of 2.0V. The thickness of the films were measured via ellipsometry to be 80 to 100nm. Water contact angle (WCA) experiments were conducted using a commercial water contact machine. The contact angles of water droplets at a minimum of 5 separate locations on the deposited film were measured (to an accuracy of $\pm 2^\circ$) as a function of UV pre-irradiation time. All WCA images were captured within 1 second upon water droplet contact on the films.

Two series of WCA experiments were conducted. In the first series of WCA experiments, the films were pre-irradiated with UV light until the TiO₂ WCA reached $10 \pm 4^\circ$. Pre-illumination of the films was achieved using a UV bench lamp (Spectroline, ENF-280C) of UV light wavelength 254nm and intensity $85\mu\text{W}/\text{cm}^2$ when placed 2cm from the light source. WCAs were measured as function of UV pre-illumination durations. In the second series of WCA experiments, the effect of an organic stearic acid layer on the TiO₂ hydrophilic response time was analyzed. 0.2ml of stearic acid that had been dissolved in methanol (100ml, 20mM) was spin coated at 2500rpm onto the TiO₂ films. Spin coating of the stearic acid layers was repeated for 5 times; after each layer was coated, the layer was dried at 80°C for 5 minutes before the next layer was coated. After 5 layers of stearic acid were coated, the organic film was placed under a UV lamp (ENF-280C/FE) of centre wavelength 254nm and light intensity $85\mu\text{W}/\text{cm}^2$. The effect of organic layer decomposition on the UV-induced hydrophilicity of TiO₂ films was determined using water contact angle measurements at regular time intervals of UV illumination.

Surface Analysis of the TiO₂ films under different experiment conditions were conducted using X-Ray Photospectroscopy, XPS (Kratos Axis Ultra) with a monochromatic Al K α source of excitation 1486.71eV.

6.3 Results and discussion

6.3.1 UV light irradiation reponse of electrodeposited films

UV light irradiation of S2, S4 and S8 films resulted in surface water contact angles (WCA) of less than $10^\circ \pm 4.0^\circ$. Fig. 6.1 shows that a maximum irradiation duration of 20 minutes was required for all electrodeposited films to reach this state of hydrophilicity ($WCA < 10^\circ$) suggesting that this hydrophilic property was inherent in TiO₂ films regardless of film phase or polycrystallinity; S8 film deposits was the most crystalline compared to S2 and S4 film deposits (see section 5.3.2 for detailed XRD analysis). This is in agreement with WCA experiments carried out for polycrystalline TiO₂ materials in ref[53]. Since this is an inherent property of TiO₂ films, it is expected that the UV induced hydrophilic property and mechanism would be similar for S2, S4 and S8 films. For this reason, later mechanistic studies on the UV induced hydrophilic state of TiO₂ films are focused on S8 films.

Figure 6.1 Water contact angle response of ($\diamond$, ---)S2, ($\triangle$,)S4 and ($\square$, - · - ·)S8 TiO₂ films after UV light illumination. Inset shows the WCA images and their corresponding angles obtained during UV irradiation.

In order to determine the mechanism behind UV induced TiO₂ hydrophilicity, the real time WCA change on pre-illuminated hydrophilic S8 films were analyzed (see Fig. 6.2). During dynamic WCA measurements, WCA images were collected at a minimum sampling duration of 100 milli-seconds; some of the successive WCA

images obtained are shown in Fig. 6.2. It can be observed from Fig. 6.2 that upon water droplet contact with the pre-illuminated hydrophilic film, the droplet immediately spreads to a WCA of $4.0^\circ \pm 1.3^\circ$. The droplet continues to spread across the hydrophilic surface after settling for ~ 1 second. In the absence of UV light irradiation, approximately 3 seconds after initial contact with the hydrophilic surface, the water droplet continues to relax further across the surface until it forms an irregularly shaped thin water film. This wetting behavior (within a response time of 2 seconds) was not observed for clean uncoated surfaces exhibiting a WCA of $5^\circ \pm 1^\circ$. The dynamic WCA change of pre-illuminated TiO_2 films in the absence of UV irradiation suggests a hydrophilic conversion mechanism that is not singularly dependant on UV- induced TiO_2 catalysis.

Figure 6.2 Real-time water contact angle response of a TiO_2 film after UV light illumination of 30mins. Time labels in white indicate the time elapsed after the water droplet makes contact on hydrophilic TiO_2 films.

Accordingly, in order to determine the likely cause/s for dynamic WCA changes in pre-illuminated TiO_2 films, the changes in TiO_2 surface states during hydrophilicity were further analyzed through XPS measurements. High resolution O (1s) and Ti (2p) spectra for as-deposited and UV irradiated films were obtained and shown in Fig. 6.3. Considering Fig. 6.3(a,b), it can be observed that significant asymmetrical broadening of the major O(1s) peaks towards higher binding energy was observed for as deposited and UV pre-illuminated films. Using a combination of Gaussian and Lorentzian distributions, the O(1s) peak could be deconvoluted into 3 peaks, each peak indicating

the presence of a different oxygen species.[184] The O(1s) peak profiles for both the as-deposited and UV irradiated films shown in Fig. 6.3 (a,b) exhibited a major peak (530.3~530.4eV) that can be attributed to the bulk oxygen within the TiO₂ crystalline network,[113,184,185] a sub peak (531.4~531.8eV) that is associated with O species from bridging acidic OH groups and physisorbed water, and finally, a tail peak (533.0~533.2eV) that can be associated with basic terminal OH groups.[186,187] The details of the deconvoluted O(1s) peaks are presented in Table 6.1.

Figure 6.3 O(1s) and Ti(2p) XPS spectra of (a, c) as deposited (b, d) UV irradiated S8 TiO₂ films respectively. (—) refers to the original XPS spectra, (---) plots the Shirley fitted background, (- - -) and (···) represent the fitted peak and the deconvoluted components respectively.

Table 6.1 Binding Energy and % relative area of deconvoluted O(1s) peaks

Experiment Conditions	Elements	Binding Energy (eV)	Relative Area (%)
As deposited	Lattice O ₂	530.397	58.10
	Ti-OH, physisorbed H ₂ O	531.517	38.72
	Ti-OH terminal groups	533.042	3.16
UV irradiated	Lattice O ₂	530.338	59.00
	Ti-OH, physisorbed H ₂ O	531.444	39.26
	Ti-OH terminal groups	533.252	1.74

Comparing the % rel. peak areas for the O(1s) peaks of the as-deposited and UV irradiated films shown in Table 6.1, it can be observed that UV irradiation on the film resulted in a higher fitted % rel. peak area for the peak associated with O species of bridging OH groups and physisorbed water (by 1.395%), and lattice O₂ groups (by

1.549%). In addition, a concomitant decrease in the fitted % rel. peak area for the peaks associated with terminal basic OH groups (by 44.937%) was observed. These findings suggest that UV irradiation is likely to have caused an increase in hydroxylation of the film surface by either molecularly or dissociatively adsorbed water. However, contrary to the UV initiated oxygen vacancy model proposed,[113,179-181] the O₂²⁻ % rel. peak area was observed to increase in our experiments suggesting a slight increase in adsorbed oxygen after UV irradiation. Additionally, no significant changes were observed in the Ti 2p_{1/2} and Ti 2p_{3/2} peak position and relative peak areas (see Fig. 6.3(c,d)). The similar Ti(2p) doublet peaks before and after UV irradiation suggested that the presence of Ti³⁺ defect states (associated to oxygen vacancies) was negligible. While it is likely that the UV-induced hydrophilicity of TiO₂ surfaces may be associated with surface hydroxylation by physisorbed water, it is unclear if hydroxylation is a consequence or prequence of some other processes like UV-driven removal of functionalized hydrocarbon species[117,182] and/or UV- initiated structural changes of the film surface.[183]

Figure 6.4 Micro-FTIR investigation of adsorbed OH groups (2500 to 4000cm⁻¹) and H₂O (1800 to 1500cm⁻¹) on TiO₂ films before and after UV irradiation.

The increase in surface adsorbed water and OH groups observed in the XPS spectra were also detected in in-situ UV light irradiated FTIR measurements. The FTIR spectra obtained prior to and during UV irradiation (after 20 minutes had lapsed) is presented in Fig. 6.4. The increase in the peak intensity and area at wavenumber 3300cm⁻¹ for dissociated and molecularly adsorbed water[188] was observed. A

similar increase in peak intensity was also observed for the peak at 1623cm^{-1} that is associated to the bending of molecular H₂O bonds[188] during UV irradiation of the film. A brief consideration shows that both XPS and FTIR measurements are in agreement with each other and indicate an increase in surface hydroxylation during and after UV irradiation. An interesting feature associated to surface adsorbed hydrocarbons[115] at wavenumber 3000cm^{-1} was also detected during in-situ FTIR measurements. The concomitant increase in surface hydroxylation and decrease in CH₂ adsorbed contaminants suggests that UV- driven removal of hydrophobic hydrocarbons on TiO₂ surfaces could possibly be associated to UV induced hydrophilicity.

6.3.2 Effect of hydrophobic stearic acid layer on TiO₂ hydrophilicity- A model of photon induced hydrophilicity

The effect of hydrophobic hydrocarbon layers on the TiO₂ UV-induced surface hydrophilicity could be analyzed by measuring the changes in WCA during the UV initiated degradation of a stearic acid layer. The stearic acid molecule comprises of a hydrophilic COOH carboxylic hydrophilic 'head' and a long hydrophobic CH₂ tail as shown schematically in Fig. 6.5. Prior to the deposition of stearic acid layers on TiO₂ films, the films were pre-irradiated with UV light and the film WCA were checked and found to be $<10^\circ$. After spin coating the stearic acid layers on the pre-illuminated TiO₂ films, the WCA of the films were found to increase to $108.0^\circ \pm 2.2^\circ$ (see Fig.6.6). The relative hydrophobicity of the stearic acid coated film was attributed to the bulk presence of hydrophobic CH₂ groups on the TiO₂ film.

Figure 6.5 Stearic acid hydrophobic-hydrophilic molecular structure.

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Figure 6.6 Water contact angles (WCA) of stearic layers on a S8 TiO_2 film after (a) 0mins: $\text{WCA}=108.0^\circ \pm 2.2^\circ$, (b) 125mins: $\text{WCA}=18.8^\circ \pm 3.8^\circ$ and (c) 155mins: $\text{WCA}=7.0^\circ \pm 2.2^\circ$. WCAs are measured between the tangent and the horizontal line.

Figure 6.7 Water contact angle (WCA) response during the degradation of hydrophobic stearic acid layers on UV irradiated (Δ) S8 TiO_2 films. The dotted lines are fitted to indicate the 3 different rates of WCA decrease.

The WCA response during stearic acid photocatalysis on the TiO_2 film was measured and is presented in Fig. 6.6 and 6.7. In Fig. 6.6, the collected images showed a decrease in WCA as UV irradiation of the stearic acid layer covered TiO_2 film continued. Fig. 6.7 presents the measured WCAs as function of UV irradiation time. It can be observed that there are 3 phases of WCA decrease. During the initial phase of UV irradiation for 70 to 80 minutes, the observed decrease in WCAs occurs at a slow

rate. After ~80 minutes of UV irradiation, the WCA decreases rapidly from ~100° to ~30°. WCA observations at this phase demonstrated a large variability in the water contact angle across the TiO₂ film (see error bars in Fig. 6.7) indicating island degradation of the stearic acid layer; this 'island' degradation of stearic acid layers by TiO₂ films photocatalysis has previously been observed in in-situ AFM studies of stearic acid photocatalysis.[109] This rapid WCA decrease was then observed to plateau after ~120minutes, when the film started to exhibit surface hydrophilicity.

Figure 6.8 Model of UV light photon driven removal of hydrophobic stearic acid layers and the corresponding effect on water contact angles (a) before, (b) during and (c) after photocatalysis.

Based on previous FTIR photocatalysis experiments and the present WCA, FTIR and XPS investigations of the electrodeposited TiO₂ films, a possible mechanism of UV-induced TiO₂ film hydrophilicity is suggested and schematically shown in Fig. 6.8. Previous FTIR investigations of stearic acid layer degradation on UV-illuminated TiO₂ films (presented in section 4.3.4 and 5.3.4) showed that upon UV irradiation of $\lambda = 254\text{nm}$ and intensity = $85\mu\text{W}/\text{cm}^2$, S8 films were found to degrade approximately

the same amount of stearic acid (as in the present case) after UV irradiation of ~110 minutes. This information can be correlated to the UV-induced change in WCA decreases presented in Fig. 6.7. It is likely that during initial UV irradiation, the rate of WCA decrease is slow as the microscopic degradation of stearic acid is not adequate to induce a macroscopic response in WCAs as illustrated in the proposed model shown in Fig. 6.8(a). Once bulk stearic acid degradation occurred, the hydrophobic stearic acid spatial area would have become relatively smaller than the exposed hydrophilic TiO₂ spatial area, hence resulting in the onset of larger WCA decreases (see Fig. 6.7 and associated model suggested in Fig. 6.8(b)). The island degradation of stearic acid monolayers on TiO₂ films previously demonstrated in AFM studies[109] further support this suggestion. After UV irradiation of ~120 minutes, when less than 5% of initial stearic acid layer was present (deduced based on FTIR observations presented in section 4.3.4 and 5.3.4), the WCA decrease exhibited an exponential decrease into hydrophilicity (WCA < 10°) similar to the trend observed for films that had not been spin coated with stearic acid (see Fig. 6.1). This exponential decrease in WCA at this stage is postulated to occur due to the rate equilibration of adsorbing and desorbing/degrading ambient hydrocarbons, and the rate at which surface hydroxylation occurs (see Fig 6.8(c)). It is unlikely that water dissociation on oxygen defects (Fujishima *et al.*[113,179-181] model) or OH dangling bonds (Gao *et al.*[183]) resulted in TiO₂ hydrophilicity since present XPS investigations of UV irradiated TiO₂ films did not register an increase in O₂ lattice defects and OH terminal groups. Correspondingly, the increase in surface adsorbed water followed by a concomitant decrease in FTIR observed CH₂ species suggest that hydrocarbon adsorbed sites recover their hydrophilic nature after the occupying hydrocarbon was degraded and the clean TiO₂ surface was exposed.

The model shown schematically in Fig 6.8 is in agreement with earlier work carried out by Zubkov *et al.*[117] and White *et al.*[182] on the effect of heterogenous catalysis of gaseous hydrocarbons on water adsorption on TiO₂ surfaces. In studies detailed by Zubkov *et al.*[117], the hydrophilicity of TiO₂ films in a highly controlled vacuum environment was found to occur suddenly after an initial induction period. It was thus proposed that this induction period was required to photo-oxidize hydrophobic hydrocarbons that had adsorbed onto the TiO₂ films. Investigations of water droplet motion on the TiO₂ surface adsorbed hydrocarbon layer was found to

induce spatial preference for water droplet wetting; this observation is similar to ours where hydrophilicity and relative hydrophobicity of the TiO₂ film was observed to occur across TiO₂ exposed areas and stearic acid islands respectively. Similarly, findings of improved water adsorption after significant photocatalysis of adsorbed hydrophobic trimethyl acetate on the TiO₂(110) surface through temperature programmed desorption analysis was presented in the White *et al.* study. Although these studies provided evidence of the role of hydrocarbons on TiO₂ surface hydrophilicity, several areas require further quantification. While the White *et al.* study analyzed the entire trimethyl acetate photocatalysis process on TiO₂(110) to deduce surface wetting behavior, water contact angle measurements to determine water droplet behavior on UV irradiated TiO₂ was not performed. On the other hand, the setup suggested in the Zubkov *et al.* study analyzed the change in water droplet behaviour during UV-driven organic (hexane gas) photocatalysis but did not quantify the amount of hexane gas that had actually adsorbed or desorped/degraded on the TiO₂ surface during UV-induced hydrophilicity.

In the present study, the parallel quantification of the actual amount of stearic acid degradation on electrodeposited films (by FTIR) and the WCA response during the degradation process suggests that the effect of hydrocarbons on UV-induced hydrophilicity depends on the surface coverage of the hydrocarbon on the photocatalytic surface. The surface reactions occurring after catalysis of the adsorbed hydrocarbon, however remains unclear and is not within the scope of the present study. From a practical point of view, the present room temperature, ambient environment study has several implications: 1) Aerated conditions with abundant O₂ supply is required for both photocatalysis and hydrophilicity, 2) Film hydrophilicity can only proceed after macroscopic degradation of adsorbed organics, 3) brief on site wettability checks of TiO₂ films as a function of UV irradiation time can provide an indication of the relative photo efficiency between different TiO₂ films without the use of specific chemical measurement tools like FTIR or liquid/gas chromatography.

6.4 Conclusions

Electrophoretically deposited TiO₂ films were observed to exhibit UV-induced hydrophilicity. XPS analysis of the UV irradiated TiO₂ films suggested that neither an increase in oxygen vacancies nor an increase in OH terminal groups occurred during UV irradiation. Corresponding FTIR analysis during in-situ UV irradiation of TiO₂ films highlighted the role of adsorbed hydrocarbons on surface hydrophilicity. When covered with stearic acid, the TiO₂ surfaces exhibited non-wetting behaviour; during UV irradiation, island degradation of the organic layer resulted in preferential wetting on TiO₂ clean exposed film while hydrocarbon covered areas exhibited non-wetting. The results suggest that surface hydrophilicity of TiO₂ films can be used as an indication of film photoactivity towards functionalized hydrocarbon compounds.

7. Anti-bacterial properties of electrophoretically deposited TiO₂ films

Chapter Summary

The anti-bacterial properties of electrodeposited TiO₂ films was investigated by subjecting *E.coli* DH5α cell strains to direct and indirect UV irradiation. In direct UV irradiation experiments, the photocatalytic effect of TiO₂ films was found to exacerbate the rate of cell killing solely induced by direct UV irradiation. Analysis of in-situ FTIR data showed that lipid peroxidation products were formed during TiO₂ photocatalysis, thus suggesting the presence of reactive oxygen species and their role in cell deactivation. Subsequent indirect UV irradiation experiments conducted revealed that cell inactivation was still possible even after UV light irradiation was terminated. These observations suggest that reactive oxygen species exist transiently in the vicinity of TiO₂ films and maintain their oxidizing abilities towards biological cells even after UV irradiation is terminated.

7.1 Introduction

TiO₂ photocatalysts are known to exhibit a photo-sensitized oxidizing ability towards both biological[55-59,61,189] and organic compounds.[88,89,190] Photo-generated reactive species like hydroxyl radicals (•OH), superoxide anions (O₂⁻), oxygen radicals (•O), singlet oxygen (¹O₂) and hydrogen peroxide (H₂O₂) have been proposed to deactivate cells via the lipid peroxidation of cell membrane walls.[61,67,189,191-193] For example, *Escherichia Coli*,[55-59] *Pseudomonas aeruginosa*,[59] and *Micrococcus luteus*,[189] among many other bacteria types, have been shown to deactivate on UV light illuminated TiO₂ photocatalyst. Likewise, the disinfection mechanism of TiO₂ films has also been found to be effective in penetrating tumor cells, inducing cytotoxicity in *HeLa* cultured animal cells under UV illumination.[61]

However, the photocatalytic disinfection process has almost always been associated with the presence of UV light irradiation. The time dependence of the TiO₂ surface reactivity after the termination of UV light illumination, has largely been neglected albeit a few studies.[91,194,195] Several types of reactive species like O₂⁻

and ¹O₂ have been found to exist even after UV illumination was stopped. These oxidative compounds were found to continue to generate hydrogen peroxide (H₂O₂) in the presence of water via the protonation of oxygen species.[194,197,198] Similarly, the long-lived reactive species were shown to cause oxidative damage to polymeric films such as Poly (2-methoxyaniline-5-sulfonic acid), Polystyrene, Octadecyltriethoxysilane, and even copper after diffusing through a gap of 12.5 ~ 500μm in an UV irradiated lithography process. The lithographic application required the mobility of ROS, and the lack of deactivation of the reactive species in air; suggesting that ROS existed in a gas phase without becoming deactivated, within the vicinity of irradiated TiO₂ films.[91] This long lasting oxidative effect has also been observed to prevent bacteria recovery for a maximum duration of three hours[58] after photocatalysis was carried out.

In the present work, the direct and residual effect of reactive species from TiO₂ photocatalytic surfaces on the *E.coli* DH5α bacteria strain is discussed. The existence of reactive species after UV irradiation has several implications on the design of self cleaning systems, i.e., the existence of photocatalytic long- lived reactive species after photocatalysis would imply that self cleaning systems like water and air purification reactors would likely only require an intermittent UV light source. Furthermore, the biological reactivity of pre-illuminated TiO₂ photocatalyst would be important in terms of the health safety of workers or researchers in constant contact or within the vicinity of the material.

7.2 Experimental

The TiO₂ films used were obtained via EPD under an applied deposition voltage of 2V and after a deposition duration of 75 seconds. The deposited films of thickness 80~120nm were dried in air for 2 hours and the total effective planar film area was measured to be ~6cm².

7.2.1 Bacterial strain and growth medium

Escherichia coli (*E. coli*) cells (DH5α strain) were grown aerobically in Luria Bertani (LB) medium containing 1% Bacto tryptone, 0.5% Bacto yeast extract and 1%

NaCl. *E. coli* cells were grown to mid-log phase and had an optical density (O.D₆₀₀) of 0.5 corresponding to $\sim 5 \times 10^8$ cells/ml of bacteria suspension. Cell viability assays were conducted by plating appropriate dilutions onto LB agar plates and counting colonies after 24 hours of incubation at 37°C. The number of colonies formed on the agar plates were then counted and calculated in terms of colony forming units per millilitres of suspension spread on the agar plates. The specific assays for bacteria harvesting and agar plate production are summarized in Appendix C.

Three replicate cell viability experiments were conducted for each experiment condition and the reported results are the arithmetic mean of the triplicate results. Error bars on Fig 7.1 and 7.3 indicate the standard deviations (SD) of triplicate results within single data sets. The SD of the obtained results was calculated using the following formula:

$$SD = \sqrt{\frac{\sum (X - \bar{X})^2}{n}} \quad (\text{E 7.1})$$

where Σ is the sum of, X is a value in the data set, $\bar{X}$ is the arithmetic mean of the data set and n is the total number of values within the data set.

7.2.2 UV irradiation and disinfection procedures

A 50kW black light bulb lamp with an emitted wavelength peak at around 254nm and light intensity of c.a. $85 \mu\text{W}/\text{cm}^2$ was used during UV light illumination. The effect of UV light irradiation on TiO₂ films was tested by applying two experiment protocols (see Fig. 7.1):

(1) 250 μL of *E. coli* cell suspension (2.5×10^8 cells) was spread onto TiO₂ films and uncoated stainless steel control specimens; these bacteria coated specimens were subsequently exposed to UV illumination of various durations and the cell suspensions were then collected and plated. A second experiment protocol was then applied to ascertain if simultaneous UV light irradiation is a necessary pre-requisite for photocatalytic killing of *E. coli* cells on TiO₂ films.

(2) TiO₂ films and uncoated stainless steel control specimens were first UV irradiated for different durations, following which 250μL of *E. coli* cell suspension was spread onto the illuminated films without further UV light exposure. The bacteria coated specimens were then left in a dark incubator to determine if bacteria recovery would occur on UV light irradiation TiO₂ surfaces after the light source was cut off. The incubated cell suspensions were then collected and plated.

Figure 7.1 In-situ and ex-situ UV irradiation protocols performed to determine the photoactivity of TiO₂ films.

7.2.3 Determination of lipid peroxidation by FTIR spectroscopy

The concentration of fatty acids within the *E. coli* cell membrane was analyzed as a function of in-situ and ex-situ UV irradiation. The extent of bulk lipid peroxidation occurring within an *E. coli* layer applied on top of photoactive TiO₂ films was determined through microscopic FTIR Spectroscopy (Biorad, Excalibur series). The *E. coli* layer was applied on TiO₂ films that had previously been treated with polylysine. The instrument was equipped with a microscope that allowed spatially focusing of the surface prior to measurements. The instrument beam was first focused on a gold

mirror for background spectrum measurements and subsequently focused on the test samples to determine the spectra associated to the biological *E. coli* layer. The spectra were collected from 64 scans, at a resolution of 4cm⁻¹, within the wavenumber range of 400-6000cm⁻¹. The gold mirror ATR mode was utilized to ensure that the same spatial diameter of 1µm was measured after each sample had undergone different experiment conditions. The absorbance peak areas reported for peaks assigned to cell membrane organics and peroxidation organic by-products are the mean values of three repetitive FTIR spectra measurements, and the error bars are the standard deviations of the absorbance peak areas recorded within three replicate measurements.

7.3 Results and Discussion

7.3.1 In-situ UV irradiation effects on cell killing

The oxidative effects of UV irradiated TiO₂ films are known to have deleterious effects on biological cells such as *E.coli* bacteria.[55-59,61,189] The pathways leading to cell membrane oxidation and later cell inactivation have been associated with the production oxygen and hydroxyl radicals in the presence of molecular O₂ and H₂O via the following possible reaction schemes:[55]

These UV generated oxygenated radicals are highly reactive towards the polyunsaturated fatty acids that exist within the cell membrane. Radical attack on these acids result in cell membrane destruction, thereby affecting the respiratory functions of *E. coli* cells that depend on an intact membrane structure.[55-59] In the presence of adsorbed water on the TiO₂ films, the reactive O₂^{•-} and HO[•] species may produce by products such as hydrogen peroxide (H₂O₂) through reaction schemes (E7.6) to (E7.8).[196] The oxidizing effect of H₂O₂ are also considerably damaging to *E.coli* cell membranes.[56]

The effect of UV irradiation in the presence of photocatalytic TiO₂ films was found to cause *E.coli* cell inactivation. Data obtained from cell viability assays under different operating conditions is presented in Fig. 7.2 and Table 7.1. It can be observed from Fig 7.1 that of both UV light irradiation (regardless of wavelength) and TiO₂ film photocatalysis led to an appreciable decrease in colony forming units after 15 minutes of irradiations. In the presence of both TiO₂ film and UV irradiation of 254nm,

residual colonies formed after a reaction time of 15 minutes were almost undetectable (1.48×10^4 cfu/ml). A similar decrease in colonies formed in the presence of TiO₂ film and UV irradiation of 365nm after the course of reaction duration.

Figure 7.2 Bacteria colony forming units per ml of bacteria suspension during the following experiment conditions: (Δ)365nm & no film, (□)254nm irradiation & no film, (▲)365nm & TiO₂ film and (■)254nm & TiO₂ film.

The decrease due to both TiO₂ photocatalysis and UV irradiation was significantly greater than the decrease that was solely attributed to UV light initiated injury to *E.coli* cells, regardless of the wavelength of UV light irradiation. An increase in *E.coli* cell death by 6.10×10^4 cfu/ml and 4.54×10^6 cfu/ml was achieved by the sole effect TiO₂ photocatalysis under 254nm and 365nm irradiation respectively. Noticably, the *E.coli* colony decrease progressed faster in the presence of both TiO₂ films and UV irradiation as compared to when the TiO₂ film was absent.

Further evidence of the effect of TiO₂ film catalysis during UV irradiation was observed when comparing samples under control 1 and 2 operating parameters. In table 7.1, the cell death observed under control 1 and 2 operating parameters were negligible within the reaction course of 15minutes, suggesting that UV-initiated TiO₂ catalysis was required to induce complete *E.coli* cell inactivation.

Table 7.1 Comparisons of *E.coli* disinfection under various operating parameters.

Sample conditions	Colonies formed	Cfu/ml after 15mins irradiation	Survival Ratio (%)
Control 1: No film, dark	2.0×10^8	2.0×10^{13}	100.00
No film, 254nm for 15mins	12.0	9.0×10^{11}	4.50
No film, 365nm for 15mins	1.1×10^8	1.4×10^{12}	7.00
Control 2: TiO ₂ film, dark	1.2×10^7	1.6×10^{11}	97.00
TiO ₂ film, 254nm	2.0	2.0×10^4	<0.00
TiO ₂ film, 365nm	8.0	8.0×10^5	<0.00

⁺ Time taken for *E.coli* survival ratio to reach 10% of initial inoculated *E.coli* suspension grown to the stationary phase.

7.3.2 Micro FTIR analysis of photocatalytic degradation of *E.coli* membrane structure

Gram negative bacteria like *E. coli* have two thin and slack cell membranes consisting mainly of a nonsymmetrical outer lippopolysaccharide bilayer (LPS), a phospholipid layer, a peptidoglycan segment and the cytoplasmic membrane. The detailed cell wall structure is illustrated in Fig.7.3. During photocatalytic oxidation of the cell membrane, decomposition of the cell membrane chemical structure via lipid peroxidation can be observed by micro FTIR spectroscopy.[192,193,199] Micro FTIR analysis of the *E.coli* layer provides an indication of the CH₂ rocking, stretching, bending and scissoring band progressions that can subsequently be used to probe the physical state of lipids under different UV exposure conditions.

Figure 7.3 Cell Wall structure of Gram- Negative Bacteria such as *E.coli*. [199]

The micro FTIR spectra obtained for the UV irradiated *E.coli* liquid layer applied on TiO₂ films was obtained after correction for earlier adsorbed organics on the TiO₂ films (i.e. $\text{Spectrum}_{E.coli} = \text{Spectrum}_{(E.coli + TiO_2 \text{ film})} - \text{Spectrum}_{(TiO_2 \text{ film})}$). The *E.coli*

spectra were subsequently normalized on the same scale in order to compare the individual peak intensities. Fig 7.4 shows significant changes in the spectra of the *E.coli* liquid layer applied to TiO₂ films that were obtained as a function of UV light (254nm) irradiation time. The lipid compounds/by-products formed or degraded during TiO₂ photocatalysis are indexed to their respective wavenumbers as summarized in Table 7.2. The fingerprint region between 900 to 700cm⁻¹ exhibited peaks associated to organic compounds that could not be assigned to any *E.coli* associated compounds.

Figure 7.4 Micro FTIR spectra of the *E.coli* layer on TiO₂ films as a function of in-situ UV irradiation durations. (a) and (b) show the normalized peaks within the spectral region of 3600 to 2600cm⁻¹ and 1900 to 700cm⁻¹ respectively.

Table 7.2 Assignment of organic compounds within the *E.coli* bacteria (Wavenumbers: 900 to 1800cm⁻¹ and 3600 to 2600 cm⁻¹) to their corresponding ATR- FTIR bands and references.

Wavenumber (cm ⁻¹)	Assignment	References
2959	Asymmetric vibrations of C-CH ₃	[192]
2873	Assymetric vibrations of CH ₃	[192]
1653	Amide I	[193]
1683	Symmetric vibrations of C=O in aldehydes	[192]
1546	Amide II	[192]
1462	Aromatic Ring Stretch	[193]
1410	Carboxylic Groups -COO- stretch COO ⁻ symmetrical vibrations	[192]
1343	δ _s (CH ₃) Umbrella progression of the CH ₂ wagging modes	[192,199]
1246	PO ₂ ⁻	[192]
1118	C-O linkage	[199]
1053-1056 989	Oligosaccharides	[199]

The main observations relating to FTIR spectra changes during TiO₂ photocatalysis can be summarized as follows: (1) The decrease in CH₃ vibrations at 2959cm⁻¹, 2873cm⁻¹ and 1343cm⁻¹ after UV irradiation of 15minutes suggest the continuous peroxidation of fatty acids that are present within the cell membrane phospholipids. (2) After UV irradiation of 9 mins, the peak intensity at 1683cm⁻¹ increased, indicating an increase in C=O groups commonly present in Malondialdehyde (MDA). MDA formation has been known to occur during initial stages of lipid peroxidation.[56,192-194] During the later stages of cell peroxidation, however, MDA itself has been observed to completely oxidize. This was similar to the present observations of MDA peak decrease after UV irradiation of 15min. (3) Complete mineralization of the *E.coli* layer was observed after UV irradiation of 15 minutes when peaks associated to the *E.coli* layer became undetectable.

7.3.3 Long lasting effects of residual ROS on cell killing (Ex-situ UV irradiation)

In addition to the direct bio-reactivity of TiO₂ films during UV illumination, pre-illuminated TiO₂ films were found to exhibit long-lasting bio-reactivity. Residual species on pre-illuminated TiO₂ were found to cause a decrease in the concentration of viable cells after a maximum incubation duration of 45mins in the dark (see Fig. 7.5).

Figure 7.5 Survival Rate of *E.coli* cells after exposure to residual reactive species on TiO₂ films. (□), (■) and (■) represent cell viability on TiO₂ films that were pre-illuminated with 254nm UV light for 45, 60 and 90 mins respectively. Error bars are ± standard deviation of triplicate experiments.

From Fig. 7.5, it can be observed that in the absence of UV irradiation, the survival ratio of *E.coli* colonies formed on pre-illuminated TiO₂ films reduced from 100 ± 3.2 % (control) to a minimum of 3.2 ± 1.3 %. Longer UV light pre-illumination durations did not improve the rate of cell killing, suggesting that a minimum UV light irradiation duration of 45mins was sufficient to induce cell killing later on. Furthermore, the survival ratio for all the pre-illuminated samples did not increase at *E.coli* incubation durations in the dark after 45minutes, indicating the persistent effect of the reactive species present on TiO₂ films.

The cell killing effect was considered to be related to the presence of residual ROS since this reduction in cell viability was not observed in cell suspensions on TiO₂ that were not pre-illuminated (see Fig 7.2 and Table 7.1). It is known that during UV light illumination of wavelength less than 380nm, the photon energy produced is greater than the band gap of TiO₂, thus resulting in electron- hole separation (equation E7.2). The positive “holes” (h^+) generated react with surface adsorbed H₂O or OH groups to form hydroxyl radicals. The corresponding excess electrons produced during electron-hole separation react with molecular oxygen to produce superoxide anions through equation E7.4. The photosensitization of TiO₂ surfaces was also found to generate singlet oxygen (see equation E7.3) In pre- illuminated TiO₂ surfaces, it has been shown that reactive and low mobility species like O_2^- and 1O_2 are present in the vicinity of the photocatalyst as a gas phase.[91,194,195,196-198] These low mobility species have been observed from photoluminescence experiments to remain active for nearly 1 minute near the TiO₂ film surface.[91,194,195,196-198] The activity of these reactive oxidative species after UV irradiation could possibly suppress *E.coli* cell reactivation by continual radical oxygen attack on the carbon backbone of cell membrane walls. However, it is unclear if the oxidative species are consumed during reaction with organic/ biological compounds or regenerative in the absence of radical scavengers such superoxide dismutase and catalase. Superoxide dismutase and catalase are known to be produced by bacteria cells as a self-defence mechanism against oxidative stress.[55,56,192,199] The exact mechanism behind the long lasting effect of pre-illuminated TiO₂ films on cell inactivation is possibly a combination of reactive oxygen species kinetics and dynamic bacteria cell behaviour under oxidative stress. At this junction, the reason for the persistent cell inactivation of pre-illuminated TiO₂ films is speculative and further work is required to clarify the pathways in which

reactive oxygen species decay and the dynamic interactions between the bacteria cell membrane and these reactive oxygen species.

7.4 Conclusions

In summary, the direct and residual effect of TiO₂ photocatalytic films on an *E.coli* liquid layer was demonstrated. The direct irradiation of TiO₂ films with 254nm and 365nm UV light resulted in the complete disinfection of *E.coli* cells. Based on preliminary micro FTIR investigations, the mineralization of *E.coli* cells during photocatalysis was found to occur as a consequence of peroxidation of the *E.coli* cell membrane. Additional experiments carried out to show the residual effect of pre-illuminated TiO₂ films indicated that bacteria cell counts did not increase after incubation in the dark. The suppression of *E.coli* cell growth in the dark was speculated to be a result of long-lived reactive O₂^{2·-} and ¹O₂ species even in the absence of UV irradiation. Future clinical tests using biological kits to test for K⁺ and Ca²⁺ ion leakages that occur during cell wall puncture may be required to further elucidate the pathways in which TiO₂ photocatalysis causes cell inactivation.

8. Summary and Outlook

This section summarizes the work completed in this thesis, and introduces the future work that can be done.

8.1 Project Summary

In summary, we have successfully developed an electrodeposition technique capable of depositing TiO_2 nanocrystalline particles on stainless steel substrates. The development and characterization of a nanocrystalline TiO_2 colloid suitable for electrodeposition was also achieved. The specific tasks achieved from Jul 2005 to Jul 2007 are listed as follows:

- Low temperature synthesis of nanocrystalline colloidal suspensions with high zeta potentials
- Development of an aqueous based electrodeposition technique suitable for depositing nanocrystalline TiO_2 thin films on stainless steel substrates
- Development and Characterization of nanocrystalline TiO_2 deposits
- Hydrophilic functionalization of nanocrystalline TiO_2 deposits resulting in the low temperature fabrication of TiO_2 films on stainless steel substrates with hydrophilic properties

The tasks completed above resulted in the discovery of several interesting findings. These novel findings are listed as follows:

- Synthesis of an aqueous- based nanocrystalline TiO_2 suspension that has a high zeta potential of greater than -60mV within a neutral pH of 7.5~8.5
- Discovery of the correlation between TiO_2 film topography and TiO_2 film photocatalytic reaction rates
- Development of an aqueous based electrodeposition technique suitable for large scale industrial applications (environmentally friendly as compared to other organic solvent based or acidic electrodeposition techniques)

8.2 General conclusions

The observations made during the deposition of TiO_2 nanoparticles and the analysis of the photocatalytic functions of the resultant films can be concluded in the following areas:

TiO_2 nanoparticle suspension characteristics: Stabilization of anatase TiO_2 particles within peroxo-titanium suspensions could be attributed to surface adsorbed peroxo-titanium species. The presence of peroxo-titanium species has a direct impact on particle zeta potential and hence colloidal stability. Colloidal stability was not present in solutions that had been crystallized via heat refluxing for more than 8 hours. Colloidal stability was considered to be a pre-requisite to the formation of uniform TiO_2 films via the EPD route. AFM analyses provided direct evidence that the size of grains deposited could be easily controlled by varying the size of particles within the EPD suspension. Due to the anatase content within the EPD suspensions, all the deposited films were found to be photoactive against an organic contaminant (stearic acid). It was found that the TiO_2 thin films developed via this EPD fabrication method had controllable and reproducible nanostructures.

Control of deposited TiO_2 film morphology and photocatalytic performance: The manipulation of TiO_2 film physical properties such as film crystallinity/grain structure and roughness could be achieved by employing electrophoretic deposition of TiO_2 films at voltages above water electrolysis overpotentials. The films produced from electrophoretic deposition were photoactive towards the degradation of a generic stearic acid layer. Analysis of catalytic rates demonstrated that films which consisted of larger grains ($\sim 50\text{nm}$) were more photoactive ($\sim 45\%$) than films containing smaller grains of $\sim 30\text{nm}$. The synergistic effect of an increase in both crystal size and film crystallinity also resulted in enhanced catalytic rates. The improvement in catalytic rates due to surface morphology was considered to be a consequence of the increased molecular permeativity of stearic acid molecules on rougher film structures. During the course of experiments, it was discovered that for TiO_2 particulate film surfaces, particle packing density is a critical parameter. The particle packing density has a direct correlation to catalytic rates as it determines the permeativity of organic molecules onto photocatalytic sites. Thus, the fabrication of efficient photocatalytic

films was as much an issue of tweaking TiO₂ material properties as it was of tweaking film surface morphology.

Assessment of superhydrophilic functions of TiO₂ films: Electrophoretically deposited TiO₂ films were observed to exhibit UV-induced hydrophilicity. XPS analysis of the UV irradiated TiO₂ films suggested that neither an increase in oxygen vacancies nor an increase in OH terminal groups occurred during UV irradiation. Corresponding FTIR analysis during in-situ UV irradiation of TiO₂ films highlighted the role of adsorbed hydrocarbons on surface hydrophilicity. When covered with stearic acid, the TiO₂ surfaces exhibited non-wetting behaviour; during UV irradiation, island degradation of the organic layer resulted in preferential wetting on TiO₂ clean exposed film while hydrocarbon covered areas exhibited non-wetting. The results suggest that surface hydrophilicity of TiO₂ films can be used as an indication of film photoactivity towards functionalized hydrocarbon compounds.

Assessment of bioreactive functions of TiO₂ films: The direct irradiation of TiO₂ films with 254nm and 365nm UV light resulted in the complete disinfection of *E.coli* cells. Based on preliminary micro FTIR investigations, the mineralization of *E.coli* cells during photocatalysis was found to occur as a consequence of peroxidation of the *E.coli* cell membrane. The suppression of *E.coli* cell growth in the dark was speculated to be a result of long-lived reactive O₂²⁻ and ¹O₂ species even in the absence of UV irradiation.

8.3 Project Outlook

The following section highlights several areas that can be explored to further study the technology developed in the present work.

8.3.1 EPD Experiments

The successful development of an electrophoretic deposition technique involves characterization of the entire EPD process such that the quality of deposits obtained can be predicted. The determination of such EPD parameters enables the transference of the deposit technique to large scale production with different electrode dimensions and variable EPD suspension properties.

8.3.1.1 In-situ conductivity and deposit weight measurements

The determination of suspension conductivity during the duration of deposition helps to ascertain if the changes in current density is a consequence of ionic depletion or increasing deposit resistance. If the changes in current density are due largely to deposit resistivity, it can be deduced that there is a maximum deposition time and deposit thickness in which the deposit obtained has little or no defects. Conducting EPD after this time would probably result in the development of extremely porous and low density deposits. Conversely, if ionic depletion is a factor of consideration, constant ionic concentration should be maintained by replenishing the suspension at an appropriate flow rate during EPD.

Similarly, deposition weight increase during EPD can be charted to determine if there is maximum deposition duration (after which the deposit weight peaks and decreases due to deposit spalling) and if deposit accumulation occurs linearly, exponentially or erratically. Determination of deposit weight accumulation during EPD helps to predict the most effective deposition durations and voltages to form coatings of adequate thicknesses.

8.3.1.2 Variation of EPD strategy

The current EPD strategy can be varied to result in improvements in coating performance such as a higher mechanical strength, improved adhesion and durability.

Two variations of the EPD strategy can be performed: Firstly, the production of composite film layers to improve adhesion and mechanical strength of coatings, i.e. substrate to binder to TiO_2 composite layers. Secondly, the development of poly-composite colloids: the inclusion of polymer electrolytes within the suspension that can initiate long chain polymer intercalation within the deposit to promote deposit strength and adhesion.

8.3.2 Testing for TiO_2 film mechanical and physical properties

The mechanical strength of electrophoretically deposited nanoparticulate TiO_2 films can be tested quantitatively through microindentation in an effort to determine the coating strength on the stainless steel substrates. In terms of testing for film robustness, scrub tests could also be used to ascertain the strength of the coating upon abrasive cycles of scrubbing.

8.3.3 Use of TiO_2 materials for novel applications

Currently, the areas of intense study in TiO_2 technologies include the modification of TiO_2 materials for visible light photocatalysis, the interaction between TiO_2 film function (photocatalysis and wettability) and morphology, and the development of robust TiO_2 films for prolonged reactivity towards biological reagents. Recently, the use of TiO_2 films have branched out from conventional photocatalytic applications towards surface energy based applications. Interesting studies on the use of TiO_2 films in microfluidic devices for controllable wetting have very recently been reported[200] and this area has become an extension of our current work.[201]

REFERENCES

- [1] TOTO Ltd, "Patent licensing of super hydrophilic photocatalyst technology", [Online Document] Jun 2006. [2006], Available at HTTP:
http://www.toto.co.jp/docs/hyd_patent_en/index.htm
- [2] Daikin Inc., "How does the 7-layer filtering system work?", [Online Document] Jun 2006, Available at HTTP:
<http://www.daikin.co.uk/airconditioning-products/air-purifiers/dust-filters.jsp>
- [3] X. Z. Li and H. S. Lin, *Environ. Sci. Tech.*, 2005, **39**(12), 4614.
- [4] A. Fujishima, K. Hashimoto and T. Watanabe, *TiO₂ Photocatalysis: Fundamentals and Applications*, Tokyo: BKC, 1999.
- [5] S. Hideki, B. Ryo, H. Kazuhito, K. Yoshinobu and F. Akira, *Chem. Lett.*, 1995, **3**, 185.
- [6] F. Heidenau, W. Mittelmeier, R. Detsch, M. Haenle, F. Stenzel, G. Ziegler and H. Gollwitzer, *J. Mater. Sci.: Mater. Med.*, 2005, **16**(10), 883.
- [7] G. Andonegi, "Hygienic surfaces, biocidal and self-cleaning coatings", [Online Document] Jun. 2006, [2005 Sept 13], Available at HTTP:
http://www.innovationsreport.com/html/reports/materials_science/report49090.html?bcsi_scan_04262C8E8694A3D4=0&bcsi_scan_filename=report-49090.html
- [8] Nordisk Innovation centre, "FUNCOAT – Enhanced functionality of self-cleaning and antibacterial surface coatings", Jun 2006, [2006 Jul], Available at HTTP:
<http://www.nordicinnovation.net/article.cfm?id=1-834-770>
- [9] Laboratory for Environmental Research, Nova Gorica Polytechnic at Nova Gorica- Solvenia, "TiO₂ Thin Films for Air & Water Purification", Jun 2006, [2005 December], Available at HTTP:
[http://www.growthconsulting.frost.com/web/images.nsf/0/82BF83246E775195652570FA001D971D/\\$File/TI%20Alert.htm](http://www.growthconsulting.frost.com/web/images.nsf/0/82BF83246E775195652570FA001D971D/$File/TI%20Alert.htm)
- [10] T.-W. Ethan, "In 2011 You'll Never Have to Clean Your House Again", Jun 2006, [2006 Jun], Available at HTTP:
<http://www.popsci.com/popsci/technology/ac213ab81df8b010vgnvcm1000004eeccdcrcrd.html>
- [11] SunCleanTM, "About SunClean Self Cleaning Glass", Jun 2006, "n.d", Available at HTTP:
<http://www.suncleanglass.com/AboutSunClean.html>
- [12] Pilkington, "Pilkington ActivTM - Self-cleaning glass", Jun 2006, "n.d", Available at HTTP:
<http://www.pilkington.com/International+Products/Activ/default.htm>
- [13] Z. R. Ulberg and Y. F. Deinega, *Electrophoretic Composite Coatings*, England: Ellis Horwood, 1992.
- [14] J. H. Masliyah and S. Bhattacharjee, *Electrokinetic and Colloid Transport Phenomenon*, New York: Academic Press, 2006.
- [15] H. Helmholtz, *Wied. Ann.*, 1879, **7**, 337.
- [16] G. Gouy, *J. Phys. Radium.*, 1910, **9**, 457.

- [17] D. L. Chapman, *Phil. Mag.*, 1913, **25**, 475.
- [18] O. Stern, *Z. Elektrochem.*, 1924, **30**(4), 508.
- [19] M. Smoluchowski, *Phys. Chem.*, 1917, **92**(1), 129.
- [20] E. Hückel, *Phys. Z.*, 1924, **25**, 204.
- [21] D. C. Henry, *Proc. Roy. Soc.*, 1931, **A103**, 106.
- [22] B.V. Derjaguin, *B.V. Kolloid Z.*, 1934, **69**, 155.
- [23] B.V. Derjaguin, *Trans. Faraday Soc.*, 1940, **36**, 203.
- [24] H. C. Hamaker, *Physica*, 1937, **4**, 1058.
- [25] L. Bergström, *Advances in colloid and interface science*, 1997, **70**, 125.
- [26] J. N. Israelachvili, *Intermolecular and surface forces* (2nd edition), New York: Academic Press, 1992.
- [27] H. Koelmans and J. T. G. Overbeek, *Discuss. Faraday Soc.*, 1954, **18**, 52.
- [28] H. C. Hamaker and E. J. W. Verway, *Trans. Faraday Soc.*, 1940, **36**, 180.
- [29] P. Sarkar and P. S. Nicholson, *J. Am. Ceram. Soc.*, 1996, **79**, 1987.
- [30] P. Sarkar, O. Prakash, and P. S. Nicholson, *Proc. Ceram. Eng. Sci.*, 1994, **15**, 1019.
- [31] M. Giersig and P. Mulvaney, *J. Phys. Chem.*, 1993, **97**, 6334.
- [32] I. Zhitomirsky, *Adv. Coll. Inter. Sci.*, 2002, **97**, 277.
- [33] I. Zhitomirsky, *NanoStruc. Mater.*, 1997, **8**, 521.
- [34] F. Grillion, D. Fayeulle, and M. Jeandin, *J. Mater. Sci. Lett.*, 1992, **11**, 272.
- [35] M. Gernie, M. Gillot and S. Riffat, *Int. J. Green Energy*, 2006, **3**, 101.
- [36] J. H. Park and O. O. Park, *Appl. Phys. Lett.*, 2006, **89**, 163106.
- [37] J. H. Park, S. Kim and A. J. Bard, *Nanolett.*, 2006, **6**(1), 24.
- [38] J. Qiu, Z. Jin, Z. Liu, X. Liu, G. Liu, W. Wu, X. Zhang and X. Gao, *Thin Solid Films*, 2007, **5**, 2897.
- [39] L. Miao, S. Tanemura, S. Toh, K. Kaneko, M. Tanemura, *J. Crys. Growth*, 2004, **264**, 246.
- [40] Y. Lin, *Mater. Lett.*, 2008, **62**, 1246.
- [41] S. Lebrette, C. Pagnoux and P. Abélard, *J. Colloid and Inter. Sci.*, 2004, **280**, 400.
- [42] Marquardt, C. and Allen, M.G., "Fabrication of micromechanical structures of titania and titanium with electrophoretic deposition", *Digest of Technical Papers of the 11th International Conference on Solid-State Sensors and Actuators.*, 2001, **1**, 616-619.
- [43] F. Tang, T. Uchikoshi, K. Ozawa and Y. Sakka, *J. Eur. Ceram. Soc.*, 2006, **26**, 1555.
- [44] N. Wang, H. Lin, J. Li, X. Yang and B. Chi, *Thin Solid Films* 2006, **496**, 649.
- [45] Y. Sayaka, N. Akira, K. Yoshikazu, Y. Naoya, W. Toshiya and O. Kiyoshi, *Mater. Res. Bull.*, 2005, **40**, 1335.
- [46] Uchida, S. Hirao, T. Torimoto, S. Kuwabata, T. Sakata, H. Mori and H. Yoneyama, *Langmuir*, 1995, **11**, 3725.
- [47] C. K. Lin, T. J. Yang, Y. C. Feng, T. T. Tsung and C. Y. Su, *Surf. Coat. Tech.*, 2006, **200**, 3184.

- [48] J. Widegren and L. Bergström, *J. Am. Ceram. Soc.*, 2002, **85**(3), 523.
- [49] W. Sugimoto, O. Terabayashi, Y. Murakami and Y. Takasu, *J. Mater. Chem.*, 2002, **12**, 3814.
- [50] E. Stoll, P. Mahr, H. –G. Kruger, H. Kern, B. J. C. Thomas and A. R. Boccaccini, *J. Eur. Ceram. Soc.*, 2006, **26**, 1567.
- [51] V. Tohver, J. E. Smay, A. Braem, P. V. Braun and J. A. Lewis, *PNAS*, 2001, **98** (16), 9850-8954.
- [52] M. Miyauchi, A. Nakajima, A. Fujishima, K. Kazuhito and T. Watanabe, *Chem. Mater.*, 2000, **12**, 3.
- [53] R-D. Sun, A. Nakajima, A. Fujishima, T. Watanabe and K. Hashimoto, *J. Phys. Chem. B*, 2001, **105**, 1984.
- [54] V. Ramamurthy, Semiconductor photochemistry and photophysics (1st edition), New York: Marcel Dekker Inc, 2003.
- [55] T. Matsunaga, R. Tomoda, T. Nakajima and H. Wake, *FEMS Microbiol. Lett.*, 1985, **29**, 211.
- [56] P. C. Maness, S. Smolinski, D. M. Blake, H. Zheng, J. E. Wolfrum and W. A. Jacoby, *Appl. Environ. Microbiol.*, 1999, **65** (9), 4094.
- [57] Y. Kikuchi, K. Sunada, T. Iyoda, K. Hashimoto and A. Fujishima, *J. Photochem. Photobiol. A: Chem.*, 1997, **106**, 51.
- [58] H. Yasuhiko, A. D.Diago, T. Masahito and T. Setsuji, *Ind. Eng. Chem. Res.*, 1996, **35**, 3920.
- [59] K. P. Kühn, I. F. Chaberny, K. Massholder, M. Stickler, V. W.Benz, H-G. Sonntag and L. Erdinger, *Chemosphere*, 2003, **53**, 71.
- [60] L. C. Latxague and A-M.Merlin, *Spectroscopy*, 2005, **19**, 17.
- [61] R. Cai, Y. Kubota, T. Shuin, H. Sakai, K Hashimoto, K. Itoh and A. Fujishima, *Cancer Res.*, 1992, **52**, 2346.
- [62] S. N. Frank and A. J. Bard, *J. Phys. Chem.*, 1977, **81**, 1484.
- [63] B. Ohtani and S. Nishimoto, *J. Phys. Chem.*, 1993, **97**(4), 920.
- [64] A. L. Pruden and D. F. Ollis, *J. Catal.*, 1983, **82**, 404.
- [65] C. Y. Hsiao, C. L. Lee and D. F. Ollis, *J. Catal.*, 1983, **82**(2), 418.
- [66] T. Nguyen and D. F. Ollis, 1984, *J. Phys. Chem.*, **88**(16), 3386.
- [67] D. F. Ollis, C. Y. Hsiao, L. Budiman and C. L. Lee, *J. Catal.*, 1984, **88**(1), 89.
- [68] M. Barbeni, M. Morello, E. Pramauro, E. Pelizzetti, M. Vincenti, E. Borgarello, and N. Serpone, *Chemosphere*, 1987, **16**(6), 1165.
- [69] R. W. Matthews, *J. Phys. Chem.*, 1987, **91**(12), 3328.
- [70] R. W. Matthews, *J. Catal.*, 1988, **111**, 264.
- [71] W. Choi, A. Termin and M. R. Hoffmann, *J. Phys. Chem.*, 1994, **98**, 13695.
- [72] P. Y. Simons and F. Dachille, *Acta Crystal.*, 1967, **23**, 334.
- [73] C. Sureh, V. Bijju, P. Mukundan and K. G. K. Warriier, *Polyhedron*, 1998, **17**, 3131.
- [74] F. C. Gennari and D. M. Pasquevich, *J. Mater. Sci.*, 1998, **33**, 1571.
- [75] C. K. Chan, J. F. Porter, Y. G. Li, W. Guo and C. M. Chan, *J. Amer. Ceram. Soc.*, 1999, **82**, 566.
- [76] S. R. Kumar, C. S. Asha, K. Vasudevan, R. Suja, P. Mukundan and K. G. K. Warriier,

- Mater. Lett.*, 1999, **38**, 161.
- [77] A. L. Linsbigler, G. Q. Lu and J. T. Yates Jr., *Chem. Rev.*, 1995, **95**(3), 735.
 - [78] K. Tanaka, M. F. V. Capule and T. Hisanaga, *Chem. Phys. Lett.*, 1991, **187**, 73.
 - [79] K. N. P. Kumar, K. Keizer and A. J. Burrgraaf, *J. Mater. Chem.*, 1993, **3**(11), 1141.
 - [80] S. J. Tsai and S. Cheng, *Catal. Today*, 1997, **33**, 227.
 - [81] A. Fujishima, K. Honda and S. Kikuchi, *Kogyo Kagaku Zaasshi*, 1969, **72**, 108.
 - [82] A. Fujishima, K. Honda, *Nature*, 1972, **238**, 37.
 - [83] B. Ohtani and S. Nishimoto, *J. Phys. Chem.*, 1993, **97**(4), 920.
 - [84] S. D. Mo and W. Y. Ching, *Phys. Rev. B*, 1995, **51**, 13023.
 - [85] K. Ishibashi, A. Fujishima, T. Watanabe, K. Hashimoto, *J. Photochem. Photobio. A: Chem.*, 2000, **134**, 139.
 - [86] A. Fujishima, T. N. Rao and D. A. Tryk, *J. Photochem. Photobio. C: Photochem. Rev.*, 2000, **1**, 1.
 - [87] M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi and T. Watanabe, *Nature*, 1997, **388**, 431.
 - [88] A. Mills and S. Le Hunte, *J. Photochem. Photobio. A: Chem.*, 1997, **108**, 1.
 - [89] M. R. Hoffmann, S.T. Martin, W. Choi and D.W. Bahnemann, *Chem. Rev.*, 1995, **95**(1), 69.
 - [90] P.C. Maness, S. Smolinski, D. M. Blake, H. Zheng, J. E. Wolfrum and W. A. Jacoby, *Appl. Environ. Microbiol.*, 1999, **65**(9), 4094.
 - [91] T. Tatsuma, S-I. Tachibana and A. Fujishima, *J. Phys. Chem. B.*, 2001, **105**, 6987.
 - [92] K. Kida, K. Hirota, K. Tajima and K. Hashimoto, *Chem. Mater.*, 2006, **18**(6), 1386.
 - [93] M. H. Park, Y. J. Jang, H. M. Sung- Suh and M. M. Sung, *Langmuir*, 2004, **20**(6), 2257.
 - [94] Y. Hori, A. Nakatsu and S. Suzuki, *Chem. Lett.*, 1985, **9**, 1429.
 - [95] J. M. Herrmann, J. Disdier and P. Pichat, *J. Catal.*, 1988, **113**(1), 72.
 - [96] S.N. Frank and A. J. Bard, *J. Phys. Chem.*, 1977, **81**(15), 1484.
 - [97] H. Hidaka, T. Nakamura, A. Ishizaka, M. Tsuchiya and J. Zhao, *J. Photochem. Photobio. A: Chem.*, 1992, **66**, 367.
 - [98] E. Borgarello, R. Harris and N. Serpone, *Nouv. J. Chimie*, 1985, **9**(12), 743.
 - [99] J. M. Herrmann, C. Guillard and P. Pichat, *Catal. Today*, 1993, **17**(1), 7.
 - [100] K. Tanaka, K. Harada and S. Murata, *Solar Energy*, 1986, **36**, 159.
 - [101] A. Lozano, J. Garcia, X. Domenech and J. Casado, *J. Photochem. Photobio. A: Chem.*, 1992, **69**, 237.
 - [102] A. Mills, A. Belghazi and D. Rodman, *Water Res.*, 1996, **30**(9), 1973.
 - [103] H. Mozzanega, J. M. Herrmann and P. Pichat, *J. Phys. Chem.*, 1979, **83**, 2251.
 - [104] A. P. Xagas, E. Androulaki, A. Hiskia and P. Falaras, *Thin Solid Films*, 1999, **357**, 173.
 - [105] A. Mills and P. Sawunyama, *J. Photochem. Photobio. A: Chem.*, 1994, **84**(3), 305.
 - [106] N. Serpone, G. Sauve, R. Koch, H. Tahiri, P. Pichat, P. Piccinini, E. Pelizzetti and H. Hidaka, *J. Photochem. Photobio. A: Chem.*, 1996, **94**, 191.
 - [107] J. T. Remillard, J. R. McBride, K. E. Nietering, A. R. Drews and X. Zhang, *J. Phys. Chem. B*, 2000, **104**, 4440.

- [108] A. Mills, N. Elliott, I. P. Parkin, S. A. O'Neill and R. J. Clark, *J. Photochem. and Photobio. A: Chem.*, 2002, **151**, 171.
- [109] P. Sawunyama, L. Jiang, A. Fujishima and K. Hashimoto, *J. Phys. Chem. B*, 1997, **101**, 11000.
- [110] K. Rajeshwar, C. R. Chenthamarakshan, S. Goeringer and M. Djukie, *Pure Appl. Chem.*, 2001, **73**(12), 1849.
- [111] L. C. Chen and T. C. Chou, *Ind. Eng. Chem. Res.*, 1993, **32**, 1520.
- [112] A. Mills, A. Lepre, N. Elliott, S. Bhopal, I. P. Parkin and S. A O'Neill., *J. Photochem. Photobiol. A: Chem.*, 2003, **160**, 213.
- [113] R. Wang, N. Sakai, A. Fujishima, T. Watanabe and K. Hashimoto, *J. Phys. Chem. B*, 1999, **103**, 2188.
- [114] R. D. Sun, A. Nakajima, A. Fujishima, T. Watanabe and K. Hashimoto, *J. Phys. Chem. B*, 2001, **105**(10), 1984.
- [115] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi and T. Watanabe, *Adv. Mater.*, 1998, **10**(2), 135.
- [116] W. Rong, N. Sakai, A. Fujishima, T. Watanabe and K. Hashimoto, *J. Phys. Chem. B*, 1999, **103**, 2188.
- [117] T. Zubkov, D. Stahl, T.L. Thompson, D. Panayotov, O. Diwald and J.T. Yates, Jr., *J. Phys. Chem.*, 2005, **109**, 15454.
- [118] Y. Ohko, Y. Utsumi, C. Niwa, T. Tatsuma, K. Kobayakawa, Y. Satoh, Y. Kubota and A. Fujishima, *J. Biomed. Mater. Res.*, 2001, **58**, 97.
- [119] A. Mills, N. Elliott, I. P. Parkin, S. A. O'Neill and R. J. Clark, *J. Photochem. Photobiol. A: Chem.*, 2002, **151**, 171.
- [120] Y. Paz, Z. Luo, L. Rabenberg and A. Heller, *J. Mater. Res.*, 1995, **10**, 2842.
- [121] T. Watanabe, S. Fukayama, M. Miyauchi, A. Fujishima and K. Hashimoto, *J. Sol-Gel Sci. Tech.*, 2000, **19**, 71.
- [122] X. Zhang, A. Fujishima, M. Jin, A. V. Emeline and T. Murakami, *J. Phys. Chem. B.*, 2006, **110**, 25142.
- [123] A. Mills, M. Crow, J. Wang, I. P. Parkin and N. Boscher, *J. Phys. Chem. C.*, 2007, **111**, 5520.
- [124] G. Goutailler, C. Guillard, S. Daniele and L. G. Hubert-Pfalzgraf, *J. Mater. Chem.*, 2003, **13**, 342.
- [125] J. Yu, X. Zhao and Q. Zhao, *Thin Solid Films*, 2000, **379**, 7.
- [126] Y. Ohko, T. Tatsuma, T. Fujii, K. Naoi, C. Niwa, Y. Kubota and A. Fujishima, *Nat. Mater.*, 2003, **2**, 29.
- [127] S. Lianrong and L. Zuhong, *Spectrochim. Acta Part A: Mol. Biomol. Spectro.*, 1997, **53**, 1719.
- [128] R. Nussbaumer, J. Caseri, R. Walter and P. Smith, *J. Nanosci. Nanotech.*, 2006, **6**, 459.
- [129] S. J. Yoo, J. W. Lim, B. Choi and Y.-E. Sung, *J. Electrochem. Soc.*, 2007, **154**, 6.
- [130] J.-H. Yum, S.-S. Kim, D.-Y. Kim, and Y.-E. Sung, *J. Photochem. Photobiol. A: Chem.*, 2005, **173**, 1.

- [131] M. Y. Song, D. K. Kim, K. J. Ihn, S. M. Jo and D. Y. Kim, *Nanotech.*, 2004, **15**, 1861.
- [132] S. Karuppuchamy, K. Nonomura, T. Yoshida, T. Sugiura and H. Minoura, *Solid State Ionics*, 2002, **151**, 19.
- [133] J. Margit and P. Fuierer, *J. Sol-Gel Sci. Tech.*, 2006, **39**, 229.
- [134] M. Mikula, V. Brezová, M. Čěppan, L. Pach and Ľ. Karpinský, *J. Mater. Sci. Lett.*, 1995, **14**, 615.
- [135] S. J. Limmer and G. Cao, *Adv. Mater.*, 2003, **15**, 427.
- [136] G. Hyett, M. Green and I. P. Parkin, *J. Amer. Chem. Soc.*, 2006, **128**, 12147.
- [137] M. F. Tobias, R. C. Hoffmann, T. P. Niesen, H. Tew, J. Bill and F. Aldinger, *J. Mater. Chem.*, 2002, **12**, 1597.
- [138] Y. Masuda, T. Sugiyama, H. Lin, W. S. Seo and K. Koumoto, *Thin Solid Films* 2001, **382**, 153.
- [139] J. Aarik, A. Aidla, H. Mändar and T. Uustare, *Appl. Surf. Sci.*, 2001, **172**, 148.
- [140] T. P. Niesen, J. Bill and F. Aldinger, *Chem. Mater.*, 2001, **13**, 1552.
- [141] A. M. Peiró, E. Brillas, J. Peral, X. Domènech and J. A. Ayllón, *J. Mater. Chem.*, 2002, **12**, 2769.
- [142] N. Koura, T. Tsukamoto, H. Shoji and T. Hotta, *Jpn. J. Appl. Phys.*, 1995, **34**, 1643.
- [143] Y. Lin, G. S. Wu, X. Y. Yuan, T. Xie and L. D. Zhang, *J. Phys.: Condens. Matt.*, 2003, **15**, 2917.
- [144] H. Uchida, S. Hirao, T. Torimoto, S. Kuwabata, T. Sakata, H. Mori and H. Yoneyama, *Langmuir*, 1995, **11**, 3725.
- [145] P. Kern, P. Schwaller and J. Michler, *Thin Solid Films*, 2006, **494**, 279.
- [146] J. Georgieva, S. Armyanov, E. Valova, I. Poullos and S. Sotiropoulos, *Electrochim. Acta*, 2006, **51**, 2076.
- [147] I. Zhitomirsky, *Mater. Lett.*, 1998, **33**, 305.
- [148] I. Zhitomirsky, *J. Eur. Ceram. Soc.*, 1999, **19**, 2581.
- [149] Powder Diffraction File 2, ICDD, 1994.
- [150] J. Calvert and J. N. Pitts, *Photochemistry*, John Wiley & Sons, New York, 1967.
- [151] J. Muhlebach, K. Muller and G. Schwarzenbach, *Inorg. Chem.*, 1970, **9**, 2381.
- [152] F. P. Rotzinger and M. Graetzel, *Inorg. Chem.*, 1987, **26**, 3704.
- [153] R. Cai, K. Itoh, and C. Q. Sun, *Materials Research Society Symposium Proceedings*, Boston, USA, 2006, p. 05.1
- [154] G. Anné, K. Vanmeensel, J. Vleugels and O. Van der Biest, *Colloids Surf. A: Physicochem. Eng. Aspects*, 2004, **245**, 35.
- [155] D. De and P. S. Nicholson, *J. Amer. Ceram. Soc.*, 1999, **82**, 3031.
- [156] H. C. Hamaker, *Trans. Faraday Soc.*, 1940, **36**, 187.
- [157] J. Ovenstone and K. Yanagisawa, *Chem. Mater.*, 1999, **11**, 2770.
- [158] B. D. Cullity and S. R. Stock, *Elements of X-Ray Diffraction*, Prentice Hall, New Jersey, 2001.
- [159] Z. Zhang, C- C. Wang, R. Zakaria, and J. Y. Ying, *J. Phys. Chem. B.*, 1998, **102**, 10871.

- [160] T. Minabe, D. A. Tryk, P. Sawunyama, Y. Kikuchi, K. Hashimoto and A. Fujishima, *J. Photochem. Photobiol. A: Chem.*, 2000, **137**, 53.
- [161] P. Evans, S. Mantke, A. Mills, A. Robinson and D. W. Sheel, *J. Photochem. Photobiol. A: Chem.*, 2007, **188**, 387.
- [162] F. Kimura, J. Umemura and T. Takenaka, *Langmuir*, 1986, **2**, 96.
- [163] T. Watanabe, T. Takizawa and K. Honda, *J. Phys. Chem.*, 1977, **81**, 1845.
- [164] Y. Li, T. White, and S. H. Lim, *Rev. Adv. Mater. Sci.*, 2003, **5**, 211.
- [165] D. F. Ollis, E. Pellizzetti, N. Serpone, *Environ. Sci. Technol.*, 1991, **25**, 1523.
- [166] D. F. Ollis, *Environ. Sci. Technol.*, 1985, **19**, 480.
- [167] H. Al-Ekabi, N. Serpone, E. Pelizzetti, C. Minero, M. A. Fox and R. B. Draper, *Langmuir*, 1989, **5**, 250.
- [168] J. F. Porter, Y. G. Li and C. K. Chen, *J. Mater. Sci.*, 1999, **34**, 1523.
- [169] A. Sdafani, L. Palmisano and M. Schiavello, *J. Phys. Chem.*, 1990, **94**, 829.
- [170] M. Anpo, T. Shima, S. Kodama and Y. Kubokawa, *J. Phys. Chem.*, 1987, **91**, 4305.
- [171] C. B. Almquist, P. Biswas, *J. Catal.*, 2002, **212**, 145.
- [172] L. Zhou, K. Kato, N. Umenara and Y. Miyake, *Nanotech.*, 1999, **10**, 363.
- [173] B. Renard, J. Barbier Jr., D. Duprez and S. Duréu, *Appl. Catal. B: Environ.*, 2005, **55**, 1.
- [174] N. Serpone, D. Lawless, R. Khairutdinov and E. Pelizzetti, *J. Phys. Chem.*, 1995, **99**, 1665.
- [175] K. Eufinger, D. Poelman, H. Poelman, R. D. Gryse and G. B. Marin, *J. Phys. D: Appl. Phys.*, 2007, **40**, 5232.
- [176] X. Wang, J. C. Yu, H. Y. Yap, L. Wu, P. K. Wong and S. Y. Lai, *Chem. Eur. J.*, 2005, **178**, 321.
- [177] L. Wu, J. C. Yu, X. Wang, L. Zhang and J. Yu, *J. Sol. State Chem.*, 2005, **178**, 321.
- [178] D. Takajo, T. Nemoto and S. Isoda, *Jpn. Soc. Appl. Phys.*, 2004, **43(7B)**, 4667.
- [179] N. Sakai, A. Fujishima, T. Watanabe and K. Hashimoto, *J. Phys. Chem. B.*, 2001, **105**, 3023.
- [180] N. Sakai, A. Fujishima, T. Watanabe and K. Hashimoto, *J. Phys. Chem. B.*, 2003, **107**, 1028.
- [181] N. Sakai, R. Wang, A. Fujishima, T. Watanabe and K. Hashimoto, *Langmuir*, 1998, **14**, 5918.
- [182] J. M. White, J. Szanyi and M. A. Henderson, *J. Phys. Chem. B.*, 2003, **107**, 9029.
- [183] Y. Gao, Y. Masuda, and K. Koumoto, *Langmuir*, 2004, **20**, 3188.
- [184] K. E. Healy and P. Ducheyne, *J. Biomed. Mater. Res.*, 1992, **26**, 319.
- [185] J.-C. Dupin, D. Gonbeau, P. Vinatier and A. Levasseur, *Phys. Chem. Chem. Phys.*, 2000, **2**, 1319.
- [186] T. K. Sham and M. S. Lazarus, *Chem. Phys. Lett.*, 1979, **68**, 426.
- [187] L. Q. Wang, D. R. Baer, M. H. Engelhard and A. N. Shultz, *Surf. Sci.*, 1995, **344**, 237.
- [188] J. Fan and J. T. Yates Jr, *J. Am. Chem. Soc.*, 1996, **118**, 4686.
- [189] C. Latxague-L and A.-M. Merlin, *Spectroscopy*, 2005, **19**, 17.
- [190] D. F. Ollis, E. Pellizzetti and N. Serpone, *Environ. Sci. Technol.*, 1991, **25**, 1523.
- [191] K. Sunada, T. Watanabe and K. Hashimoto, *J. Photochem. Photobiol. A: Chem.*, 2003, **156**, 227.
- [192] J. Kiwi and V. Nadtochenko, *J. Phys. Chem. B*, 2004, **108**, 17675.

- [193] V. Nadtochenko, A. G. Rincon, S. E. Stanca and J. Kiwi, *J. Photochem. Photobiol. A: Chem.*, 2005, **169**, 131.
- [194] K-I. Ishibashi, Y. Nosaka, K. Hashimoto and A. Fujishima, *J. Phys. Chem. B.*, 1998, **102**(12), 2117.
- [195] T. Tatsuma, S-I. Tachibana, T. Miwa, D. A. Tryk and A. Fujishima, *J. Phys. Chem. B.*, 1999, **103**(38), 8033.
- [196] Y. Nosaka, M. Nakamura and T. Hirakawa, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1088.
- [197] R. F. Howe and M. Grätzel, *J. Phy. Chem.*, 1987, **91**, 3906.
- [198] V. H. Damme and K. W. Hall, *J. Am. Chem. Soc. Comm.*, 1979, **101**(15), 4373.
- [199] J. Kiwi and V. Nadtochenko, *Langmuir*, 2005, **21**, 4631.
- [200] G. Takei, M. Nonogi, A. Hibara, T. Kitamori and H-B. Kim, *Lab Chip*, 2007, **7**, 596.
- [201] G. G. A. Toh, G. M. Nolan, R. Cai and D. L. Butler, "Reversible wetting of Titanium dioxide films", *Proceedings of the SPIE*, 2007, 680004.

Appendix A: Photon Flux and Quantum Efficiency Calculations

Calculation of Total Photon Flux from UV light sources

UV light source used was a Spectroline Model, ENF- 280C/FE with a 230V, 0.17A, 50Hz. The UV light intensities of the UV wavelengths were obtained from a Solatell Solacheck system which measures UV wavelengths, λ at two ranges: 240 to 280nm and 300nm to 400nm, at a sensitivity of $< 10\text{nW}/\text{cm}^2/\text{nm}$. The UV light used has a wavelength of 254nm and the light intensity of the lamp was measured within the range of 240 to 280nm. The intensity values were first measured in this range and in the range of 300 to 400nm to determine the wavelength range emitted by the lamp. The intensity values are listed in the following table:

	λ Range: 240 to 280nm	λ Range: 300 to 400nm
Incident light intensity (W/cm^2)	85×10^{-6}	0

The measured light intensity can then be used to calculate the light photon flux, F using the photon flux energy equation derived from ferrioxalate actinometry:

$$\text{Total photon flux, } F = \left(\frac{\lambda}{hc} \right) P$$

where F is the photon flux ($\text{photons}/\text{cm}^2\text{s}$)

λ is the source wavelength (m),

h is Planck's constant ($6.626068 \times 10^{-34} \text{ J.s}$),

c is the speed of light ($299\,792\,458 \text{ m/s}$),

and P is the power density (W/cm^2).

Calculation of TiO₂ film Quantum Efficiency from incident UV Photon Flux

The quantum efficiency values of the TiO₂ films were obtained from FTIR analysis of the stearic acid layer that was spin coated on the films prior to photocatalytic

experiments. The FTIR peak area under a stearic acid FTIR profile can be correlated to the number of molecules within the stearic acid layer under detection. A detected FTIR peak area of 1cm^{-1} for a generic stearic acid layer can be associated to 3.1667×10^{15} molecules.[112, 119] The rate of the photo reaction is the number of molecules degraded for per unit of photocatalysis duration. The rate of FTIR peak area decrease can be converted into the rate of photoreaction by:

$$\text{rate of photoreaction} = \text{rate of FTIR peak area decrease}(\text{cm}^{-1}\text{s}^{-1}) \times 3.1667 \times 10^{15}(\text{molecules cm}^{-1})$$

$$(\text{molecules s}^{-1})$$

The rate of photoreaction can then be used to calculate the quantum efficiency, δ of the TiO_2 film against stearic acid degradation:

$$\delta = \frac{\text{rate of photo reaction}(\text{molecules s}^{-1})}{\text{incident light intensity}(\text{photons s}^{-1})}$$

An example calculation for the stearic acid degradation of stearic acid on S8 films, deposited at an applied voltage of 2.0V is shown below:

FTIR peak area decrease from wavenumber 2700cm^{-1} to 3000cm^{-1} can be plotted as follows:

Assuming zero order degradation kinetics, the rate of absorbance area decrease can be then be converted to the rate of photoreaction:

$$\begin{aligned}\text{rate of photoreaction} &= \frac{0.0016986}{60} \times 3.1667 \times 10^{15} \\ &= 8.96492 \times 10^{10} \text{ molecules } s^{-1}\end{aligned}$$

The incident photon flux provided during the photocatalytic reaction is calculated from the photon flux equation:

$$\begin{aligned}F &= \left(\frac{\lambda}{hc} \right) P \\ &= \left(\frac{254 \times 10^{-9}}{6.626068 \times 10^{-34} \times 299\,792\,458} \right) \times 85 \times 10^{-6} \\ &= 1.08687 \times 10^{14} \text{ photons } s^{-1}\end{aligned}$$

The quantum efficiency, δ of the TiO_2 film can be calculated as:

$$\delta = \frac{8.96492 \times 10^{10} \text{ (molecules } s^{-1})}{1.08687 \times 10^{14} \text{ (photons } s^{-1})} = 8.24841 \times 10^{-4} \text{ molecules photon}^{-1}$$

In summary, the quantum efficiency of the TiO_2 film against a layer of stearic acid can be obtained by the rate of FTIR peak absorbance change by utilizing the above calculations.

Appendix B: AFM micrographs of S2, S4 and S8 films

Figure B1 S2 films deposited at (a,b) 1.2V, (c,d) 1.5V and (e,f) 2.0V, (a,c,e) and (b,d,f) are obtained from 1 μm and 0.5 μm square scan area respectively.

Appendix B: AFM micrographs of S2, S4 and S8 films

Figure B2 S4 films deposited at (a,b) 1.2V, (c,d) 1.5V and (e,f) 2.0V, (a,c,e) and (b,d,f) are obtained from 1 μm and 0.5 μm square scan area respectively.

Appendix B: AFM micrographs of S2, S4 and S8 films

Figure B3 S8 films deposited at (a,b) 1.2V, (c,d) 1.5V and (e,f) 2.0V, (a,c,e) and (b,d,f) are obtained from 1 μm and 0.5 μm square scan area respectively.

Appendix C: *Escherichia coli* preparation and cell viability assay

E. coli DH5 α preparation

E. coli strain DH5 α glycerol stock was prepared by aliquot 800 μ l of *E. coli* suspension into a cryotube and subsequently added 200 μ l of 80% glycerol. The glycerol stock suspension was then vortex until homogeneous and kept at -80°C. The *E. coli* strain was subsequently grown to mid-log phase in Luria- Bertani (LB) medium. The recipe used to formulate the LB medium is as follows:

Formulation of LB medium (1L volume)

Bacto- tryptone	10g
Bacto-yeast extract	5g
NaCl	10g

Add above ingredients together with 800ml of milliQ distilled water. Adjust suspension pH to 7.0 with 5M of NaOH.

Cells viability assay

In the cell viability assay, the bacteria on the TiO₂ films were first transferred into a microcentrifuge tube. The TiO₂ films were then rinse with 250 μ L Luria-Bertani medium and collected the remaining bacteria into the same microcentrifuge tube. The number of viable cells was determined by plating 10 μ L of the bacteria in serially diluted bacteria suspension directly on to LB agar plates

Figure C 1 Serially diluted bacteria suspension on LB agar

Appendix D: Reference crystallographic information files**TiO₂ Anatase reference cif**

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#©2007 by Fachinformationszentrum Karlsruhe, and the U.S. Secretary of
#Commerce on behalf of the United States. All rights reserved.
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Appendix D: Reference crystallographic information files

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TiO₂ Rutile reference cif

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Appendix D: Reference crystallographic information files

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TiO₂ Brookite reference cif

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Appendix D: Reference crystallographic information files

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Appendix E: List of Publications

- [1] Toh G. G. A., Butler D. L., and Cai R., “Electrophoretically deposited TiO₂ superhydrophilic thin films”, *Proceedings of the 3rd International Conference on Technological Advances of Thin Films & Surface Coatings*, Singapore, 2006, pg 169, ETF 635.
- [2] Toh G. G. A., Butler D. L., and Cai R., “The influence of surface topography on the photocatalytic activity of electrophoretic deposited Titanium dioxide thin films”, *Proceedings of the 11th International Metrology and Properties of Engineering Surfaces conference*, Huddersfield/ United Kingdom, 2007, pg 191-196.
- [3] Toh G. G. A., Nolan G. M., Cai R., and Butler D. L., “Reversible wetting of Titanium dioxide films”, *Proceedings of the SPIE*, Canberra/ Australia, 2007, pg680004-680010.
- [4] Toh G. G. A., Butler D. L., and Cai R., “Anodic electrophoretic deposition of titanium dioxide thin films: an aqueous peroxo-titanium stabilization route”, *Journal of Materials Chemistry*, 2007 (pending submission)