A Forensic Approach to Elucidate the Factors that influence the Photocatalytic Activity of Nanostructured Anatase-Rutile-Carbon Composite Coatings by PP-MOCVD

A thesis submitted towards the fulfilment of requirements for the degree of Doctor of Philosophy

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AEMS Lab
Advanced Energy and Material Systems
To all the explorers, dreamers & investigators who believe the sky is NOT the limit.

To my dad and mom for my wings.

To my brother, my best friend and my partner in crime.
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A Forensic Approach to Elucidate the Factors that influence the Photocatalytic Activity of Nanostructured Anatase-Rutile-Carbon Composite Coatings by PP – MOCVD

PhD Thesis
Rukmini Gorthy

Abstract
Titanium dioxide has been of high interest because of its UV-light absorbing properties and its ability to produce electron-hole pairs that are capable in catalyzing surface reactions. The discovery of the photocatalytic properties of TiO₂ was first reported by Akira Fujishima in 1967. Since then, TiO₂ nanomaterials have attracted tremendous interest for self-cleaning, energy harvesting, antimicrobial, and pollution mitigation applications. Research in semiconductor photocatalysis has recently included nanoparticles and nanostructured materials that possess the advantages of a robust material while retaining the unique properties of nanoscale particles.

The Pulsed-Pressure Metalorganic Chemical Vapor Deposition (pp-MOCVD) process has previously been studied for preparing antimicrobial nanostructured TiO₂ coatings on 3D surfaces for healthcare facilities. The pp-MOCVD process is a single step deposition technique that produces conformal coatings of TiO₂ on microscale features and on glass and stainless-steel substrates. The TiO₂ coatings exhibit enhanced photocatalytic activity (PCA) under low energy visible light compared to the conventional TiO₂ materials. Scanning electron microscopic (SEM) investigations revealed that the more active TiO₂ thin films exhibit a rarely observed morphology of TiO₂. Figure 1 shows the unique morphology of the TiO₂-C coatings prepared by pp-MOCVD.
Figure 1 (a) Plan-view image & (b) cross-sectional view of a TiO$_2$-C coating prepared via pp-MOCVD
X-ray diffraction studies (Figure 2 a) showed that the coatings consist of anatase and rutile phases of TiO₂. The results showed that the columnar nanostructured TiO₂ coatings are composed of highly textured anatase and polycrystalline-rutile. The characterization of the coatings showed that the films were composed of TiO₂ with co-deposited carbon (Figure 2 b). Early results showed that the visible light active TiO₂ coatings exhibit high-grade durability, and enhanced water splitting efficiency.
Figure 2 (a) XRD spectrum and (b) Raman spectrum of a TiO$_2$-C composite coating
The pp-MOCVD process has five relevant deposition parameters that produce a wide range of multi-phase TiO$_2$-C composites with complex nanostructures and characteristics. Preliminary work by the research group demonstrated that some variants of the nanostructured TiO$_2$ coatings are more effective than others. The hypothesis is that specific combinations of the different processing parameters of pp-MOCVD produce polycrystalline TiO$_2$ solid films that are active under visible light. The mechanisms of the deposition process are responsible for producing crystals with instabilities that are capped with stabilizing amorphous carbon. This doctoral dissertation is aimed at validating or disproving the hypothesis of the role of carbon in the formation of the unique microstructure and enhanced PCA. The approach is to study the influence of the pp-MOCVD processing parameters on resulting characteristics and properties, and then link the performance of the coatings to their characteristics. A novel approach based on Forensic Investigation Principles was used to design and carry out the investigations using less than 15 samples deposited under carefully selected sets of parameters.

The proposed forensic materials science investigation differs from the standard materials science approach. Normally, one holds all processing parameters constant except one, then studies the material characteristics and properties as a function of that parameter. However, with five processing parameters to investigate, this would require more than 120 samples. The forensic investigation approach proposed in this dissertation sets out to solve the mystery behind active and non-active variants of the TiO$_2$ coatings. Evidence of all the statistically possible combination of parameters was generated. Finally, the factors behind the high PCA of the coatings were deduced based on the evidence of properties and performance and testing of combinatorial hypothesis.
The most active samples were identified Methylene Blue Dye (MBD) degradations tests. The active samples were analyzed using High-Res Transmission Electron Microscopy (HRTEM). The carbon location on the exposed facets of the samples was mapped using atomic resolution Electron Energy Loss Spectroscopy. Figure 3(a) shows the HRTEM images and the facets on the most active sample. The HRTEM analysis showed that NsARC coating has exposed A{105} surfaces at the top of the anatase crystal and exposed A{112} facets on the nanoscale structures that are present along the length of the columns.

The EELS maps of the carbon location for H2 are shown in Figure 4. The EELS map shows that carbon caps and stabilizes the exposed high-energy A{112} surfaces.
Figure 3 (a) SEM image of the plan-view morphology of NsARC; (b) Corresponding HRETM image with annotated exposed facets on an anatase column of NsARC
Figure 4 EELS map showing the carbon location on the exposed [112] facets of the nanoscale features
Finally, the mechanical behavior of the coatings was analyzed, and the results demonstrated that the TiO$_2$-C composite materials exhibit high adhesion and robustness. Figure 5 shows a TiO$_2$-C composite coating subjected to ASTM D3359 scratch test. The result is categorized as grade 5B as 0% of the coatings area is removed from the substrate surface. This behavior makes them ideal antimicrobial coatings for high-touch surfaces in healthcare facilities.

*Figure 5* ASTM Scotch™ tape test on TiO$_2$-C composite film on stainless-steel substrate
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td></td>
</tr>
<tr>
<td>ACOM</td>
<td>Automated Crystal Orientation Mapping (also known as ASTAR™)</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>AMA</td>
<td>Antimicrobial Activity</td>
</tr>
<tr>
<td>AMCSAD</td>
<td>American Mineralogist Crystal Structure Database</td>
</tr>
<tr>
<td>ARM</td>
<td>Atomic Resolution Microscope</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction Band</td>
</tr>
<tr>
<td>CDC</td>
<td>Center for Disease Control, USA</td>
</tr>
<tr>
<td>CIF</td>
<td>Crystallographic Information File</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory (calculations)</td>
</tr>
<tr>
<td>DI</td>
<td>De-ionized</td>
</tr>
<tr>
<td>DOE</td>
<td>Design of Experiments</td>
</tr>
<tr>
<td>E. coli</td>
<td>Escherichia Coli – a gram-negative coliform bacterium</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency, USA</td>
</tr>
<tr>
<td>FDA</td>
<td>Food and Drug Administration, USA</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>GR</td>
<td>Growth-Rate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>h+</td>
<td>Hole, a quasiparticle with a net positive charge</td>
</tr>
<tr>
<td>HAIs</td>
<td>Hospital Acquired Infections</td>
</tr>
<tr>
<td>hn</td>
<td>Photon energy in eV</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-Resolution Transmission Electron Microscope</td>
</tr>
<tr>
<td>ICU</td>
<td>Intensive Care Unit</td>
</tr>
<tr>
<td>MBD</td>
<td>Methylene Blue Dye</td>
</tr>
<tr>
<td>MO</td>
<td>Metal Oxide</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metalorganic Chemical Vapor Deposition</td>
</tr>
<tr>
<td>MRSA</td>
<td>Methicillin Resistant Staphylococcus Aureus – a gram-positive bacterium</td>
</tr>
<tr>
<td>NIOSH</td>
<td>National Institute for Occupational Safety and Health, USA</td>
</tr>
<tr>
<td>NsARC</td>
<td>Nanostructured Anatase Rutile Carbon (composite coating)</td>
</tr>
<tr>
<td>OSHA</td>
<td>Occupational Safety and Health Administration, USA</td>
</tr>
<tr>
<td>OVAT</td>
<td>One-Variable-At-a-Time</td>
</tr>
<tr>
<td>paii</td>
<td>Photocatalytic Activity Indicator Ink</td>
</tr>
<tr>
<td>PB</td>
<td>Plackett-Burman</td>
</tr>
<tr>
<td>PCA</td>
<td>Photocatalytic Activity</td>
</tr>
<tr>
<td>PEC</td>
<td>Photoelectrochemical (reaction)</td>
</tr>
<tr>
<td>pp-MOCVD</td>
<td>Pulsed-Pressure Metalorganic Chemical Vapor Deposition</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>R</td>
<td>Rutile</td>
</tr>
<tr>
<td>Redox</td>
<td>Simultaneous reduction-oxidation chemical reactions</td>
</tr>
<tr>
<td>Response</td>
<td>Measured result (For example, PCA)</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive Ion Etching</td>
</tr>
</tbody>
</table>
RMS  Root Mean Squares
ROI  Region of Interest
ROS  Reactive Oxygen Species
RRUFF  Raman Research Used For Fun (Academic & Science Database)
SEM  Scanning Electron Microscope
SI  Spectrum Imaging (Digital Micrograph software version)
SSA  Specific Surface Area
STEM  Scanning-Transmission Electron Microscope
TC  Texture Coefficient
TEM  Transmission Electron Microscope
TTIP  Titanium tetra-isopropoxide (C\textsubscript{12}H\textsubscript{28}O\textsubscript{4}Ti)
UV  Ultraviolet radiation/light (\(\lambda = 10\) nm to 400 nm)
UV-Vis  Ultraviolet – Visible light (Spectrophotometer)
VB  Valence Band
VESTA  Software for visualization of crystal, volumetric and morphology data
VOC  Volatile Organic Compound
WCA  Water Contact Angle
WHO  World Health Organization
XRD  X-ray Diffraction
ZLP  Zero-Loss Peak (of an EELS spectrum)
\(\lambda\)  Wavelength of radiation
List of Publications


Conference Presentation

Poster Presentation

Chapter 1: Introduction

This chapter provides groundwork for the application of semiconductor TiO$_2$ materials as antimicrobial touch surface coatings.

- Section 1.1 presents a brief literature survey on the prevalence of Hospital Acquired Infections (HAIs), their transmission in healthcare facilities and the existing methods to combat the spread of the HAIs.
- Section 1.2 provides an insight into the different categories of self-cleaning surfaces and their applications. The literature on the application of the self-cleaning surfaces as antimicrobial materials is discussed briefly.
- Definitions of different types of nanoscale materials are provided in section 1.3.
- Section 1.4 provides detailed literature on the heterogeneous photocatalysis of TiO$_2$. The section presents a brief overview of semiconductor photocatalysis and the underlying mechanisms of photocatalytic materials. The photocatalytic performance of TiO$_2$ is described for different applications. The section also provides the background on current methodologies pertaining to the enhancement of the photocatalytic performance of TiO$_2$.
- Section 1.5 provides the scope of the thesis and an outline of the thesis organization.
1.1 Hospital Acquired Infections

1.1.1 Prevalence

Healthcare-associated of Hospital Acquired Infections (HAIs) are among the leading causes of patient mortality in healthcare services and facilities. Health-care environments, particularly high-touch surfaces, play a role in a patient or a staff member contracting a HAI. Dancer et al. estimate that high touch surfaces like door handles, elevator lift buttons, bed rails in rooms that previously were occupied by infected patients facilitate transmission of bacteria like Escherichia coli (E. coli), Methicillin-resistant Staphylococcus aureus (MRSA) and Clostridium difficile [1]. The probability of a person contracting an HAI increases with the duration of stay [2]. HAIs occur not only in patients but are also an occupational problem among healthcare professionals [3].

The crisis of HAIs is spreading at an alarming rate. In 2018, the World Health Organization (WHO) estimated that 7 – 10 % of hospitalized patients acquire at least one HAI [4]. The Center for Disease Control, USA, estimates that on any given day, 1 in 31 patients has an HAI. Magill SS et al. estimate that the direct and indirect global costs of HAIs amount to 97 – 147 billion USD per year [5].

The incidence of HAIs is most common in patients admitted to intensive care units (ICUs). HAIs are contracted by means of different medical procedures, like the implantation of contaminated urinary catheters and central IV lines. The central IV-line infections are particularly threatening in the neonatal ICUs [6].
1.1.2 Transmission of HAIs

A study by Boyce performed to assess the contamination of high-touch surfaces with HAI-causing bacteria, shows that the following surfaces are the most contaminated [7].

- 67% of bedrails and bedside tables
- 33% of call buttons
- 32.5% of toilets (including door handles and faucets).

A case study of 500 near-patient sites in a hospital in Scotland, UK revealed that 47% of the hand-touch sites in an ICU failed the standard hygiene tests. A more disturbing result obtained from this facility is the air quality standard. The authors find that the 50% of passive air samples and 37.5% of active air samples obtained failed to meet the hygiene standards [8]. The air samples were collected from an ICU ventilator in the hospital. A more recent study performed by Reynolds et al. shows that microbes in an outpatient clinic reach maximum contamination levels within 2 hours of contamination [9]. The authors observe highest contamination on examination room door handles and nurses’ station chairs.

1.1.3 Prevention of HAIs

HAIs from touch surfaces are preventable and can be reduced through vigilant enforcement of established hygiene standards and cleaning protocols. Methods to potentially decrease the frequency and level of microbial contamination in hospital touch surface include routine disinfection with strong chemical germicides [10] like quaternary ammonia compounds. High-touch surfaces should be cleaned at least every 4 hours using high concentration ethanol-based disinfectant [9].
A medical research team from the University of North Carolina Health Care System prepared an extensive list of guidelines and protocols for the CDC, USA that recommends using strong chemicals like 60-90% ethanol in water, hypochlorite-based solutions, formaldehyde, hydrogen peroxide, peroxycetic acid and phenolics. These chemicals, however, are known to cause occupational concerns to the hospital and cleaning-staff. Glutaraldehyde causes adverse health effects like dermatitis and asthma [11]. Cleaning products based on hydrogen peroxide, peracetic acid and acetic acid exacerbate asthma due to their chemical composition. These products are also responsible for causing dermal problems like dermatitis and eczema. The CDC, USA has an established guideline for use of the aforementioned chemicals [10, 12]. National Institute of Occupational Safety and Health (NIOSH, USA) and the Occupational Safety and Health Administration (OSHA, USA) provided similar guidelines but the enforcement of these protocols is not as vigilantly monitored as necessary. A survey published by Henn et al. reports that 17% of the respondents have not been trained to handle high-level disinfectants and 19% of them report that the employers either do not have standard procedures in place or were unaware of their existence [11].

Weber et al. recommend using ‘no touch’ methods of terminal and routine room disinfection with UV or aerosolized H$_2$O$_2$ [13, 14]. UV disinfection requires the removal of the patients and the healthcare personnel from the room. This method is not currently recognized by the Food and Drug Association of America (FDA), the Environmental Protection Agency (EPA), USA or the CDC [15]. UV irradiation is a line-of-sight method of disinfection and would not affect the microbes in the shadowed areas of the facility.
1.2 Self-Cleaning Surfaces

Self-disinfecting or self-sanitizing surfaces could be an efficient additional passive measure to the methodologies mentioned in the previous sections to combat HAIs. The motivation to use passive measures is to make the healthcare facility less hospitable to microbial growth while not affecting the workers or require more measures. There are different surface modification strategies which have been explored with a range of objectives. The standard surface modification strategies are imbuing the target surfaces with superhydrophobic, superhydrophilic or photocatalytic properties.

1.2.1 Superhydrophobic Surfaces

Surface modification to achieve superhydrophobicity was inspired by natural phenomena observed in lotus leaves and gecko feet [16]. Superhydrophobic surfaces have water contact angles (WCA) greater than 150°. The surfaces repel water providing reduced opportunity for microbial colonization from liquid contaminant sources. Figure 1. 1 provides an illustration of the behavior of a water droplet on a nano-patterned surface.

![Figure 1. 1 Schematic of a water droplet on a nano-patterned superhydrophobic surface.](image)
Artificial superhydrophobic surfaces with self-cleaning properties are prepared via surface modification or by coating the target object with a coating that exhibits superhydrophobicity [17]. Reported methods for modifying surfaces are nanolithography or Reactive Ion Etching (RIE) to create nanostructures on surfaces and Focused Ion Beam (FIB) milling to precisely design nanoscale patterns on target surfaces. Surfaces with superhydrophobic properties are fabricated by vacuum casting to replicate natural surfaces (for example, gecko’s feet) onto polymer and silicon substrates [18]. Hydrothermal synthesis [19] and Chemical Vapor Deposition (CVD) [20, 21] have been used by researchers to produce nanoscale materials that exhibit superhydrophobic behavior.

The production of superhydrophobic materials involves high fabrication costs. There is existing literature that reports the fragility and instability of nanoscale structures reduce the efficiency of the superhydrophobic materials [17]. Research has also shown that the nanoscale patterns in a superhydrophobic coating are not entirely effective in repelling bacteria like S. aureus. S. aureus cells mainly adhered to the crevices in the patterned surfaces and were protected from the anti-microbial action of the superhydrophobic surface [18].

Polytetrafluoroethylene is a well-known superhydrophobic material that is commonly used in coating implantable medical devices to prevent microbial colonization on the surfaces [22].
1.2.2 Superhydrophilic Surfaces

Fujishima et al. first observed the superhydrophilicity of TiO2 photocatalysts, under UV light, in 1995 in collaboration with a Japanese company, Toto [23]. The authors were working on developing anti-fogging glass and mirrors for the automotive industry. On a superhydrophilic surface, the water contact angle is less than 5° (illustrated in Figure 1.2). This allows liquids to spread completely across and roll off the surface. The antimicrobial properties of superhydrophilic surfaces result from reduced contamination due to the non-adhering behavior of liquid contaminants.

![Figure 1.2 Schematic of a water droplet on a superhydrophilic surface.](image)

Superhydrophilicity can be achieved by surface modification or by applying a superhydrophilic coating (e.g. Plikington Activ™) to the target specimen. Fujishima et al. used thermal hydrolysis of titanium sulfate to prepare superhydrophilic coatings on glass substrates [23]. Since then, researchers have used electrospinning to produce titania nanofibers with superhydrophilic and antimicrobial properties [24]. Common methods of achieving superhydrophilic surfaces is via patterning the surfaces at a microscopic level and introducing nanoparticles to the surface to increase the surface roughness [25]. Superhydrophilic surfaces in the form of metal oxide coatings have been synthesized via different technologies like Metalorganic Chemical Vapor Deposition [26, 27].
The limitations to using superhydrophilic surfaces for antimicrobial applications are the durability of the coatings, the difficulty to pattern the surfaces etc. [25, 26]. The superhydrophilicity of some of these materials is activated only under direct photo-stimulation [28].

A widely used superhydrophilic coating, Pilkington Activ™, is commercially manufactured for self-cleaning glass in building applications [29].

1.2.3 Photocatalytic Materials

The term Photokatalyse was probably introduced by Plotnikov in 1910 [30]. Photocatalysis is the process of altering the rate of a chemical reaction or its initiation by direct photon irradiation in the presence of a photocatalyst. A photocatalyst absorbs photonic energy and catalyzes reduction-oxidation (redox) reactions on its surface. Redox potential of a photocatalyst is defined as the capability of the material to acquire or release electrons and is measured in Volts.

Semiconducting materials with high photon absorption have attracted the most interest as photocatalytic materials. Photocatalytic reactions are mostly heterogeneous with a few exceptions like the Fenton process [31] and the ozonation technique for water treatment [32, 33]. Conventional photocatalysts consist of metal oxides and/or their composites.

Bandgap of a semiconductor is the energy range between its Valence Band (VB) and Conduction Band (CB). The photonic source must possess enough energy to overcome the bandgap of the semiconductor. Figure 1. 3 shows the relationship between the CB and the VB for different types of materials.
Photoexcitation of semiconductors like TiO$_2$ and ZnO in aqueous or nonaqueous solutions or gaseous mixtures leads to simultaneous oxidation and reduction reactions. Photonic irradiation of semiconducting materials excites the electrons in the valence band causing them to migrate from the VB to the CB. The migration of the negatively charged electrons to the CB leaves a vacancy or an electron hole in the VB that has a net positive charge. The photocatalytic behavior of the material is due to the generation and migration of the electron hole pairs at the semiconductor surface. The excited in the CB freely react with O$_2$ and H$_2$O in the surrounding and produce Reactive Oxygen Species (ROS) such as superoxide (·$O_2^{-}$), hydroxyl radicals (·OH) and peroxides ($H_2O_2$). Figure 1. 4 illustrates the photocatalysis of TiO$_2$ and the accompanying reactions detail the generation of ROS.

**Figure 1. 3 Schematic representing the VB, CB and bandgap for different types of materials.**
Figure 1.4 Schematic showing the transition of a photo-excited electron from the VB to the CB accompanied by reactions detailing the production of ROS species.
1.3 Nanomaterials

“There’s plenty of room at the bottom” – a concept proposed by Dr. Richard Feynman paved the pathways for the development of nanotechnology [34]. The term nanotechnology was coined by Prof. Norio Taniguchi in 1974 and was popularized in the 1970s and 80s by Dr. K Eric Drexler [35]. Nanotechnology refers to the field of applied science and technology, which is based on synthesizing, controlling and processing, materials and devices at the range of a billionth of a meter. Nanoscale materials [36] are broadly classified as:

- Nanoparticles: these particles have all three dimensions in the 1-100 nm range. For example, gold quantum dots, Degussa P25, Fullerenes [37]. Figure 1.5 shows the schematic of a C\textsubscript{60} fullerene nanoparticle.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{C60.png}
\caption{Schematic of a C\textsubscript{60} fullerene particle.}
\end{figure}

- Nanotubes/Nanowires: these materials have 2 dimensions in the 1-100 nm range. For example, Carbon Nanotubes (CNTs), TiO\textsubscript{2} nanotubes [38, 39]. Figure 1.6 shows a transmission electron microscope image of a multi-walled CNT.
Nanosheets: These materials have only one dimension in the 1-100 nm range. For example, graphene. Figure 1. 7 shows the schematic of a 2-dimensional graphene nanosheet.
Nanostructured Materials: These are solid materials with one or more characteristic structural length in the nanoscale. For example, surface of a lotus leaf, nanoflowers of TiO$_2$ [41]. Figure 1. 8 shows the nanostructures on a micron-sized TiO$_2$ particle.

*Figure 1. 7 Schematic of a 2D graphene sheet.*

*Figure 1. 8 Scanning electron microscope image of a nanostructured TiO$_2$ puffball.*
Naturally occurring nanomaterials are found in volcanic ash, soot from forest fires, carbon black and soil phyllosilicates (nano clay) [42]. Nanomaterials exhibit unique behaviours because of their size. They have high surface to volume ratios. Nanomaterials also exhibit optical and electronic properties that are very different from their bulk counterparts. The change of electronic and optical properties of a material from macroscale to nanoscale is referred to as Quantum Confinement [43].

Commercial applications of nanomaterials are found in a wide range of industries – food, cosmetics, pharmaceuticals, computers, cellular devices and textiles [42]. As the research in nanotechnology progressed, certain disadvantages of nanomaterials came to light. These applications have inadvertently caused nanomaterials to enter the environment and now pose a significant threat to plant, animal and human life. Handy et al. report that CNTs can cause lung damage at intratracheal exposure levels [44]. Nel et al. state that nanomaterials with the ability to generate ROS induce lung injuries [45]. ROS preferentially attack guanine residues in DNA leading to cell and tissue damage [46-48]. Nanomaterials also induce phytoxicity and are known to affect aquatic ecosystems [49-51]. Research groups working in analyzing the environmental concentrations of nanomaterials have proved that the removal of these materials is a difficult task [47, 52, 53].

Nanostructured materials unlike nanomaterials exhibit the unique properties of nanoparticles whilst in a solid form. Nanostructures or nano-scale patterns are synthesized on the surface of bulk materials via fabrication techniques like nanolithography or FIB machining. Nanostructured materials are also manufactured using technologies like CVD.
Research interest in nanostructured materials is wide ranging. Schoonmann reviewed the improved performance of nanostructured ceramic electrodes over electrodes composed nanoparticles. The electrode performances were tested and compared in lithium-ion batteries [35]. Hashimoto et al. theorize that selective nanostructuring will improve the hydrophilicity of TiO$_2$ surfaces [54]. A review by Arico et al. shows that nanostructured materials have improved energy-storing capabilities when compared to the nanoparticles of the same chemical composition [55]. A review by Cavallo et al. describes the advantage of nanostructured materials over nanoparticles. Nanostructured materials possess the advantages of high surface area and are easier to handle. 3D nanostructures such as mesoporous titania have demonstrated improved photoanodic efficiency over Degussa P25 [56].

Nanoparticles in comparison to nanostructured materials and state that nanoparticles pose a greater threat to the environment. The reason – free nanoparticles have lesser constraint than nanostructured materials and spread more easily through the environment [57].
1.4 Titanium Dioxide

Titanium dioxide is among the most investigated single crystal materials and has a wide range of applications. It is represented with the chemical formula TiO$_2$. TiO$_2$ has a molecular weight of 79.90 g/mol. It is primarily extracted as a white powder with particles sized between 200-300 nm in diameter from natural ores containing ilmenite, rutile and anatase. TiO$_2$ has three main natural phases – anatase, rutile and brookite and a rarer phase – akaogiite. The anatase and rutile phases of TiO$_2$ are the most investigated for various practical applications. The anatase phase of TiO$_2$ has a wider bandgap (3.2 eV) than the rutile phase (3.0 eV). Rutile is the most stable phase of TiO$_2$ while anatase is the metastable phase. Anatase shows a higher surface-adsorption rate of hydroxyl radicals. Anatase also exhibits a slower charge recombination rate than rutile [58]. Due to this reason, some studies on TiO$_2$ were directed at tapping the benefits of anatase for photocatalytic applications.

Table 1. 1 lists the crystallographic properties of the four phases of TiO$_2$ [59, 60]. The crystallographic structures of the three widely researched phases of TiO$_2$ – anatase, rutile and brookite are illustrated in Figure 1. 9.

The commercial production of TiO$_2$ began in the early 20$^{th}$ century and it is used as a pigment in products like sunscreens [61], paints, toothpastes, and pigments [62]. The use of TiO$_2$ as a pigment is the result of the opacity of the powder due to its high refractive index. The pigments derived from TiO$_2$ mainly consist of anatase and rutile phases.
Table 1.1 Crystallographic properties of TiO$_2$ phases.

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>Density (g/cm$^3$)</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>Cell Parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>3.83</td>
<td>Tetragonal</td>
<td>I4$_1$/amd</td>
<td>3.785 3.785 9.514</td>
</tr>
<tr>
<td>Rutile</td>
<td>4.24</td>
<td>Tetragonal</td>
<td>P4$_2$/mnm</td>
<td>4.594 4.595 2.959</td>
</tr>
<tr>
<td>Brookite</td>
<td>4.17</td>
<td>Rhombohedral</td>
<td>Pbca</td>
<td>5.456 9.182 5.143</td>
</tr>
<tr>
<td>Akaogiite</td>
<td>4.72</td>
<td>Monoclinic</td>
<td>P2$_1$/b</td>
<td>4.606 4.986 4.933</td>
</tr>
</tbody>
</table>

Figure 1.9 Crystal structures of Anatase, Rutile and Brookite phases of TiO$_2$. 
1.4.1 Photocatalytic Activity (PCA) of TiO$_2$

The discovery of the capability of TiO$_2$ to split water under UV light by Fujishima and Honda in 1972 prompted a vast amount of research in the field of heterogeneous photocatalysis [63-66]. The photocatalytic decomposition of water by TiO$_2$ under UV light is called the Honda-Fujishima effect. TiO$_2$ materials were initially of interest for pigments in paints and sunscreens due to their high refractive index [67]. Clear, adherent, abrasion resistant films of TiO$_2$ were also used as heat mirrors in insulating windows [68]. The chemical stability of TiO$_2$ has made the material one of the most widely used photocatalysts for self-cleaning applications [54]. TiO$_2$ has also been explored for energy harvesting applications [69] and organic pollutant decomposition [70].

1.4.1.1 Self-Cleaning Properties of TiO$_2$

TiO$_2$ is a chemically inert and this property along with its optical properties make it an attractive option for self-cleaning applications. The most extensively used TiO$_2$ product, Pilkington Activ™ has superhydrophilic surface properties [71]. The self-cleaning performance of the TiO$_2$ thin film is activated by solar UV light. The high surface redox potential of TiO$_2$ (3.0 V) makes it capable of photocatalytically decomposing most organic contaminants on the surface. The superhydrophilicity of the coating ensures that any loose on the surface are washed off with relative ease. Titania coated surfaces remain photoactive over an extended service life. Researchers also found that the desired PCA mechanism does not consume or degrade the material [72]. The ROS generated due to PCA of TiO$_2$ increased the rate of *E. coli* cell-death by attacking the cell membranes of the bacteria cells [73].
1.4.1.2 Pollution Mitigation Properties of TiO₂

One of the earliest reports of harnessing the photocatalytic properties of TiO₂ for environmental remediation was from Oliver et al. The authors reported the use of nanosized TiO₂ powders in the form of a suspended sediment for photolysis of organic pollutants in the presence of sunlight [74]. Odenbrand et al. used V₂O₅ supported on precipitated SiO₂-TiO₂ as a novel catalyst system to understand the reduction of NOₓ and ammonia in water [75]. Fujishima et al. describe the use of TiO₂ films on transparent tiles or glass to purify indoor air via solar irradiation [23]. Hashimoto et al. constructed a practical water purification system for agricultural wastewater and soil polluted with volatile organic compounds (VOC) [54]. Chen et al. evaluated using TiO₂ nano-powders in modified concrete surfaces for NOₓ and VOC degradation [76]. Other research groups have demonstrated the use of nanostructured TiO₂-based materials for pollution control and environmental remediation [77, 78].

1.4.1.3 Energy Harvesting Applications of TiO₂

The growing demand for reduction in the emissions of greenhouse gases has led to an exponential increase in the research for sustainable technologies. Mills et al. explore the use of TiO₂ powders as photosensitizers for the production of hydrogen from biomass and water under UV light irradiation [79]. Hashimoto et al. theorized that dye sensitization of TiO₂ would utilize the longer wavelength lights for water photoelectrolysis [54]. Barreca et al. functionalized TiO₂ with Fe₂O₃ for increasing the efficiency of solar water oxidation by lowering the bandgap of the material to 2.1 eV [80, 81]. The authors report a 15% theoretical solar-to-hydrogen conversion efficiency. 1D nanostructured TiO₂ thin films and nanometal decorated TiO₂ hybrid structures are among the later technologies being explored by scientists for solar energy conversion [77]. Gardecka et al. have reported high efficiency water-splitting with visible light
active nanostructured anatase-rutile composite photoelectrodes [69]. Wang, S et al. describe different mechanisms of facet engineering of TiO$_2$ to enhance the photoelectrochemical water splitting process [82].

1.4.2 Enhancing the PCA of TiO$_2$ under Visible Light

TiO$_2$ is highly photocatalytic under UV light but is transparent to visible light. Since the discovery of the Honda-Fujishima effect, the research in TiO$_2$ photocatalysis took a giant leap. The initial work was carried out under UV light, but for practical indoor photocatalytic applications, it is necessary to lower the bandgap of TiO$_2$ to the visible spectrum.

1.4.2.1 Heterostructures for TiO$_2$ Nanomaterials

Heterostructures are created by introducing an interface within a semiconductor crystal across which the chemical or phase composition varies. The fabricated heterostructure possesses properties superior to those of the individual counterparts. For semiconductor based photocatalytic materials, heterostructures improve the photo-induced charge separation efficiency [83]. Preparation of heterostructures is one of the approaches used to improve the photocatalytic activity of TiO$_2$ and to ‘functionalize’ the materials. Functionalization is the process of modifying the surface chemistry of a material by the adhesion of nanoparticles by chemical bonding or absorptive reactions or binders.

TiO$_2$ nanoparticles were functionalized to be photocatalytic under visible light by creating heterostructures of TiO$_2$ with materials like CdS quantum dots or by cocatalyst coupling with noble metals [77]. Heterostructures of TiO$_2$ and Fe$_2$O$_3$ were reported to exhibit 15% solar-to-hydrogen conversion efficiency [81]. Surface heterostructures TiO$_2$ nanobelts functionalized with metal oxide (Ag$_2$O, CeO$_2$, ZnO and
MoS$_2$) nanoparticles were reported to have narrower bandgaps making them photoactive under visible light. The photoactivity of the metal oxide/TiO$_2$ heterostructures was analyzed using Methyl Orange (MO) degradation under visible light. The authors reported that the heterostructures exhibited improved performance when compared to photoactive behavior of TiO$_2$ nanobelts [84]. Visible light driven TiO$_2$/CdS photocatalytic heterostructures prepared for quantum dot-sensitized solar cells exhibited a 12% solar-to-hydrogen conversion efficiency [85, 86]. Huang et al. investigated Cu nanowires dip-coated with TiO$_2$ nanoparticles for solar-water electrolysis. The dip-coated nanowires performed 2.5 time better than TiO$_2$ nanoparticles under visible light [87]. Friedmann et al. reviewed fabricated epoxy-resin impregnated with TiO$_2$ using laser stereolithography for methanol degradation under visible light [88]. Vanadia-titania visible light photocatalysts prepared by ion-exchange were used for xylene oxidation [89].

Another widely used yet simple heterostructure is the ‘Schottky junction’, formed between a metal and a semiconductor. Schottky junctions promote charge-carrier separations and as a result, photo-excited electrons tend to move more freely through the composite materials. The free motion of the charge carriers implies an increase in the photocatalytic capability of the materials. TiO$_2$ nanomaterials functionalized with metals like Pt, Pd, Au, Cu, and Ag have exhibited superior photocatalytic performance in comparison with pure TiO$_2$ [78].

Heterostructures can also be formed between different phases of the same chemical compound. Sclafani et al and Augustynski report that anatase demonstrates a significantly higher PCA than rutile [90, 91] while other researchers believe that rutile is more useful for certain photocatalytic applications [92, 93]. Ohno et al. report that a combination of anatase and rutile facilitates improved redox reactions [94]. Song
et al. report that anatase aggregates embedded with rutile nanorods have demonstrated enhanced Photoelectrochemical (PEC) response for photovoltaic applications [95]. Yu et al. prepared a multiphase TiO$_2$-Ag nanocomposite by liquid phase deposition method for degradation of methyl orange in an aqueous solution [96]. A review of TiO$_2$ heterostructures by Mutuma et al reports that the samples containing multi-phase titania nanoparticles have demonstrated enhanced visible light photocatalytic performance [97]. Wang et al. report that the an aqueous solution of Rhodamine B dye degraded faster in the presence of a heterostructured catalyst with anatase-rutile surface junction when compared to the degradation of the dye in the presence of either anatase or rutile [98]. Cheng et al. demonstrated that a catalyst with an anatase-rutile-tin oxide heterostructure has enhanced PCA due to the incorporation of Schottky junctions with multi-phase band alignment [99].

Heterostructures can also be formed between different phases of the same chemical compound. Anatase and rutile are the most widely researched phases of TiO$_2$ for photocatalytic applications. Rutile has a smaller bandgap than anatase but the synthesis of nanoparticulate anatase is less challenging than rutile nanoparticles [100]. Despite the wider bandgap, anatase shows a higher surface-adsorption rate of hydroxyl radicals. Anatase also exhibits slower charge recombination rates than rutile. Thus, the majority of the studies on TiO$_2$ photocatalysis are directed at using a combination of anatase and rutile for practical applications [90, 91, 95].

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As the metastable phase, anatase transforms into rutile when processing temperatures are sufficiently high [101]. Yu et al. have used a liquid phase deposition technique to prepare anatase thin films and then treated the films with an AgNO$_3$ solution at different levels to tailor the phase transformation of anatase to rutile. The resultant heterostructured film photocatalytically performed 6.3 times better than pure TiO$_2$ thin films [96].
1.4.2.2 Facet Engineering of TiO₂ Crystals

Surface structures for metal-oxide ceramics have a strong influence on the surface chemistry. The influence of exposed surfaces or ‘facets’ can be particularly noticed in photocatalysis as this is a surface phenomenon. This section gives a brief insight into the surface energies and their influence on TiO₂ PCA for anatase and rutile.

**Anatase (A):**

Natural anatase crystals have two main exposed facets – A{101} and A{001} with A{101} family of facets being more prevalent for anatase nanocrystals. Theoretically, the surfaces with higher surface energy demonstrate higher photocatalytic activity. Gong et al used Density Functional Theory (DFT) calculations to predict that the A{111} and A{001} facets have much higher surface energies and hence having a large percentage of these facets exposed will lead to higher photocatalytic performance [102]. Xu et al used DFT calculations to predict the surface energies of the different anatase facets [103]. A review by Chen et al. states that as the surface energy increases, the stability of the facets decreases. This explains, the occurrence of natural anatase in with exposed A{101} facets [104]. Table 1. 2 lists the surface energies for different widely-researched facets of anatase.
Table 1. Surface energies of different anatase facets.

<table>
<thead>
<tr>
<th>Facet</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A{101}</td>
<td>0.44 J/m²</td>
</tr>
<tr>
<td>A{010}</td>
<td>0.53 J/m²</td>
</tr>
<tr>
<td>A{001}</td>
<td>0.90 J/m²</td>
</tr>
<tr>
<td>A{111}</td>
<td>1.61 J/m²</td>
</tr>
</tbody>
</table>

Yang et al. employed fluorine mediation to expose and stabilize the minority A{001} facets [105]. Based on first principle calculations, the authors also state that anatase crystals with exposed A{001} facets have promising applications in solar cells and photocatalysis. Xu et al. studied the effect of exposed A{111} facets for the evolution of H₂ from water in comparison to the photocatalytic effect of the A{101} and A{001} facets. They reported that exposing the A{111} facets largely enhanced the photocatalytic activity of TiO₂ nanocrystals [103]. Surprisingly, the A{010} facets regardless of their higher energy, demonstrate lower PCA when compared to the A{101} facets [106].

Apart from the aforementioned crystal facets, the A{10l} (l>1) family of planes have been reported to possess superior photocatalytic capabilities. Jiang et al. prepared anatase nanocrystals with high index A{105} facets and demonstrated that these crystals cleaved water photocatalytically better than anatase crystals with exposed A{101} facets [107]. Figure 1. 10 provides illustrations for the location of the different facets for an anatase TiO₂ crystal with respect to the naturally occurring A{101} facets. The facets were generated using the VESTA software [108] and the raw Crystallographic Information File (cif) for anatase was obtained from the American Mineralogist Crystal Structure Database.
Database (AMCSD) and the Raman Research Used for Fun Academic and Science Database (RRUFF) [109, 110].

**Figure 1.** Anatase crystal with (a) $A\{101\}$ facets exposed – natural form; (b) a large percentage of the high energy $A\{001\}$ facets exposed; (c) $A\{001\}$ and $A\{111\}$ facets exposed; (d) $A\{10\}$ family of planes exposed.
**Rutile (R):**

Naturally occurring rutile has two main crystal facets – R\{110\} and R\{100\} of which, the R\{110\} facet is the stable one. The higher energy facets for rutile are R\{101\}, R\{001\}, R\{011\} and R\{111\}. Zhang et al. report that rutile nanorods with exposed R\{111\} facets have a bandgap of 2.8 eV which is significantly less than the conventional 3.0 eV [111]. Yang et al. have reported that rutile TiO$_2$ with dominant R\{001\} facets demonstrated superior photocatalytic behavior [112]. Jiang et al. have used First-Principle atomistic Wulff constructions to calculate the surface energies for the different rutile facets [113]. Table 1. 3 lists the surface energies for different rutile facets reported in literature. Figure 1. 11 details the location of the facets listed in Table 1. 3 with respect to the naturally occurring R\{110\} facets.

**Table 1. 3 Surface energies of different rutile facets**

<table>
<thead>
<tr>
<th>Facet</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>R{110}</td>
<td>0.74 J/m$^2$</td>
</tr>
<tr>
<td>R{100}</td>
<td>0.83 J/m$^2$</td>
</tr>
<tr>
<td>R{101}</td>
<td>1.11 J/m$^2$</td>
</tr>
<tr>
<td>R{011}</td>
<td>1.50 J/m$^2$</td>
</tr>
<tr>
<td>R{111}</td>
<td>1.51 J/m$^2$</td>
</tr>
<tr>
<td>R{001}</td>
<td>1.65 J/m$^2$</td>
</tr>
</tbody>
</table>
Figure 1.11 Rutile crystal with exposed R\{110\}, R\{100\} and (a) R\{001\}; (b) R\{011\}; (c) R\{111\} and (d) R\{101\} families of facets.

Surface structures of the two phases of TiO$_2$ also play a role in the phase transformation of anatase to rutile. Hanaor et al. report that the kinetics of the phase transformation of anatase to rutile may be controlled by exposure of certain facets. The authors theorize that in pure anatase, rutile is likely to nucleate as the (112) twin interfaces as these sites are structurally comparable to rutile [58].
1.4.2.3 Doping TiO$_2$

The wide bandgap range of TiO$_2$ (3.0 – 3.2 eV) is responsible for TiO$_2$ being transparent to visible light. The bandgap of a semiconductor can be lowered by introducing an impurity into its lattice to modify the material’s optical and electronic properties. This process is referred to as doping. Metallic or nonmetallic dopants can be introduced into the interstitial or substitutional sites of TiO$_2$ crystals to alter the electronic properties and make it more responsive to photonic radiation with energies lower than 3.0 eV. Interstitial doping is achieved when the introduced impurity occupies a site that is typically vacant. Substitutional doping is achieved by replacing a host atom in the crystal lattice. The illustration in Figure 1. 12 demonstrates the bandgap modification of a TiO$_2$ crystal with dopants.

![Diagram showing bandgap modification of TiO$_2$ with dopants](image.png)

**Figure 1. 12** Schematic showing the bandgap modification of a TiO$_2$ crystal with dopants.

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29 | Introduction
**Metallic Dopants:**

Metal doped TiO$_2$ nanomaterials have been extensively investigated for photocatalytic degradation of organic pollutants under visible light [101] [Chen X 07]. The electron-hole recombination is reduced if the dopants are situated closer to the surface of the TiO$_2$ materials rather than the bulk [114]. Noble metals like Pt, Au, Cu and Ag are some commonly used dopants for PCA enhancement apart from transition metals like Sn, and Fe. Low et al. reviewed studies on the improved light response of TiO$_2$ nanomaterials doped with cu for photocatalytic CO$_2$ reduction [115]. Cu and Ag are well-known antimicrobial agents. Leyland et al. prepared a visible light active Cu-doped TiO$_2$ coating for antimicrobial applications [116]. The authors reported a 4-fold reduction in bacterial cell-count after 24 hours of exposure to the coating. Charpentier et al. reported that Ag doped nanoparticles of titania killed about 40% of *E. coli* population under UV illumination [117]. When the fabrication costs of Ag-doped and Cu-doped TiO$_2$ nanomaterials are compared, Cu-based dopants have a considerable cost advantage over Ag-dopants [118, 119]. Primo et al. have reviewed TiO$_2$ nanomaterials doped with varying concentrations of Au$^{3+}$ ions. The authors proposed that gold-doped TiO$_2$ could find applications in solar irradiation-based environmental remediation and H$_2$ production [120]. Pt$^{4+}$ ion-doped TiO$_2$ nanoparticles have exhibited high rates of phenol degradation under visible light [121]. TiO$_2$ nanobelts synthesized via CVD were deliberately doped with Fe in-situ to enhance their PCA performance. These materials exhibited efficient visible light degradation of Methylene Blue Dye (MBD) solution and possess a narrower bandgap than pure TiO$_2$ [122]. The limitations of using metal dopants for PCA enhancement are the prohibitive costs involved
in using precious metals, photo-corrosion of the materials and promoted charge recombination at the metal sites [123].

**Non-metallic Dopants:**

Carbon, nitrogen, fluorine and sulfur are the most widely used nonmetallic dopants for enhancing the PCA of TiO$_2$. The versatility of carbon-based materials in enhancing the PCA of TiO$_2$ nanomaterials is a vast field of research in itself and thus, the materials in this category are described in the next section.

One of the main reasons for using nitrogen as a dopant for TiO$_2$ is its similar atomic size to oxygen atoms [123]. N$_2$ based dopants induce bandgap narrowing in TiO$_2$ nanoparticles [124, 125]. Belver et al. reported that, combining titanium precursor with N$_2$-containing ligand resulted in an N-doped TiO$_2$ nanomaterial with a bandgap of 2.3 eV [126]. N-doped TiO$_2$ nanobelts synthesized by hydrothermal processing followed by ammonia heat treatment exhibited organic pollutant degradation in the visible light spectrum [127]. N-doped TiO$_2$ nanotubes exhibited decomposition of isopropanol under visible light irradiation [101]. The limitation of doping TiO$_2$ nanomaterials with N$_2$ is the possible increase of electron-hole recombination rate due to oxygen vacancies in the TiO$_2$ crystal lattice [128].

Doping TiO$_2$ with F promotes the charge separation in the materials and improves the efficiency of the photocatalytic processes [129]. Padmanabhan et al. reported an F-doped TiO$_2$ material that proved to be more photocatalytically active than Degussa P25 under UV light. The limitation to using F as a dopant is that the bandgap of TiO$_2$ remains unchanged [130]. The underlying photocatalytic mechanisms of fluorine doped TiO$_2$ remain controversial and necessitates further research [131]. Sulfur-doped TiO$_2$ nanomaterials have exhibited some unique
properties. These materials are known to exhibit higher PCA under visible light but lower PCA in the UV region when compared to pure TiO$_2$ nanomaterials. S-doped TiO$_2$ thin films were particularly effective in degrading microcystin-LR, a toxin produced by cyanobacteria, under visible light irradiation [123].

TiO$_2$ co-doped with multiple elements has also been researched for visible light photocatalysis. N-F co-doped TiO$_2$ have the synergistic effects of high visible light response due to N$_2$ and effective charge separation due to F [132, 133]. N-F co-doped TiO$_2$ exhibited high visible light decomposition of acetaldehyde and trichloroethylene [101].
1.4.2.4 Carbonaceous TiO$_2$

Carbon-based nanomaterials are among the most widely used functionalizing materials for TiO$_2$ because of their visible light absorptive capabilities. Carbonaceous nanomaterials possess unique, controllable electronic properties and stable physio-chemistry. The synthesis processes of these materials are straightforward and the materials can be tailored to the requirements of different applications. The well-known carbonaceous nanomaterials are activated carbon, CNTs, graphene, Graphene Oxide (GO), Reduced Graphene Oxide (RGO), carbon dots, fullerene and mesoporous carbon [134]. Of these, CNTs and graphene-based nanomaterials are most widely used to prepare carbonaceous TiO$_2$ photocatalytic nanomaterials. Carbonaceous TiO$_2$ nanomaterials include C-doped TiO$_2$, heterostructures of carbon-based materials with TiO$_2$, nanocomposites of TiO$_2$ with carbon nanomaterials and carbon coated TiO$_2$ nanoparticles. The enhancement of the photocatalytic activity of carbonaceous TiO$_2$ nanomaterials is primarily attributed to the photonic adsorption of the materials in the visible light spectrum (~400 nm to 700 nm).

C-doped TiO$_2$ with a bandgap of 2.3 eV was synthesized by controlled combustion of metallic Ti in ambient air by Khan et al. for visible PEC water splitting [135]. Irie et al. prepared C-doped TiO$_2$ nanotubes by oxidative pyrolysis of TiC for the degradation of 2-propanol under visible light [136]. The visible light photocatalytic performance of C-doped TiO$_2$, when investigated in comparison with N-doped TiO$_2$, revealed that materials doped with C are more active under visible light irradiation [137]. The limitation to using C-doped TiO$_2$ for photocatalysis is the complexity of their synthesis. Most of the current synthesis techniques involve multiple stages and unstable precursors [138].
Heterostructures of TiO$_2$ with carbonaceous materials are also widely researched. Xu et al. used a wet impregnation method to fabricate CNT-TiO$_2$ nanocomposite photocatalysts that exhibited high visible light organic dye degradation when compared to pristine TiO$_2$ [139]. Polymer composites embedded with CNTs and TiO$_2$ were also analyzed for visible light photocatalysis. Composite nanofibers embedded with TiO$_2$ nanoparticles and multi-walled CNTs dispersed in a polyacrylonitrile support were reported to degrade Rhodamine dye twice as fast when compared to the performance of TiO$_2$ nanoparticles [140].

Graphene sheets have a theoretical surface area of $\sim$2500 m$^2$/g making them highly attractive photocatalyst supports. Akhvan et al. used a sol-gel technique to prepare a photocatalytic antimicrobial GO-TiO$_2$ nanocomposite, which performed 7.5 time better than pure anatase TiO$_2$ [141]. Zhang et al. have reported a GO-TiO$_2$ nanocomposite prepared by hydrothermal synthesis with the capability to degrade MB dye under visible light. The authors report that the PCA of GO-TiO$_2$ composite was higher than that of CNT-TiO$_2$ composite [142]. Amorphous carbon has been reported to stabilize the exposed high-energy facets of anatase TiO$_2$. This unique feature was exploited by Chen et al. where carbon-supported anatase nanosheets were used as anode materials for fast reversible lithium storage [143].
1.4.3 Processing Methods for Visible-Light Antimicrobial Coatings

The following sections provide a brief overview of the various synthesis methods currently being employed to produce visible light-activated TiO$_2$ coated surfaces.

1.4.3.1 Chemical Vapor Deposition

CVD is one of the most popular industrial technologies used in the synthesis of semiconductors. Thin films are deposited on the substrate surfaces by a chemical reaction (pyrolysis or decomposition) of vapor-phase precursors [144]. Chemical reactions are initiated or promoted by different techniques like heat, high frequency photonic radiations, or plasma. Common precursors used for CVD of TiO$_2$ nanoparticles and thin films are titanium tetra-isopropoxide (TTIP), titanium tetrachloride (TiCl$_4$), titanium tetranitrate (Ti(NO$_3$)$_4$) and tetrabutyltitanate [145]. Conventional CVD processes are limited in terms of substrate geometry and dimensional changes.

Fractal-like TiO$_2$ nanoparticles were prepared using an in-house built CVD reactor by Kandjani et al. for visible light Rhodamine dye degradation [146]. TiO$_2$ nano powders were prepared by Ayllon et al in a cold-walled plasma-enhanced CVD system were tested for organic carbon degradation under visible light [147]. Thermal CVD process has been reported to provide phase control during the synthesis of TiO$_2$ nano particles. Wu et al reported the synthesis of well-aligned anatase and rutile nanorods at 630 °C and 535 °C respectively. TiO$_2$ nanoparticles were coated on glass beads using a T-junction CVD for degradation of indoor organic pollutants [148].

Porphyrin sensitized anatase-TiO$_2$ thin films were prepared via cold-walled MOCVD process for visible light PEC applications [149]. Antimicrobial anatase thin
films were deposited using electric field-assisted CVD [150]. Goossens et al. reported the use of gas-phase MOCVD process to produce nanostuctured TiO$_2$ coatings with enhanced active surface area [41].

### 1.4.3.2 Physical Vapor Deposition (PVD)

In a PVD process, vaporized titanium is condensed on a target substrate in low-pressure O$_2$ environment to form a solid TiO$_2$ coating. Prominent PVD methods include pulsed laser vaporization, sputtering, electron beam deposition and molecular beam epitaxy [151]. PVD processes provide a good control of homogeneity and thickness on flat surfaces. PVD processes are line-of-sight processes and this limits the types of substrate geometries that can be coated.

Martin et al. modified the microstructure of oxidized surfaces with nanoparticulate TiO$_2$ synthesized via reactive magnetron sputtering [152]. Pyun et al. employed an oblique angle e-beam variation of PVD to produce 20-35 nm large TiO$_2$ nanoparticles for photocatalytic applications [153]. Magnetron sputtering is a PVD-based industrial process reported to produce high quality TiO$_2$ films at low substrate temperatures [154]. TiO$_2$ thin films with variable optical properties were prepared using magnetron sputtering for diverse photocatalytic efficiencies [155].

### 1.4.3.3 Sol-Gel

Sol-gel method is a simple process used to prepared products with high purity and controlled stoichiometry. It is a dip-coating or spin-coating method used in the processing of glass, ceramic and other oxide materials since the 80s [156]. Sols are colloidal suspensions of solid particles (1-100 nm in diameter). A gel is an interconnected network of pores (< 1 µm) and micro-scale polymeric chains. The three approaches used to make sol-gel monoliths [157] are:
(a) gelation of a colloidal suspension
(b) hydrolysis and polycondensation of chemical precursors (TTIP, Ti(NO$_3$)$_4$) followed by hypercritical drying of the resulting gel
(c) hydrolysis and polycondensation of alkoxide precursors followed by aging and drying in ambient conditions

Sol-gel methods are also time-consuming processes that involve lengthy drying times. If the drying rate is too high, TiO$_2$ coatings have been reported to crack and peel-off from the substrate [101].

TiO$_2$ nanoparticles were produced by acid-catalyzed hydrolysis of TTIP for antimicrobial applications [158]. TiO$_2$ inverse opal photo-crystals were prepared using sol-gel method with tetrabutyl titanate as the precursor. The inverse opal photocrystals were used in photocatalytic degradation of organic dye and have a potential application in clinical medicine [159]. Li et al. prepared crystalline anatase nanoparticles through ethanol-catalyzed polycondensation of TTIP for potential photocatalytic applications [160].

Nanostructured TiO$_2$ thin films can be prepared via sol-gel methods involving alkoxide precursors in the presence of templating agents. But this is an expensive technique as the templating agents are sacrificed after synthesis [161].

1.4.3.4 Atomic Layer Deposition

ALD is a variation of CVD that is widely used in the field of microelectronics. In ALD, vaporized reactants are intermittently introduced into the reactor with periodic inert gas purging of the reactor chamber. The precursor molecules form the desired material through surface chemical reactions on the target substrate. The periodic purging of inert gas mitigates gas-phase reactions of the injected precursor. ALD is
governed by self-limiting surface reactions that lead to uniformly thick conformal coatings. The number of iterations of the reactions dictates the film thickness. Current ALD methodologies are slow and expensive processes. Additionally, the long purge cycles considerably increase deposition times [162].

TiS$_2$ nanosheets were coated with nanoscale TiO$_2$ particles to fabricate PEC electrodes for water splitting [163]. Li et al. produced Al$_2$O$_3$ coated anatase TiO$_2$ nanorods via ALD for catalytic CO$_2$ reduction [164]. King et al. used ALD to deposit nanoscale TiO$_2$ particles on silica spheres for wastewater treatment [165]. Sree et al. used ALD to deposit nanoparticles of TiO$_2$ inside the microstructure of mesoporous silica for textile dye degradation [166]. ALD was also used to generate arrays of titania on inorganic substrates for various photocatalytic applications [83].

ALD is one of the few technologies that facilitates conformal deposition of thin films on complex 3D structures [167]. Nanolayers of TiO$_2$ were deposited on a Si electrode via ALD for oxidation of organic dyes [168]. ALD-TiO$_2$ layers were shown to improve the corrosion resistance of Si electrodes [169]. Multilayer TiO$_2$ nanocomposites were prepared by ALD for CO$_2$ scrubbing [162].

1.4.3.5 **Flame Aerosol Technology**

Flame aerosol technology or combustion flame-chemical vapor condensation is used for industrial scale manufacture of ceramic powders. This is one of the oldest technologies and has been practiced in cave paintings and later in Chinese ink artwork [170]. The technology is based on the generation of ultrafine or nanoscale particles from vaporized precursors in flames. Flame aerosol technology is used to synthesize nanopowders with no agglomeration, uniform particle size and high purity. Flame aerosol synthesis is complex process and rate of production of the TiO$_2$ particles is
particularly high. This leads to a lack of control on the process and the produced powders coagulate post synthesis [170, 171]. The most well know commercially available TiO$_2$ product, Degussa P25 is produced by means of gas-flame synthesis [172].

**1.4.3.6 Pulsed-Chemical Vapor Deposition (Pulsed-CVD)**

The earliest reported use of pulsed-CVD was by Xie et al. [173]. Pulsed-CVD is variant of CVD based on periodic injection of gaseous precursors into a low-pressure reactor chamber. A chemical reaction is initiated at the substrate’s surface producing a coating of the desired material on the substrate. Pulsed-CVD is analogous to ALD except for the short-purge times. Pulsed-CVD facilitates high degree of coating conformality. The thickness of the coating is controlled by the number of cycles in the process [174]. Pulsed-CVD has the potential to produce large-scale synthesis of nanostructured coatings with on complex-shaped objects [175].

TiO$_2$-rutile nanorods were produced using pulsed-CVD to conformally coat complex-shaped confined spaces. The authors propose that the nanoarchitectures produced by pulsed-CVD could find applications as photocatalysts [176].

Thin films of rutile TiO$_2$ were produced on sapphire substrates using pulsed-CVD with direct liquid-injection of atomized precursor [177]. TiO$_2$ nanocomposites for antimicrobial applications were prepared using pulsed direct liquid-injection CVD on stainless steel substrates [178].
1.5 Scope of Research and Thesis Organization

TiO$_2$ is non-toxic but its capability to produce ROS is a desired property for antimicrobial performance. To produce a viable coating on touch surfaces for healthcare facilities the following challenges need to be addressed:

- The production of a nanostructured material with high specific surface area as a robust solid coating.
- The extension of PCA to visible spectrum in order to activate the coating using indoor light.
- The development of an up-scalable process for producing the coatings on touch-surfaces.

Pulsed-pressure Metalorganic Chemical Vapor Deposition (pp-MOCVD) is a single-step commercial-grade process that is capable of producing thick uniform metal oxide coatings on complex shaped objects [179]. The current research project started out with investigating antimicrobial TiO$_2$ coatings for hospital fixtures [180]. Early studies yielded a surprising result. An error in temperature measurement during deposition process produced a black coating that exhibited the stoichiometry of TiO$_2$. Preliminary tests for PCA using a photocatalytic activity indicator ink (païi) RZ test pen (not publishable result) appeared to show photoactivity in visible indoor light. Scanning Electron Microscope imaging (SEM) showed that the coatings had morphologies rarely observed in TiO$_2$ materials.

The pp-MOCVD process has five relevant deposition parameters that produce a wide range of multi-phase TiO$_2$-C composites with complex nanostructures and characteristics. Preliminary investigations into the material properties revealed that some variants of the nanostructured TiO$_2$ coatings are more effective than others. The
hypothesis is that specific combinations of the deposition parameters are responsible for producing visible light active TiO₂ coatings. The aim of this doctoral research project is to elucidate the factors that are responsible for the visible light activity of the polycrystalline coatings. In order to achieve this, I applied Forensic Science Principles to the materials science investigations. The novel approach is based on studying the influence of the pp-MOCVD processing parameters on films’ characteristics and properties and then link the performance of the coatings to their observed characteristics. The results from this study present a restricted set of pp-MOCVD processing parameters that can be used to produce solid TiO₂ coatings with ensured visible light PCA.

The thesis is organized in seven chapters according the following outline

*Chapter 1*

The current chapter provides the background literature for the research project. It demonstrates the need for antimicrobial touch-surfaces in hospitals and health care facilities. The various surface modification methods are reviewed with an emphasis on self-cleaning properties of the materials. The literature survey also covers the photocatalytic applications of titania with an emphasis on visible light driven PCA. The final section of the chapter provides the motivation and scope of the current research project.

*Chapter 2*

This chapter presents the background on pp-MOCVD deposition technique. The preliminary investigations carried out on the photocatalytic coatings produced for potential antimicrobial applications are provided and the structural evolution of the TiO₂ composite coatings is discussed.
The chapter also provides the research methods employed in carrying out the experimental work for this doctoral thesis.

Chapter 3

The chapter discusses the growth-rate study performed to analyze the nanostructure evolution of the TiO$_2$ coatings with coating thickness. The thickest sample exhibited unique structural morphologies that were investigated in detail. Preliminary antimicrobial tests performed on the sample showed that the coating exhibits antimicrobial activity under low-energy indoor visible light. The mechanical behavior of the coatings was also studied to investigate the robustness of the coatings for touch surface applications.

Chapter 4

The chapter is the first stage in the Forensic analysis of TiO$_2$ composite coatings prepared by pp-MOCVD. The Forensic approach to materials investigation is described in detail. The chapter also describes the Design of Experiments (DOE) methodology. A set of 12 samples was prepared using this methodology. The influence of the five processing parameters on the performance, structure and composition of the coatings was evaluated by linking the performance of the coatings with the resulting characteristics of the coatings. The results of the study identified two samples that exhibited high photocatalytic activity under visible light.

Chapter 5

This chapter is the second stage in the Forensic Investigation of TiO$_2$ composite coatings. The two most photocatalytically active samples from the DOE set were analyzed using advanced material characterization methods. The chapter
aims to answer the question – do the samples have the characteristics suspected to exhibit high PCA? The results were used to determine whether the samples possess high energy exposed crystal facets.

Chapter 6
The third stage of the Forensic Investigation into TiO$_2$ coatings is presented in this chapter. The location of carbon content and its distribution in the micro and nanostructure of the coatings was analyzed using atomic-scale resolution electron energy loss spectroscopy. The results were used to establish the role of carbon in the stabilization of the high-energy exposed facets.

Chapter 7
This chapter is the final stage in the Forensic Materials Investigation. The gathered evidence was used to deduce the reasons behind the high PCA of the samples identified in the DOE study. The concluding remarks for the research project are provided in this chapter.
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Chapter 2: PP-MOCVD Processing, Materials & Characterization Methods

The previous chapter gave the motivation for investigating antimicrobial coatings. The chapter discussed the motivation for using photoactivated TiO$_2$ as touch-surface coating material. The inherent challenges of producing coatings on 3D surfaces have also been briefly described. The current chapter is split into the following sections.

- Section 2.1 describes the pp-MOCVD process in detail. The section includes a list of processing raw-materials and different substrates used in this research project.
- Section 2.2 provides the preliminary investigations performed to investigate the applicability of pp-MOCVD in producing commercial-grade TiO$_2$ composite coatings on touch-surfaces for healthcare facilities.
- Section 2.3 describes the research methods used in structural and morphological characterization of the TiO$_2$ composite coatings prepared by pp-MOCVD.
- Section 2.4 describes the methods used in phase and compositional investigations of the coatings prepared by pp-MOCVD.
- Section 2.5 describes the evaluation methods used to analyze the photocatalytic and antimicrobial performance of the TiO$_2$ coatings.
- Section 2.6 provides the details of the mechanical behavioral tests used in analyzing the durability and robustness of the coatings.
- Section 2.7 provides a summary of the chapter and discusses the research questions addressed in Chapter 3.
2.1 Deposition Method

The current pp-MOCVD methodology was developed by Krumdieck et al. to coat large surfaces such as turbine blades with thermal barrier coatings [1]. Pp-MOCVD is a single step technique that is capable of producing antimicrobial coatings on complex geometries such as door handles, elevator lift buttons, bed rails and other common high touch surfaces.

The pp-MOCVD process is governed by periodic injection of liquid precursor into a cold-walled reactor chamber. A single pulse cycle involves three phases:

1. **The injection phase:** Liquid precursor is directly injected into a constantly evacuated cold-walled reactor chamber through an ultrasonic atomizer from a pressurized source. The atomized precursor droplets are flash vaporized upon entry into the chamber. The flash vaporization of precursor leads to a sudden increase of pressure in the reactor chamber. The flash vaporization of the liquid precursor is also responsible for the flow conditions in the reactor chamber to approach a ‘well-mixed’ state [2]. The ‘well-mixed’ reactor condition enables the uniform coating of 3D objects and surfaces.

2. **The deposition phase:** The atomized precursor comes in contact with a heated substrate surface in the first 340 milliseconds of the pulse cycle and reacts to form a thin solid film [3].

3. **The evacuation phase:** A vacuum pump removes the by-products of the surface reactions any unreacted precursor into a liquid N\textsubscript{2} cold-trap.

The number of pulses controls the coating thickness during the operation pp-MOCVD system. Figure 2.1 shows the schematic of a typical pp-MOCVD pulse curve with the three phases labeled.
Figure 2. 1 Illustration of a pulse curve for three pulses of the pp-MOCVD process

2.1.1 Components and Operation of the pp-MOCVD System

Lee et al developed the scale-up prototype used to produce commercially viable coatings used in this research project [4]. The pp-MOCVD system consists of a liquid delivery system, a reactor chamber and an exhaust system. A Labview program is used to operate the pp-MOCVD system. Figure 2. 2 shows the pp-MOCVD system used by the AEMS lab research group at UC. The layout of the different components is provided in the image. An image of the reactor interior is provided in Figure 2. 3.
Figure 2.2 The pp-MOCVD system and its components.

1. Reactor chamber
2. Ultrasonic atomizer
3. 2-Way solenoid valve (precursor delivery)
4. Induction heating system
5. Precursor bottle (pressurized)
6. Operation control system (Labview)
7. LN$_2$ cold-trap
8. Vacuum pump
Figure 2.3 The interior of the pp-MOCVD reactor chamber showing the port for pressure measurement, the Cu induction coil and the thermocouples.

The pressure inside the chamber is measured by the means of a Pirani gauge attached to one of the ports of the reactor chamber. The pressure readout from the Pirani gauge is fed into the Labview program. The operator uses this to set the working base pressure at a desired value. The injection phase of the operation is triggered when the reactor chamber reaches a preset base pressure. A metered volume of precursor solution is delivered to the atomizer from a pressurized container via a 2-way solenoid valve. The ultrasonic atomizer injects the atomized liquid into the reactor chamber at preset time-intervals. The liquid precursor is a dilute mixture of TTIP in toluene. The target objects or substrates are placed on a susceptor, which is heated using a water-cooled induction coil. A k-type thermocouple inserted into the susceptor allows for temperature measurement. The feedback from the thermocouple (via Labview program) is used to control the induction heater power supply to maintain the susceptor temperature at a desired value.
2.1.2 Operating Parameters of the pp-MOCVD system

Preliminary investigations to understand the effects of pp-MOCVD processing parameters on the properties and conformality of TiO$_2$ coatings were conducted by Siriwongrungson et al. Table 2.1 summarizes the influence of various processing parameters on TiO$_2$ film growth as reported by the authors [5]. The preliminary investigations utilized a systematic ‘One-Variable-at-a-Time’ approach.

**Table 2.1 Processing parameters of the pp-MOCVD system and their influence on film growth**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Effect on growth</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature</strong> $(T)$</td>
<td>375 – 525 °C</td>
<td>The microstructure of the films changes from solid film to columnar microstructure (Figure 5)</td>
<td>The deposition temperature is measured at the susceptor</td>
</tr>
<tr>
<td><strong>Precursor Concentration</strong> $(C)$</td>
<td>3 – 5 mol%</td>
<td>The microstructure of the films remains columnar, but the thickness of the films increases with increasing concentration</td>
<td>This is the molar percentage of TTIP diluted in toluene</td>
</tr>
<tr>
<td><strong>Injection volume</strong> $(V_{inj})$</td>
<td>250 – 500 µL</td>
<td>The thickness of the films increases with the injection volume</td>
<td>The volume of precursor injected in a single pulse</td>
</tr>
<tr>
<td><strong>Pulse</strong></td>
<td>500 – 1000</td>
<td>The higher the number of pulses, the thicker the coating</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>------------</td>
<td>-----------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Base pressure</strong> ( (P_{\text{min}}) )</td>
<td>85 – 115 Pa</td>
<td>At lower base pressures, the evaporation efficiency of the injected precursor is higher.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>This is the number of times the precursor is injected into the chamber during a single deposition. The number of pulses for a deposition is preset at the beginning of a deposition in the Labview program.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>The reactor is pumped down to a set pressure after each pulse. It is measured by a Pirani gauge attached to one of the ports on the reactor chamber.</td>
<td></td>
</tr>
</tbody>
</table>
2.1.3 Materials

The chemicals and raw materials used to prepare the TiO₂ composite coatings for this research project are listed in Table 2.2.

Table 2.2 List of source materials and substrates used in the research project

<table>
<thead>
<tr>
<th>Material/Substrate</th>
<th>Supplier</th>
<th>Source and additional details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium tetra-</td>
<td>Supplier: Sigma-Aldrich Chemical Co., USA</td>
<td>99.5% pure (as received)</td>
</tr>
<tr>
<td>isopropoxide</td>
<td>Purity:</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>Supplier: Distilled in-house</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Purity: High-performance liquid chromatography</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(HPLC) grade</td>
<td></td>
</tr>
<tr>
<td>Fused Silica (substrate)</td>
<td>Supplier: Esco Optics, USA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dimensions: 25 mm × 25 mm × 1 mm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Surface finish: 0.05 μm</td>
<td></td>
</tr>
<tr>
<td>Stainless-steel (substrate)</td>
<td>Supplier: AISI (grade 304)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dimensions: 75 mm × 25 mm × 1 mm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Surface finish: 0.1 μm</td>
<td></td>
</tr>
</tbody>
</table>
2.2 Preliminary Investigations on TiO$_2$ Coatings prepared by pp-MOCVD

Preliminary tests on the micro and nano-conformality of TiO$_2$ thin films produced by pp-MOCVD were performed by Siriwongrungson et al. [6]. Conformality investigations performed on the TiO$_2$ coatings on an impellor showed that pp-MOCVD eliminates the dependency of thin film deposition on reactor and substrate geometry. This makes pp-MOCVD a versatile technique to coat 3D objects [4].

2.2.1 Temperature Dependence of TiO$_2$ coatings by pp-MOCVD

The initial-stage investigations of the current research project were targeted at determining the temperature at which the deposition process tips into the mass-transport controlled regime [7, 8]. This is the key to obtain a well-mixed reactor condition and eventually conformal coatings on 3D objects.

TiO$_2$ coatings were prepared at different temperatures ranging from 375 – 525 °C. The deposition times were adjusted to produce 2.5 – 3.0 µm thick films. The coatings were deposited on 25 mm × 25 mm × 1 mm FS substrates. The photographs of the samples prepared for the temperature dependence study and their corresponding microstructures are provided in Figure 2.4. The Scanning Electron Microscope (SEM) images show that the morphologies of the coatings at low temperatures are vastly different from the ones deposited at 525 °C. The morphology of the coatings changes from a solid film at 375 °C to a film that exhibits loosely packed columnar microstructure at 525 °C.
Figure 2.4 Photographs and SEM images showing the plan-view and fracture surface morphologies of TiO$_2$ films deposited at (a) 375 °C, (b) 450 °C and (c) 525 °C. Images reproduced with permission from Krumdieck et al. [8].

Photoactivity of the samples was measured using methylene blue dye degradation tests. The PCA results showed that the sample deposited at 525 °C was remarkably active under laboratory bench top light. Table 2.3 summarizes the results of this study.
Table 2.4 Summary of results from the temperature dependence study [8].

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Color</th>
<th>Observations and performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>375 °C</td>
<td>Opaque white</td>
<td>➢ 2.1 μm thick solid film</td>
</tr>
<tr>
<td></td>
<td></td>
<td>➢ 0.91 μm average grain diameter</td>
</tr>
<tr>
<td></td>
<td></td>
<td>➢ Phase: Anatase phase of TiO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>➢ PCA – 3.09×10⁻⁴ min⁻¹</td>
</tr>
<tr>
<td>450 °C</td>
<td>Translucent gray</td>
<td>➢ 2.9 μm thick film with rough columnar microstructure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>➢ 0.32 μm average grain diameter</td>
</tr>
<tr>
<td></td>
<td></td>
<td>➢ Phase: Anatase TiO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>➢ PCA – 7.53×10⁻⁴ min⁻¹</td>
</tr>
<tr>
<td>525 °C</td>
<td>Opaque black</td>
<td>➢ 3.1 mm thick films with loosely packed definitive columnar microstructure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>➢ 0.21 μm average grain diameter</td>
</tr>
<tr>
<td></td>
<td></td>
<td>➢ Phase: Anatase TiO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>➢ PCA – 29.1×10⁻⁴ min⁻¹</td>
</tr>
</tbody>
</table>

Investigation by Gardecka et al. assessed the water-splitting capability of black TiO₂ coatings produced by pp-MOCVD. The results showed that the incident photon to current efficiency of the thin TiO₂ films was above 80% [9].
The following questions arise from the preliminary investigations:

1. What is the black TiO$_2$ coating?
2. How do the processing parameters influence the observable characteristics of the coatings?
3. What are the reasons for the high PCA of the TiO$_2$ coatings?
4. Are the TiO$_2$ composite films feasible for antimicrobial touch surface coatings?

This doctoral research is aimed at answering the above mentioned research questions. The research project focuses on samples deposited at 500 ± 25 °C.

2.3 Structural & Morphological Characterization

2.3.1 Electron Microscopy

Electron microscopy (EM) is used to observe and characterize the surfaces of materials on a nanometer to micrometer scale by the means of a low or high-energy source. An electron gun generates electron beams in the range of 1 – 300 kV. The electron beam generates secondary electrons, transmitted electrons, backscattered electrons, characteristic x-rays, and other photons when it interacts with the surface of the object. The electrons from the incident beam also undergo elastic and inelastic scattering. The different types of signals generated from the interaction of electron beams with a sample surface is illustrated in Figure 2.5. The signals from a specific type of emission are used to analyze a particular characteristic of the sample. The Table 2.4 summarizes the characteristic information obtained a particular type of signal.
Figure 2.5 Signals generated from the interaction of an electron (e') beam and a specimen
Table 2.5 List of different types of signals arising from the interaction of a sample with a beam of electrons and the corresponding characteristic information obtained

<table>
<thead>
<tr>
<th>Type of Interaction</th>
<th>Characteristic Information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Secondary Electrons (SE)</strong></td>
<td>These are low-energy electrons emitted from the sample surface at the beam-impact area. The signals from these emissions are captured by an SE detector and are used to obtain topographical information of the sample surface. SE detectors can provide shape, size and texture information from the specimen surface.</td>
</tr>
<tr>
<td><strong>Backscattered Electrons (BSE)</strong></td>
<td>These emissions result from the interaction of the electron beam with the atomic nuclei of the sample surface. BSE detectors analyze the emitted signals provide information on the compositional variation of the sample. BSE detectors work on a probabilistic principle and the resultant information obtained is based on the atomic number ( Z ) of the sample composition. Higher ( Z ) elements appear brighter than the lower ( Z ) elements. Information from BSE is reliable for solid elements with ( Z &lt; 50 ) [10]</td>
</tr>
<tr>
<td><strong>Characteristic X-rays</strong></td>
<td>These are emitted when the incoming electron beam ejects the inner shell electrons of the sample atoms. The emitted signals provide qualitative and quantitative information on the composition of the sample surface. The technique is called Energy-Dispersive X-ray (EDX) spectroscopy</td>
</tr>
</tbody>
</table>
Transmitted Electrons

If the specimen is \( \leq 100 \) nm and the electron gun has an energy \( \geq 100 \) kV, some electrons are transmitted through the sample. An image of the sample structure is formed (on a fluorescent screen) by the interaction of sample with the transmitted electrons.

Inelastic-scattered Electrons

These electrons are emitted when the incident beam interacts with the nucleus of an atom and loses some of its energy. The signal from the amount of energy lost is used to characterize the elemental composition of the sample.

Scanning Electron Microscopy (SEM)

An illustration of an SEM in shown in Figure 2.6. A JEOL 7000F field emission SEM, equipped with a Schottky emission gun, was used for visual observation of the plan-view and fracture surfaces of the \( \text{TiO}_2 \) coatings prepared by pp-MOCVD. The \( \text{TiO}_2 \) coatings on FS substrates were scored on the uncoated side using a diamond-tipped scribe and fractured into four sections. One of the fractured pieces is sputtered with Pd/Cr/Au using a Quorum Tech rotary pumped coater prior to SEM imaging. The plan-view of the surfaces provided information on grain size, texture and surface morphology of the coatings. The fracture surfaces provided the thickness of the coatings for calculation of film growth-rates. The resolution of the SEM is 10 nm at 30 kV.

For a coating of thickness ‘\( w \)’, the Growth-rate (GR) is obtained using the formula:

\[
GR = \frac{w}{N}
\]

\( N \)= number of pulses
Figure 2.6 Schematic of an SEM
Transmission Electron Microscopy (TEM)

Figure 2. 7 illustrates the basic operating principle of a TEM.
A 200 kV Philips CM 200 TEM equipped with a LaB\textsubscript{6} electron gun was used to observe the nanostructure of the samples prepared via pp-MOCVD. For preliminary TEM investigations, TiO\textsubscript{2} coatings were scrapped off from their substrates using a diamond-tipped scribe onto a Cu grid with Formvar coating. The coating particles were affixed to the grid via carbon evaporation using the Quorum Tech rotary pumped coater. The Cu-grids were mounted on a single-tilt holder for imaging. The CM 200 has a resolution of about 0.27 nm at 200 kV.

**High-Resolution TEM (HRTEM)**

A *JEOL 2800* field emission HRTEM with a 200 kV Schottky-type field emission gun was used to analyze the crystallographic orientation of the TiO\textsubscript{2} coatings. An FEI Quanta 3D FIB-SEM was used to prepare the lamella for HRTEM imaging. The Region of Interest (ROI) was prepared in the following stages:

- A 1 \(\mu\)m \(\times\) 5 \(\mu\)m \(\times\) 0.1 \(\mu\)m thick Pt layer via e-beam deposition was used to mark the ROI.
- A 2 \(\mu\)m \(\times\)10 \(\mu\)m \(\times\)2 \(\mu\)m thick Pt layer deposited via ion-beam deposition protects the top surface of the FIB lamellae from Ga\textsuperscript{+} ion milling. This Pt layer also provides support to the FIB lamellae for lift-off and mounting.
- An Omni probe tip was used to lift-off the lamellae from the substrate and mount it on a 3-tipped Cu-TEM Grid. All the lamellae were ensured to have sufficiently thick substrate at the bottom to further stabilize to the HRTEM specimen and to enable the characterization of film and substrate interface.
- The sample was milled to a thickness of \(\sim\) 100 nm or less to make it as transparent to electrons as possible.
A Gatan Solarus plasma system was used to clean the TEM grid with the FIB lamella in Ar environment with O₂ plasma. This step ensured the removal of any organic contamination that might be present on the FIB grid and the sample.

For imaging purposes, the Cu-grid is mounted on a double tilt holder and loaded into the TEM chamber. The *JEOL 2800* has a resolution of 0.24 nm. Fast Fourier Transformation of the HRTEM images were used to obtain the lattice information of the sample. The crystallographic information for anatase and rutile obtained from AMCSD was used to analyze the orientation and lattice spacing of the crystals [11].

*Scanning-Transmission Electron Microscopy (STEM)*

A *JEOL 300CF* Grand Atomic Resolution Microscope (ARM) was used to obtain high-mag STEM images. The Grand ARM is equipped with a 300 kV cold field emission gun and a double aberration corrector. Samples for imaging are prepared the same way as the HRTEM specimens described above. A double-tilt sample holder is used to load the sample into the TEM chamber. The Grand ARM has a resolution of 82 pm in STEM mode at 300 kV.

All the TEM images were post-processed using the Spectrum Imaging (*SI*) version of Gatan Micrograph Suite (Gatan Inc.) software.
2.3.2 Surface Roughness

*Atomic Force Microscopy (AFM)*

A Digital Instruments Dimension 3100 Atomic Force Microscope (AFM) was used to characterize the surface roughness of the TiO$_2$ coatings. As-deposited samples cleaned with acetone, isopropanol and DI water (in that order) were used for AFM analysis. The AFM has a resolution of 0.1 nm. The data was post-processed using Nanoscope Freeware. This technique provided data on the microscopic and nanoscopic peaks and valleys on the TiO$_2$ coatings and the results were processed in the form of Root Mean Squares (RMS) values.

*Water Contact Angle (WCA) Measurements*

The wetting properties of the TiO$_2$ coatings prepared by pp-MOCVD were studied by measuring the water contact angles on the films surface. A Cam 100 optical contact angle meter equipped with a CCD camera was used to for this purpose. A droplet of ~5.0 μL was dropped on the surface using a syringe and the spread of the droplet was imaged using the CCD camera. The acquired images were post-processed to obtain the water contact angle of the TiO$_2$ coatings.

2.4 Phase and Compositional Analysis

2.4.1 X-Ray Diffraction

X-rays are electro-magnetic radiations with wavelengths in the order of 0.1 Å to 10 nm. X-rays used for diffractions are in the $\lambda = 0.5 – 2.5$ Å range. XRD is based on constructive interference of monochromatic X-rays and a crystalline material. Bragg’s law states that the diffraction angle is related to lattice spacing of a crystal according to the following equation:
\[ n\lambda = 2d \sin(\theta) \]

- **n**: a positive integer
- **\(\lambda\)**: wavelength of incoming radiation
- **\(\theta\)**: angle of diffraction
- **d**: lattice spacing

Figure 2.8 illustrates the diffraction of an incident photon ray after it interacts with two different atoms in a 3D crystal lattice.

**Figure 2.8 Illustration of Bragg diffraction by a 3D crystal structure.**

XRD is a non-destructive analytical technique that is used to obtain detailed information about the crystallographic signature, chemical composition and phase identities of materials. It is also used to obtain information on the phase ratios of the sample material. A cathode filament is used to generate X-rays that are collimated and directed towards a crystalline sample. The incident rays interact with the sample and
produce constructive interference and generate diffracted rays when the Bragg’s law is satisfied. The diffracted rays are detected using a scintillation detector and processed to analyze the crystallographic signature of the sample. XRD can be used to analyze powder samples and thin films.

In an XRD experimental setup, the angle of incidence, \( \theta \), cannot be determined directly. Thus, the detector traverses an arc subtending twice the value of \( \theta \), to obtain information from the deflected X-ray beam. The angle of deflection is the angle between transmitted beam and the reflected beam, \( 2\theta \). An XRD pattern for a specimen is obtained by plotting the intensity of deflected X-rays against \( 2\theta \) values. Figure 2.9 illustrates the experimental setup to obtain XRD patterns for a flat sample.

**Figure 2.9 Illustration of the Rigaku PXRD setup for obtaining XRD patterns of a specimen in \( 2\theta, \phi \) and \( \chi \).**
The as-deposited samples were mounted on a flat sample holder and the detector was set up to collect from 5° to 90° in 2θ at a scan rate of 10° per minute. The spectral-peaks were indexed using the RRUFF database.

The nonrandom distribution of crystal orientations in a polycrystalline coating is defined as the texture or preferred orientation of the material. The texture coefficient of preferred orientation for a polycrystalline film is the representation of the deviation of that particular set of planes from the growth orientation of a standard sample of similar chemical composition. The indexed spectra were used to calculate the texture coefficients (TC) of the coatings according to the correlation below:

\[
TC = \frac{\sum_{i=1}^{N} \frac{I(hkl)_i}{I_0(hkl)_i}}{\frac{1}{N} \sum_{i=1}^{N} \frac{I(hkl)}{I_0(hkl)}}
\]

I(hkl)_i = observed intensity of the (hkl)_i planes

I_0(hkl)_i = intensity of the (hkl)_i reflection of a polycrystalline sample

N = total number of reflections used in the analysis

I_0(hkl) = intensity of the most common signature peak of a particular phase

The phase ratios of the TiO₂ coatings were obtained by fixing the 2θ arms at 25.4° for anatase and 27.5° for rutile. The spectra are then collected in χ from 0° to 90° at a scan rate of 10° per minute. The ratio of the intensities of these peaks gives the anatase to rutile ratios for a particular sample. The TiO₂ samples were annealed at 500 °C for 2 hours prior to collecting the spectra in χ. This was done to remove any amorphous signatures from the coating material.
2.4.2 ASTAR\textsuperscript{TM} Automated Crystal Orientation Mapping (ACOM)

The ASTAR\textsuperscript{TM} [12] method was used to characterize the different phases and orientation of the TiO\textsubscript{2} films prepared by pp-MOCVD. These results were obtained through Dr. R. Boichot and his research team, our collaborators at the Grenoble (Institute of Engineering), France. The ACOM crystal and phase mapping technique utilizes batches of Selected Area Electron Diffraction (SAED) patterns to identify and colormap the phases and crystallographic orientation of a TiO\textsubscript{2} specimen. The SAED patterns were obtained using a \textit{JEOL 2100F} TEM with a precession angle of 1.2° and a step size of 10 nm. The ASTAR\textsuperscript{TM} matching procedure uses the crystallographic information for anatase and rutile from AMSCD to characterize the phases of TiO\textsubscript{2} crystals [11].

The samples were prepared in a similar way as for HRTEM using a \textit{Zeiss NVision 40} FIB-SEM equipped with a MEB GEMINI column and a Schottky type field emission gun. A FIB \textit{SIINT ZETA} column attached in the SEM provided the Ga\textsuperscript{+} ions for the ion beam milling. The samples were mounted on a TEM grid in the same way as for HRTEM and STEM.

2.4.3 Raman Spectroscopy

Raman spectroscopy is a non-destructive technique based on the principle of Raman scattering. Raman scattering is an optical process observed when photons incident on a material surface undergo inelastic scattering. The incident photonic radiation interacts with the sample surface and gets scattered by losing energy to the vibrational modes of the chemical bonds in the sample. The scattered light is processed and recorded in the form of spectral peaks that correspond to a specific molecular bond vibration. The spectra are post-processed to study the chemical signature of the sample.
Raman-scatter forms only a small portion of the scattered light and can be enhanced by having a rough sample surface [13]. The technique, Surface-Enhanced Raman Spectroscopy (SERS), is the primary operating principle of the Raman spectrometer used to analyze the molecular content of the coatings prepared by pp-MOCVD.

The Raman spectra for the TiO₂ coatings prepared by pp-MOCVD were recorded using a HORIBA Jobin-Vyon LabRam spectrometer equipped with an Ar-ion (514 nm) laser. The power of the laser was set at 420 μW and the sample surfaces were analyzed as deposited. The spectra were post-processed in OriginPro using a Gaussian peak-fitting algorithm to de-convolute the various peaks. The spectral peaks were then identified using the Handbook of Raman Spectroscopy for TiO₂ and a combination of HORIBA Raman application dataset and two other reviews [14-16]. The depth resolution of the SERS technique is 15 nm.

2.4.4 Electron Energy Loss Spectroscopy (EELS)

Electron energy-loss spectra provide atomic scale information on the energy distribution of the electrons that have suffered inelastic scattering. EELS involves the analysis of energy distribution of monoenergetic electrons that have interacted with a specimen [17]. Inelastic scattering of electrons occurs when a high-energy electron beam interacts with electrons that surround the nucleus of the atom (i.e., atoms located in the K-shell, L-shell and so on). As a result of the interaction, the electron beam loses a characteristic amount of energy. The amount of energy lost by the beam is equal to the excitation energy gained by the atomic electrons. Excitation energies are specific to each element and each type of shell [18].

The transmitted electron beam, after its interaction with the specimen, is directed into a high-resolution electron spectrometer where electrons are separated into
different channels according to their kinetic energy. The EELS spectrum is obtained by plotting the scattered intensity of the electrons as a function of their decrease in kinetic energy [19]. The excitation of the atomic electrons produces ionization edges in the EELS spectrum that are used to identify the different elements present in the specimen. The region of the EELS spectrum with the ionization edge information is also known as the core-loss region.

The low-loss region EELS spectrum is characterized by the Zero-Loss Peak (ZLP), which represents the electrons that did not undergo any inelastic scattering. The ZLP can used as the reference peak to accurately align the ionization edges of the core-loss region in an EELS spectrum. Sample EELS spectra for low-loss and core-loss regions are provided in Figure 2.10.

**Quantitative Analysis from EELS Data**

The areal density (N atoms/nm²) of an element in the specimen is be calculated from

\[ N_c \frac{\text{atoms}}{\text{nm}^2} = \frac{I_c}{I_{\text{low}} \sigma_c} \]

where \( I_k \) = integral of the ionization edge of C integrated over a window \( \Delta_C \) eV

\[ I_{\text{low}} = \text{low-loss intensity integrated over a window } \Delta_C \text{ eV} \]

\( \sigma_k \) = partial inelastic cross-section of C

The atomic ratio of C and Ti is obtained from

\[ \frac{N_c}{N_{Ti}} = \frac{\text{concentration of C}}{\text{concentration of Ti}} = \frac{I_c \sigma_{Ti}}{I_{Ti} \sigma_c} \]
Figure 2. 10 (a) Zero-loss peak and (b) Core-loss region showing the ionization edges of C, Ti and O in a TiO₂ composite coating.
EELS spectra for the samples prepared using pp-MOCVD were obtained using the Grand ARM. FIB lamellae of different coatings were prepared according to the sample prep method described in Section 2.3.1 for HRTEM. The STEM images were obtained using a Gatan Annular Dark Field (ADF) detector and the EELS spectra were recorded via US1000GIF/EELS. The SI-GMS software was used to post-process the EELS spectra. GMS was also used to collate spectral data from a particular ROI and generate the elemental maps that were used to determine the location of different elements in the micro/nanostructure of the TiO\textsubscript{2} coatings. The Power Law background model was used to extract the elemental signals from the EELS spectrum [20].

The resolution of the Grand ARM probe used for analytical microscopy is 0.1 nm at an operating current of 500 pA at 300 kV.

2.5 Photocatalytic Performance Evaluation

2.5.1 Estimation of Optical Bandgap

In semiconductors, the optical and electronic bandgaps are indistinguishable. TiO\textsubscript{2} is known to be spectrally absorptive to UV light but is transparent to visible light. As per this phenomenon, TiO\textsubscript{2} absorbs all photonic radiations with energies greater than 3.2 eV or wavelengths lower than 360 nm. Based on this property, the optical bandgap of TiO\textsubscript{2} can be estimated using UV-Vis spectroscopy. UV-Visible light spectroscopy is an analytical technique that measures the changes in absorbance or reflectance of a material as a function of wavelength.

When photons strike a material surface, they are absorbed, scattered and/or reflected by the material. Some unabsorbed photons are transmitted through the material. The ease with which a certain volume of material is penetrated by incident light is characterized by the absorption coefficient. Similarly, scattering coefficient is
used to determine the ability of a material to scatter photons of an incident beam of light.

In UV-Vis spectrometry, the sample surface is exposed to a range of photonic radiations with wavelengths from 260 nm to 800 nm. The sample surface interacts with the incoming radiation and absorbs, transmits, reflects and scatters the photons with altered energies. Depending on the mode of operation, the spectrometer detects the reflected/scattered/unabsorbed/transmitted radiation. The detected photonic radiations are processed in plotted as a function of wavelength of radiation. As the TiO$_2$ coatings are opaque the UV-Vis spectrometer is operated in the reflectance mode. The recorded spectra are post-processed using the Kubelka-Munk (K-M) theory. According to the K-M theory, the reflectance (R) of the coating layer is a function ($f(R)$) of its absorption coefficient ($\alpha$) and scattering coefficient (s) according to the following relation:

$$R = 1 + \frac{\alpha}{s} - \sqrt{\frac{\alpha}{s}(2 + \frac{\alpha}{s})}$$

$$\Rightarrow f(R) = \frac{\alpha}{s} = \frac{(1 - R)^{0.5}}{2R}$$

$$\Rightarrow \alpha \propto \frac{(1 - R)^{0.5}}{2R}$$

After the K-M transformation is applied to the reflectance data, the values are plotted against the energy of photon radiation. The resultant spectrum resembles a Tauc plot, which is used to determine the optical bandgap of the material. The transformed spectrum is plotted against the photonic energy of the incident. Tauc plots have distinct linear regimes which denote the onset of absorption. Jan Tauc demonstrated that extrapolating the slope of the linear absorption regime to intersect with the wavelength/energy (abscissa) estimates the bandgap of the material.
A Cintra 4040 UV-Vis spectrophotometer was used to determine the bandgap of the TiO$_2$ materials prepared by pp-MOCVD. The ROI was isolated with a 7 mm aperture and the reflectance data was collected in the wavelength range of 361 nm to 800 nm.

2.5.2 Specific Surface Area (SSA) Measurement

Specific surface area is defined as the ratio of a particle’s accessible surface area to its volume [21]. SSA is critical for a photocatalytic material. A photocatalyst with high SSA demonstrates higher PCA. The SSA for a material can be determined by quantifying the physical adsorption of a reactant on the surface of the target material.

The SSA for the TiO$_2$ thin films prepared by pp-MOCVD was assessed using Methylene Blue Dye (MBD) adsorption tests. The tests were performed inside a dark chamber to prevent any interference of physical adsorption and photocatalytic degradation of the dye in the presence of the TiO$_2$ coatings. The TiO$_2$ films on fused silica substrates were immersed in 20 mL of MBD solution (15 mg/L). The adsorption of MBD on the material surface was determined by studying the decrease in the concentration of the solution using a UV-Vis spectrophotometer. 4 mL of MBD solution was drawn at 10-minute intervals and injected into a quartz cuvette. The cuvette is placed in the UV-Vis spectrophotometer and the absorbance of the MBD solution is recorded. The drawn solution is re-injected back into the test beakers after the results are tabulated. The TiO$_2$ thin films reach physical adsorption equilibrium after about 90 minutes of exposure to MBD solution. The adsorption tests are performed using a blank sample as a control. The SSA for the TiO$_2$ films is presented in terms of m$^2$/m$^3$. The results are compared to previously reported SSA tests performed using P25 [22].
2.5.3 Photocatalytic Activity

Two different light sources were used to perform the PCA tests

1. Ultra Violet – 365 nm, 8 W.
2. Visible light – Deta DET692 white LED attached with UV filter, 18 W, 1500 lumens, 83 lm/W, 5700 K color temperature (daylight)

The PCA tests were performed in a team with Johann Land. The PCA of TiO$_2$ coatings was measured using Methylene-Blue dye (MBD) degradation over time under visible light. The relative activities of the samples are compared to a bare substrate. The samples are immersed in MBD solution for 20 mins to attain physical adsorption equilibrium. The samples are then transferred to individual beakers with 40 ml of fresh regenerated MBD solution for the PCA tests. The mass concentration of the solution is 8.0 mg or MBD per liter of molecular water. The decrease in the absorbance of the solution is measured using a Cintra 4040 UV-Vis spectrophotometer by drawing 2 ml of solution at 5-min intervals. The drawn solution is injected into a Quartz cuvette for this purpose. Once the absorbance of the solution is recorded, the drawn volume is re-injected back into the beaker with the photocatalyst for subsequent measurements. The homogeneity of the solution is maintained via a magnetic stirrer and a water bath is used to maintain the temperature of the solution constant. The absorbances change linearly with respect to time and the slopes of the lines are used to determine the PCA of the coatings.
2.5.4 Antimicrobial Activity

The AMA results were obtained through our research partners, Alibe Wasa, a PhD student in microbiology under Prof. J. Heinemann. The international standard ISO 27447:2009 with *E. Coli*, *pseudomonas*, *yeast*, and *S. Aureus* was followed. The AMA results were used as a tool to understand and evaluate the effects of TiO$_2$ coatings on microorganisms.

2.6 Mechanical Behavior Tests

2.6.1 Adhesion Test

The adherence of the coatings prepared by pp-MOCVD on SS substrates was tested using the ASTM-D3359 test standard. The coatings are subjected to 1 mm$^2$ crosscuts made with a high-carbon tool steel blade. Later, a Scotch™ 3M semi-transparent tape is used to peel off the film from the substrate. The remnants of the film on the substrate are evaluated using the classification provided in the ASTM test.

2.6.2 Three-point Bend Test

The adhesion of the TiO$_2$ coatings on SS substrates was also evaluated using a 3-point bend test. The SS sample was placed on an Al support with a span length of 20 mm with the non-film side toward the direction of loading. An MTS Criterion (C43-104) was used to apply a load of 2.5 kN on the sample, The SS substrates were bent to approximately 60° and the films were evaluated using macroscopic photographs and SEM images.
2.6.3 Microindentation Test

The TiO$_2$ coatings by pp-MOCVD were subjected Vickers Hardness test with the test parameters set to the limits of the substrate. The Vickers hardness tests were performed with a load of 500 gf. The indents were analyzed using the JEOL 7000F SEM.

References


Chapter 3: Nanostructured TiO$_2$ Coatings

Preliminary investigations into TiO$_2$ thin films prepared by pp-MOCVD showed that the black samples prepared at 525 °C exhibit PCA under visible light. The current chapter is split into the following four sections.

- Section 3.1 provides a growth-rate study performed by varying the number of pulses to obtain black TiO$_2$ coatings with different thicknesses (GR-A, B & C). The texture and composition of the coatings was analyzed using XRD. This study yielded one sample (GR-C) that exhibited unique structural morphologies.

- The section 3.2 provides a detailed description of the morphologies observed on the GR-C sample. The phase and composition characteristics of GR-C are described here. Mechanical behavioral tests performed on the GR-C coatings (deposited on SS) are also discussed in this section. The performance of the GR-C sample was evaluated using a visible light AMA test.

- Section 3.3 presents a discussion on the results obtained in the this chapter.

- Section 3.4 presents a compilation of research questions for subsequent studies.
3.1 Growth-Rate (GR) Studies

High-touch antimicrobial coatings for healthcare facilities are required to be robust, durable and adherent. In this study, the TiO$_2$ samples were prepared at 525 °C with varying number of pulses. The aim was to produce TiO$_2$ films that measured at least 10 μm in thickness. All the samples were deposited on FS with a precursor concentration of 5 mol% TTIP in toluene. The relationship between film-thickness, growth-rate and texture of the coatings were analyzed. Table 3. 1 summarizes the processing parameters for the GR study samples.

*Table 3. 1 Pulse-rate information for TiO$_2$ samples deposited for the growth rate studies.*

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Number of pulses</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR-A</td>
<td>75</td>
</tr>
<tr>
<td>GR-B</td>
<td>350</td>
</tr>
<tr>
<td>GR-C</td>
<td>735</td>
</tr>
</tbody>
</table>

$T = 525 \, ^\circ C; \quad C = 5 \, \text{mol}\% \, \text{TTIP in Toluene}; \quad V_{inj} = 500 \, mL$

3.1.1 Structural Morphology

All the coatings are different shades of black providing visual evidence of the presence of carbon in the films. The opacity of the films increases as the pulse-rate increases. Figure 3. 1 shows the photographs (taken after they were fractured for SEM) of the three different samples of the GR-study.
Figure 3. 1 Photographs of (a) GR-A; (b) GR-B; (c) GR-C.
Figure 3. 2 (a) Plan-view & (b) fracture surface SEM images of GR-A.
Figure 3.3 (a) Plan-view & (b) fracture surface SEM images of GR-B.
Figure 3.4 (a) Plan-view & (b) fracture surface SEM images of GR-C.
The plan-view and fracture surface SEMs of the GR study samples are shown in Figure 3. 2, Figure 3. 3 and Figure 3. 4. The fracture surface SEMs show that all the samples deposited at 525 °C show a rare columnar morphology. The surface SEM images of the samples show that the grain diameter of the crystals increases with increasing number of pulses. Figure 3. 4 shows that the sample GR-C exhibits twos distinct topographies in the plan-view SEM. Similar morphologies are not observed in the other two samples of the GR-studies.

The structure of the GR-study films was also analyzed using high-mag TEM images. The TEM images of the samples revealed that the crystal columns possess secondary nanoscale features. The nanostructures were measured from the core of the crystal to the tip of the plate as shown in the illustration in Figure 3. 5. Fifteen measurements from different plates on a single column were used to obtain the nanostructural dimensions of the samples. Figure 3. 6 – Figure 3. 12 show the nanostructures on the crystals of GR-A, B and C respectively.

Figure 3. 5 Cropped TEM image defining the nanostructure dimension used in the GR investigation.
Figure 3. 6 TEM image of scrapped-off columns from GR-A.
Figure 3. 7 TEM image showing the nanostructures on a single column of GR-A.
Figure 3. 8 TEM image of a scrapped off column from GR-B.
Figure 3. 9 TEM image showing the nanostructures on GR-B columns.
Figure 3. TEM image showing the scrapped-off columns from GR-C. The nanostructures on this column make a relatively large angle with the column center.
Figure 3.11 TEM image showing a column of GR-C with different morphology from the one in Figure 3.10. The nanostructures on the highlighted column exhibit a smaller angle to the center of the crystal.
The TEM images in Figure 3. 6 to Figure 3. 12 clearly show that as the pulse rate increases, the crystal diameter and the nanostructure dimensions increase. The GR-C sample exhibits two distinct columnar morphologies (Figure 3. 10 & Figure 3. 11). The nanostructures in Figure 3. 11 have a smaller angle to the center of the core than the ones in Figure 3. 10. Table 3. 2 summarizes the different measurements used to characterize the visual features of the GR-study samples.
Table 3.2 Summary of measurements for the growth-rate study samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness ($\mu$m)</th>
<th>Growth-rate ($nm$/pulse)</th>
<th>Column Diameter ($\pm 15 , nm$)</th>
<th>Nanostructure Dimension ($\pm 1.5 , nm$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR-A</td>
<td>0.52 ± 0.03</td>
<td>6.93 ± 0.40</td>
<td>100.6</td>
<td>6.5</td>
</tr>
<tr>
<td>GR-B</td>
<td>3.30 ± 0.04</td>
<td>9.43 ± 0.12</td>
<td>227.5</td>
<td>8.0</td>
</tr>
<tr>
<td>GR-C</td>
<td>11.50 ± 0.10</td>
<td>15.65 ± 0.14</td>
<td>448.2</td>
<td>16.5</td>
</tr>
</tbody>
</table>

3.1.2 Phase and Composition

The phase and composition of the GR-study samples were analyzed using XRD and Raman spectroscopy. The Figure 3.13, Figure 3.14 and Figure 3.15 show the XRD and Raman spectra of the GR-A, B and C samples respectively.
Figure 3. 13 (a) XRD spectrum & (b) Raman spectrum of the sample GR-A.
Figure 3.14 (a) XRD spectrum & (b) Raman spectrum of the sample GR-B.
**Figure 3.** 15 (a) XRD spectrum & (b) Raman spectrum of the sample GR-A.
All three samples of the GR-study are bi-phased TiO$_2$ thin films. The XRD spectra demonstrate that the films are crystalline TiO$_2$ and are not doped with any other chemical. The XRD spectra of the samples also show that the texture of the films changes with increasing pulse-rate. The spectrum in Figure 3.13 (a) shows that rutile is the dominant phase for the low-pulse coating and as the pulse-rate increases, the intensity of the anatase phase increases. The film texture also changes significantly. The anatase phase of the samples exhibits a [220] growth orientation and the rutile phase exhibits a [210] growth orientation. The texture coefficients for anatase and rutile were calculated separately. The XRD spectra show that increasing the pulse-rate of the depositions increases the anatase [220] and decreases the rutile [210] texture. The results are summarized in Table 3.3.

**Table 3.3 Texture Coefficients (TC) of anatase and rutile in the GR-Study samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anatase TC (±0.05)</th>
<th>Rutile TC (±0.05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR-A</td>
<td>1.50</td>
<td>3.30</td>
</tr>
<tr>
<td>GR-B</td>
<td>4.43</td>
<td>3.08</td>
</tr>
<tr>
<td>GR-C</td>
<td>4.65</td>
<td>1.33</td>
</tr>
</tbody>
</table>

The Raman spectra of all three samples show that the carbon is amorphous and the peak deconvolution results are listed in Appendix A1. The Raman spectrum for GR-C exhibits peaks for both anatase and rutile phases of TiO$_2$. 

116 | Nanostructured TiO$_2$ Coatings
3.1.3 Discussion of the GR-Study Results

The SEM images show that the films thickness increases with increasing the number of pulses. The increase in the number of pulses also leads to films with larger grain diameters and nanostructures. The analysis of the films’ thicknesses shows that the increasing film thicknesses are accompanied by an increase in the growth-rates. This leads to the observation that the growth-rate of the samples is accelerating with the number of pulses. The increase in the grain diameter is due to the occlusion of slow-growing grains by the fast-growing ones [1]. The plan-view surface SEMs also show that the GR-C sample (Figure 3.4) has additional microstructural features when compared to the GR-A and GR-B samples.

The major difference among the three samples in the GR-study is observed in the XRD spectra. The spectra show that the accelerating growth-rates of the pp-MOCVD process cause the TiO₂ crystals to grow in a preferred orientation. An et al observed similar behavior of TiO₂ crystals. The authors reported nanostructured anatase-TiO₂ with a preferred orientation of [112] [2]. The preferred growth of the GR-C in the [220] would also explain the high texture of anatase obtained at the higher pulse-rates. Highly textured anatase has been reported to exhibit superior photocatalytic performance [3, 4].

The black color of the coatings GR-B and GR-C provides evidence of visible light absorption. The Raman spectroscopy of the GR-study samples indicated the presence of carbon in the TiO₂ thin films. The spectra also show that the presence of carbon does not alter the stoichiometry of the TiO₂. At this stage, the distribution of carbon content through-out the depth of the coating is undetermined.
The growth-rate study resulted in one sample that possess some desirable characteristics for a photocatalytic coating. The GR-C sample is a thick, multi-phased, TiO₂-C composite coating that is most likely to be active under visible light. This sample is further analyzed using advanced characterization methods in the following sections.

3.2 What is the GR-C Sample?

3.2.1 Structure and Visual Characteristics

High-magnification SEM images of GR-C show that the sample exhibits columnar microstructure with two distinct morphologies – rough dendritic columns and layered-pyramidal columns (Figure 3. 16). The GR-C film has nanostructures observable even at the microscale level. The fracture surface SEM of the sample (Figure 3. 17) shows that the columnar structure of the films extends all the way to the film-substrate interface. The image also shows that the dendritic columns appear do not appear to extend to the entire film thickness.
Figure 3. 16 Plan-view SEM image showing the two crystal morphologies observed on GR-C.
The layered columns are further segmented into nanosized feather-like features (Figure 3. 18). The dendritic columns exhibit fractal growth with nanoscale secondary dendritic features branching out from a primary core. The dendritic features are shown in Figure 3. 19.
Figure 3. 18 SEM images showing the nanoscale features on the layered crystals from (a) plan-view & (b) fracture surface view.
Figure 3. SEM images showing the nanoscale features on the dendritic crystals from (a) plan-view & (b) fracture surface view.
3.2.2 Phase

The XRD spectrum shows that the GR-C coating possesses both anatase and rutile phases of TiO$_2$. The spectrum also demonstrates that the anatase phase is highly textured in the [220] growth direction. Figure 3. 20 (a) shows that the XRD signal from the anatase [220] planes dominates the other reflections. The other XRD reflections of the sample are observed by isolating the intensity range between 0.35 and 0.85. The limited range spectrum in Figure 3. 20 (b) shows that the rutile phase is oriented in the [210] direction. From here forth, the coatings with characteristics resembling the GR-C film are broadly labeled Nanostructured Anatase-Rutile-Carbon (NsARC) composite coatings.
Figure 3. 20 (a) Complete XRD spectrum of an NsARC coating on FS with [220] reflection; (b) Zoomed-in spectrum for the other reflections.
3.2.3 Composition

Raman spectroscopy qualitatively analyzed the carbon content of the NsARC coatings. The spectra conclusively prove that the black color of the coating is solely due to the presence of carbon in the material. The spectrum also shows that the NsARC samples are not oxygen deficient and C is not present at the interstitial sites. The amorphous carbon exhibits signatures of aromatic rings and carboxylate groups. After Gaussian deconvolution, the Raman spectra exhibit significant G and D bands. The D band at \(~1450 \text{ cm}^{-1}\) refers to disorder in the graphitic structure due to breathing modes of the aromatic rings. The G band at \(~1600 \text{ cm}^{-1}\) refers to the C-C bond stretching and is typical of all sp\(^2\) type carbon materials. Figure 3. 21 shows the deconvoluted peaks observed from the NaARC Raman spectra.
Figure 3.21 (a) Raman spectra of NsARC on fused-silica substrate; (b) Carbon peaks with Gaussian deconvolution.
The carbon signature from the samples is not attributed to adventitious carbon. This is confirmed by performing Raman spectroscopy on an annealed NsARC sample. Annealing the coatings makes the samples pure white (Figure 3. 22) and the films macroscopically resemble commercially available TiO$_2$. Figure 3. 23 shows the Raman spectrum of an annealed NsARC film on fused silica substrate.

**Figure 3. 22** Annealed NsARC films on FS.
3.2.4 Crystallographic Orientation

The ASTAR\textsuperscript{TM}-ACOM\textsuperscript{[5]} crystal and phase mapping was used to characterize the NsARC material. Figure 3. 24 (a) is the SEM image of the target crystals studied using the ASTAR technique. Figure 3. 24 (b) shows that the dendritic columns are rutile and the layered-pyramidal columns are anatase. The figure also shows that the rutile columns appear to grow on top of anatase crystal columns.

The ACOM orientation mapping in Figure 3. 25 (b) showed that the anatase columns are all single crystals. The ACOM technique provided additional confirmation on the [220] texture of anatase in the NsARC coatings. The rutile columns appear to possess polycrystalline characteristics \textsuperscript{[6]}. 

*Figure 3. 23 Raman spectrum of annealed NsARC on FS substrate.*
Figure 3.24 (a) SEM image showing the anatase and rutile crystal tops; (b) ASTAR™ phase mapping showing the pyramidal columns as anatase and dendritic columns as rutile.
**Figure 3.** 25 (a) SEM image showing the anatase and rutile crystal tops; (b) ACOM orientation mapping showing the growth orientation of the anatase [220] planes perpendicular to the substrate.
3.2.5 Specific Surface Area (SSA)

The adsorption of MBD into the NsARC coatings in dark was used to measure the SSA of the coatings. The adsorption tests showed that the SSA of a ~15 μm thick NsARC coatings is 278 m$^2$/m$^2$. This is equivalent to the SSA of 3.2 mg of commercially available Degussa P25 [7]. Figure 3. 26 shows the decrease in absorbance of MBD solution with time for a blank FS substrate and an NsARC sample.

![Graph showing the decrease of absorbance with time for an NsARC sample.](image)

**Figure 3.** 26 *Graph showing the decrease of absorbance with time for an NsARC sample.*
3.2.6 Mechanical Behavior

3.2.6.1 Durability of NsARC Coatings

The durability of the NsARC coatings was analyzed using a scratch test and a three-point bend test. The tests were performed in order to assess the applicability of NsARC coatings as antimicrobial touch surface coatings.

The adherence NsARC coatings to stainless steel was analyzed according to ASTM test standard – D3359. Seven NsARC coated substrates were tested for their adhesion. The test result classified as Grade 5B implying that the films exhibited the highest level of adhesion. The result of the Scotch™ tape test is shown in Figure 3.27.

![Scotch™ tape test showing the adherence of NsARC coating to a SS substrate.](image)

The adhesion of the NsARC coatings was further analyzed by subjecting NsARC coated substrates to 3-point bending. SS substrates (75×25×1 mm³) were bent to approximately 60° with a load of 2.5 kN. Figure 3.28 shows that the point of bend does not show any macroscopic delamination or damage.
**Figure 3.** 28 NsARC coated SS substrate that has been subjected to the 3-point bend test.

The bent SS substrate was imaged using an SEM to study the microscopic behavior of the NsARC coating. The image (Figure 3. 29) showed that the bending the substrate ‘opens’ the microstructure of the film along the columnar grain interfaces. However, no delamination of the film was observed.
3.2.6.2 Indentation Behavior

The NsARC coatings were subjected to Vickers Hardness test with test parameters set to the limits of the substrate. A unique feature of the NsARC coatings is their ductile-like behavior. The films deform like a metal rather than crack under extreme conditions with a load of 500 gf. Around 75 indents made on 15 specimens showed no cracking or delamination of the coating.

The nano-segmentation of the crystals is a possible explanation for the films to behave like a metal. It can be hypothesized that the columnar plates move against each other without undergoing any ‘breaking’ of bonds between the atomic planes. The coatings exhibit behavior similar to that of deforming shock absorbers. This would explain the lack of crack-propagation or deformation of the coating near the indent.

Figure 3. 30 shows a representative SEM image of a microindent on the surface on an NsARC Coating.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure3}
\caption{(a) SEM image showing the ‘openings’ in the microstructure of the NsARC film subjected to 3-point bending; (b) SEM image showing the ‘open’ columnar interfaces on the surface of the NsARC film.}
\end{figure}
Figure 3. (a) SEM image of 500 gf microindents on NsARC; (b) Close-up SEM image of a single indent on NsARC surface; (c) SEM image of one of the corners of the indent.
3.2.7 Antimicrobial Performance

The AMA test performed in collaboration with Prof. J. Heinemann’s research group provided crucial evidence regarding the visible light PCA of the NsARC coatings. The results, published in Nature Scientific Reports, demonstrated that the viable bacterial cell count on NsARC decreased at least 1000-fold (99.9 % reduction) under visible light and a 3-4 log AMA was observed under UV light. Additionally, a 2log reduction in bacterial cell count was observed when the AMA tests were performed in the dark. Figure 3. 31 gives the AMA test results showing the reduction in E.coli cell count after 4 hours in different illumination conditions.

![Antimicrobial Test Results](image)

*Figure 3. 31 Antimicrobial Test Results*
3.3 Discussion

The high-instantaneous vapor flux from the pulsed injection of the precursor could explain the generation of columnar microstructure via pp-MOCVD. This is supported by the review by Bryant. The nanoscale features on the films demonstrate the deposition process could enhance the available surface area by inducing nanostructures to the coatings. Similar morphologies have been reported by a few other research groups. Takahashi et al. report the dendritic crystals produced by MOCVD [8]. The authors theorize that the crystal modification is controlled kinetically rather than thermodynamically. Goossens et al. report that the fractal growth of TiO$_2$ by gas-phase deposition where the nanostructure generation was attributed to the temperature of deposition and precursor selection [9]. Fujishima et al. demonstrated that one of the key features necessary for PCA enhancement is that the film possesses superhydrophilic properties [10]. The SEM images show that the columnar microstructure extends to the entire depth of the NsARC film. The NsARC coatings also appear to have a certain amount of porosity between the nanostructured columns.

The XRD and the ASTAR$^\text{TM}$ phase mapping provide clear indication of the presence of anatase and rutile phases of TiO$_2$ in the NsARC coating. It also appears that the distribution of anatase and rutile columns in the film is random. The ASTAR$^\text{TM}$ analysis suggest that rutile grows on top of anatase crystals. The phenomena responsible for only some of the anatase columns to transform into rutile is unclear at this stage. Goto et al. studied the morphological evolution of anatase and rutile at temperatures between 525 and 925 °C. The authors report that the anatase transforms to rutile at higher temperatures (≥ 630 °C) but the rutile mixture does not demonstrate any orientation [11].
The [210] orientation of rutile has been rarely reported. Mahmoodi et al report that nanostructured rutile with a [210] growth orientation exhibits antibacterial properties. They report a 2-log reduction in bacterial cell count after 24 hours of exposure [12]. The authors, however, do not report the irradiation source that triggers the antibacterial properties of the nanostructured TiO$_2$. Only two other research groups have reported the [210] growth orientation of rutile TiO$_2$ [13, 14].

The presence of carbon has been spectroscopically confirmed but the location is yet to be determined. Calatayud et al. have demonstrated the use of carbon-containing chemicals such as oleic acid to tailor the crystal growth in a preferred orientation and stabilize high-energy facets of anatase nanocrystals [15]. It is possible that carbon is catalytically being reduced from the TTIP ligands and is selectively accumulating at the nanostructures of the NsARC crystal columns.

The black color of the NsARC coating its composition explains the visible and UV light AMA of the films. AMA in the dark was observed by Rincon et al. when microbes were exposed to a solution of aqueous formate containing mixed-phase TiO$_2$ powders[16]. The authors state that the solution can produce ROS that linger after irradiation and prove toxic to microbial activity even in the dark. Another explanation of the AMA of NsARC in dark is the zeta potential between the TiO$_2$ coating and the bacterial cell wall. Zeta potential is defined as potential difference that exists between the surface of a solid particle and conductivity of the liquid it is immersed in [17]. It is possible that the NsARC coating can modify the zeta potential of the bacterial cell membrane thus proving toxic to infection-causing microorganisms [18].
3.4 Questions for Subsequent Research

- What is the effect of the other processing parameters on the NsARC film growth and PCA?
- What is the role of growth-texture on the performance of NsARC coatings?
- How does the anatase-to-rutile phase ratio on NsARC coatings effect the PCA?
- Where is carbon located in the microstructure and nanostructure of the coating?
- What is the role of carbon co-deposition in the generation of nanostructure?

References


Chapter 4: Forensic Analysis of NsARC

Preliminary investigations showed that TiO$_2$ coatings deposited on fused silica and stainless-steel substrates in the mass transport-controlled regime (>450 °C) demonstrated interesting PCA under visible light. The highest PCA was observed for NsARC samples deposited at 525 °C. Chapter 3 focused on the samples deposited at 525 °C and described the rarely reported nanostructures of TiO$_2$ observed in NsARC coatings prepared by pp-MOCVD. NsARC coatings were primarily studied using XRD and Raman spectroscopy. The results revealed that the coatings were bi-phased composites of TiO$_2$ and carbon. The coatings exhibited promising performance as photocatalytic antimicrobial materials.

Pulsed Pressure – Metalorganic Chemical Vapor Deposition (pp-MOCVD) is a one-step process to produce thick TiO$_2$-C composite coatings that are potential visible light active photocatalytic materials. The pp-MOCVD process has 5 processing parameters (deposition temperature, precursor concentration, injection volume, working base pressure & number of pulses) that influence the structure and composition of the resulting coatings. Siriwongrungson et al. conducted preliminary experiments on the deposition process using a ‘One-variable-at-a-time’ approach [1]. This chapter describes a novel approach based on ‘Forensic Science Principles’ to develop an up-scalable coating material. The Design of Experiments (DOE) methodology was used to evaluate the influence of pp-MOCVD processing parameters on the resulting NsARC coatings.
4.1 Forensic Approach to Materials Design for Product Development

The conventional forensic investigative approach is employed to deduce the motives behind the perpetration of an anomalous incident. Possible suspects involved in the incident are identified and the most likely perpetrators are narrowed down through a series of careful evaluation processes. At the scene of the incident, forensic investigators collect, examine and analyze the physical evidence. The evidence is then used to reconstruct the incident and deduce the motive of the perpetrator. The collected evidence also helps in linking the perpetrator to the scene of the incident. Figure 4.1 illustrates the process flow of forensic investigative approach.
Figure 4. 1 Illustration of the process flow employed in forensic investigations.
In materials science, the objective is to control the process to obtain a target property that is responsible for the performance of the material. For example, fluorinating anatase TiO$_2$ nanoparticles to expose [001] facets for enhanced visible light photocatalysis.

The forensic approach differs from the standard materials characterization approach because the parameter investigation is not carried out by progressive variations and observed trends. The forensic approach is like solving a mystery of why a particular material has the observed performance. Evidence of observed performance, properties, understood science are gathered and screened. The combinatorial hypotheses are tested to determine the factors that are responsible for the visible light PCA of NsARC coatings.

The following sections describe how I set up the forensic approach for material design based on the one utilized for crime scene investigation. Table 4.1 illustrates the Forensic materials investigation approach I propose to analyze coatings prepared by pp-MOCVD.
Table 4.1 Forensic Investigative Approach for Materials Design.

<table>
<thead>
<tr>
<th>Forensic approach to solving a crime</th>
<th>Forensic approach to materials design</th>
<th>NsARC investigation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Incident</strong></td>
<td>Discovery of photocatalytic antimicrobial NsARC coating</td>
<td>Extremely high kill-rate of <em>E. coli</em> by NsARC under visible light</td>
</tr>
<tr>
<td><strong>Identification of possible suspects</strong></td>
<td>Preparation of visible light active NsARC</td>
<td>Design of Experiments (DOE) to investigate the influence of processing parameters that provide favorable deposition conditions for visible light NsARC to be deposited on the target substrate</td>
</tr>
<tr>
<td><strong>Narrowing down the perpetrators</strong></td>
<td>Determining the coatings with the most desired performance</td>
<td>Methylene Blue Dye (MBD) degradation tests under visible light were used to determine the PCA of NsARC coatings prepared in the DOE</td>
</tr>
<tr>
<td><strong>Interrogation &amp; evidence collection</strong></td>
<td>Characterization and analysis of NsARC</td>
<td>NsARC coatings are methodically analyzed using SEM, AFM, WCA and XRD</td>
</tr>
<tr>
<td><strong>Determining the means of perpetration</strong></td>
<td>Determining the key parameter(s) responsible for the characteristics</td>
<td>The influence of the different processing parameters on the performance and characteristics of the coatings is assessed.</td>
</tr>
</tbody>
</table>
| Establishing the motive(s) of the perpetrator | Identification of the characteristics responsible for the observed PCA | The active coating(s) is suspected to have the following characteristics:
- Nanostructure
- Exposed high energy facets
- Anatase-rutile polymorphic junctions
- Sensitizing carbon on the surface (for visible light absorptive capabilities)
- Dopants that lower the bandgap of the coating |

| Reconstruction of evidence to deduce the perpetration of the incident | Linking performance to characteristics of the NsARC coatings | The different characteristics of the NsARC coatings are linked to their performance by means of trend charts. The most active NsARC coating(s) are investigated further using STEM, HRTEM and EELS to deduce the reason for their high PCA. |
4.2 Design of Experiments (DOE)

The ‘One-Variable-at-a-Time’ approach to understand the influence of the processing parameters of pp-MOCVD is time-consuming and requires a large number of experiments. It is also possible that the approach may yield false optimum conditions for the process [2]. Design of experiments is a statistical approach to determine the influence of operating conditions on a resulting product by simultaneously varying the processing parameters. A DOE approach allows the evaluation of a large number of processing parameters in a limited number of experiments. The DOE approach describes the response as a linear function of the influencing parameters. The function is represented in the form of a polynomial (empirical) expression. It is important to note that DOE does not determine the optimal experimental strategy.

Experimental design for screening experiments can be performed using one of the following approaches:

- Plackett-Burman Approach
- Taguchi Methods

The following steps define the different steps employed in setting up and validating the DOE model used for this study. Figure 4. 2 provides a flowchart of the process-map used in designing of experiments.
Figure 4.2 Flowchart illustrating the different steps used in a DOE.
1. Definition of the Problem

*What combination of pp-MOCVD operating parameters is responsible for producing an NsARC coating that exhibits enhanced visible light PCA?*

The problem is to determine the relevant pp-MOCVD processing parameters responsible in generating NsARC coatings that exhibit visible light PCA. The DOE methodology was used to devise an optimal strategy of parameter variation according to a postulated model. DOE allowed the prediction of the performance of the resulting coating with high statistically significant precision in the least number of trials.

2. The objective of the DOE

The objective was to determine the statistically significant influence of different operating parameters on the features and properties of resulting NsARC films by screening them for their photocatalytic activity under visible light.

3. Responses and measurement techniques

The responses are the results of all measured features, characteristics or properties of different NsARC coatings on fused silica substrates. The NsARC films were initially tested for their visible light PCA. The coatings were studied using SEM, AFM, WCA measurements. The composition of the coatings was determined using XRD and Raman spectroscopy. The optical bandgap of the coatings was determined using UV-Vis photo-spectrometry.

4. Setting up the parameter matrix

The pp-MOCVD process has five independent controlled and measurable parameters that are suspected to influence the characteristics and performance of NsARC coatings. The independent variables ($X_m$) are:
(i) \( X_1 = \) Deposition temperature (T)  

(ii) \( X_2 = \) Precursor concentration (C)  

(iii) \( X_3 = \) Injection volume (V)  

(iv) \( X_4 = \) Base pressure (P)  

(v) \( X_5 = \) Number of pulses (Pulse)  

Prior to performing the experimental design, three experiments were performed using a constant set of deposition parameters to determine the repeatability and reproducibility of the coatings prepared by pp-MOCVD. These experiments, called Zero (Z) experiments, were also used to determine the error of the different measurements used in analyzing the performance and characteristics of the coatings. The parameter ranges used to prepare the samples for the ‘Zero’ experiments are listed below:

(i) \( X_1 = \) Deposition temperature (T) = 500 °C  

(ii) \( X_2 = \) Precursor concentration (C) = 4 mol\%  

(iii) \( X_3 = \) Injection volume (V) = 500 μL  

(iv) \( X_4 = \) Base pressure (P) = 100 Pa  

(v) \( X_5 = \) Number of pulses (Pulse) = 750 pulses  

The DOE methodology used in this thesis is based on the Plackett-Burman (PB) designs. Plackett-Burman design uses the least number of experiments to determine the significance of influence of the operating parameters on the resulting NsARC film through a linear relationship. The PB DOE design evaluates the influence of ‘m’ parameters in ‘n’ trials where n is greater than m and is the nearest power of 2. The pp-MOCVD process has \( m = 5 \), therefore the DOE was setup in \( n = 8 \) parameter sets. Each experiment is called \( H_n \) (1≤n≤8).
The quantitatively measurable responses for the DOE are listed below and are represented in the form of a matrix $R_{nj}$ where $n =$ number of the experiment and $j$ is the corresponding measurement:

- $j = 1 =$ PCA
- $j = 2 =$ Thickness
- $j = 3 =$ Growth Rates (GR)
- $j = 4 =$ Columnar Diameter
- $j = 5 =$ Surface roughness (RMS)
- $j = 6 =$ Water Contact Angles (WCA)
- $j = 7 =$ Texture coefficients for Anatase
- $j = 8 =$ Anatase-to-Rutile Phase-ratios

The deposition parameters for each experiment were assigned by setting up a Hadamard matrix. A Hadamard matrix is a square matrix with mutually orthogonal rows and possess some unique statistical properties. During the setup of the parameter matrix, the lower parameter values were assigned to the ‘-1’ position and the higher parameter values were assigned in the ‘+1’ position. This methodology of assignment was used to non-dimensionalize the different processing parameters and make them comparable to each other.
A Hadamard matrix, $H_n$, satisfies the following condition:

$$H'_n \cdot H_n = n \cdot I_n$$

where, $H_n$ = a square matrix of order $n$ with elements that are +1 or -1

$H'_n$ = the transpose of matrix $H_n$

$n = 2^p$ ($p$ is an integer $\geq 0$)

$I_n$ = unit matrix of order $n$

For $n = 8$, the Hadamard matrix, $H_8$ is given in Table 4. 2.

<table>
<thead>
<tr>
<th>ID</th>
<th>I</th>
<th>$X_1$</th>
<th>$X_2$</th>
<th>$X_3$</th>
<th>$X_4$</th>
<th>$X_5$</th>
<th>$X_6$</th>
<th>$X_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H1$</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>$H2$</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>$H3$</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$H4$</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>$H5$</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$H6$</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>$H7$</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>$H8$</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
</tr>
</tbody>
</table>

The first column, ID, represents the label assigned to each experiment of the DOE. The second column, $I$, is called the identity column and the columns $X_n$ are the parameter values used in the experiments. The responses for each of the experiments are provided in Table 4. 3.
Table 4.3 An example response matrix for the different experiments in Table 4.2

<table>
<thead>
<tr>
<th>ID</th>
<th>$R_{nj}$</th>
<th>$R_{n5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>$R_{11}$</td>
<td>$R_{15}$</td>
</tr>
<tr>
<td>H2</td>
<td>$R_{21}$</td>
<td>$R_{25}$</td>
</tr>
<tr>
<td>H3</td>
<td>$R_{31}$</td>
<td>$R_{35}$</td>
</tr>
<tr>
<td>H4</td>
<td>$R_{41}$</td>
<td>$R_{45}$</td>
</tr>
<tr>
<td>H5</td>
<td>$R_{51}$</td>
<td>$R_{55}$</td>
</tr>
<tr>
<td>H6</td>
<td>$R_{61}$</td>
<td>$R_{65}$</td>
</tr>
<tr>
<td>H7</td>
<td>$R_{71}$</td>
<td>$R_{75}$</td>
</tr>
<tr>
<td>H8</td>
<td>$R_{81}$</td>
<td>$R_{85}$</td>
</tr>
</tbody>
</table>

Calculation of the non-dimensional coefficients for the linear model

The influence of a parameters ($X_a$) on each response was evaluated through the linear model provided in Equation 4.1

$$R_{nj} = b_{n0} + \sum_{i=1}^{7} b_{ni}X_i \quad \ldots \ldots \text{4.1}$$

where, $R_{nj}$ represents one of the columns in the response matrix in Table 4.3

The coefficients $b_i$ are calculated as follows:

$$b_{10} = \frac{1}{8} (I \cdot R_{n1})$$

$$b_{10} = \frac{1}{8} (1 \times R_{11} + 1 \times R_{21} + 1 \times R_{31} + 1 \times R_{41} + 1 \times R_{51} + 1 \times R_{61} + 1 \times R_{71} + 1 \times R_{81})$$

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\[
\begin{align*}
    b_{11} &= \frac{1}{8}(1 \times R_{11} - 1 \times R_{21} + 1 \times R_{31} - 1 \times R_{41} + 1 \times R_{51} - 1 \times R_{61} + 1 \times R_{71} \\
    &\quad - 1 \times R_{81}) \\
    \ldots \\
    b_{17} &= \frac{1}{8}(1 \times R_{11} - 1 \times R_{21} - 1 \times R_{31} + 1 \times R_{41} - 1 \times R_{51} + 1 \times R_{61} + 1 \times R_{71} \\
    &\quad - 1 \times R_{81})
\end{align*}
\]

After the coefficients of the model were calculated, the responses were modeled as:

\[
\begin{align*}
    R_{n1} &= b_{10} + b_{11}X_1 + b_{12}X_2 + b_{13}X_3 + b_{14}X_4 + b_{15}X_5 + b_{16}X_6 + b_{17}X_7 \\
    R_{n5} &= b_{50} + b_{51}X_1 + b_{52}X_2 + b_{53}X_3 + b_{54}X_4 + b_{55}X_5 + b_{56}X_6 + b_{57}X_7
\end{align*}
\]

The values of the coefficients were used to evaluate the relative impact of the operating parameters on the responses of the the NsARC coatings prepared for the DOE. The significance of the influence was determined using the deviation of coefficient values above or below the 2\(\sigma\) line of the response measurements (where, \(\pm\sigma\) = error, assuming the normal distribution of error values). The 2\(\sigma\) value was used to cover 95% of the data within the analysis. This model is valid only for the pre-determined ranges of parameters. Figure 4. 3 gives an example of the chart used to determine the influence of the operating parameters on a response \(R_{nj}\).
The Figure 4. 3 shows that

- $X_2$ has a positive influence on the response $R_{nj}$
- $X_1$, and the ghost parameters do not influence the response $R_{nj}$ significantly
- $X_4$ has a negative influence on the response
- $X_3$ has some positive influence but not as significant as $X_2$
- $X_3$ has some negative influence on the response $R$ and is lower than that of $X_2$, $X_4$, and $X_5$. However, at this stage, the parameter cannot be discarded from the analysis completely.

5. **Domain region of the parameters**

The ranges of the operating parameters were set as:

(i) Deposition temperature ($T$) = $475 \degree C - 525 \degree C$

(ii) Precursor concentration ($C$) = $3 \text{ mol\%} - 5 \text{ mol\%}$

(iii) Injection volume ($V$) = $250 \mu l - 500 \mu l$

(iv) Base pressure ($P$) = $85 \text{ Pa} - 115 \text{ Pa}$

(v) Number of pulses (Pulse) = $500 - 1000$ pulses
6. Variabilities of the responses

To evaluate the variation of the responses the three ‘Zero’ experiments were conducted at the center of the domain. To reduce the setup time, the zero experiments were performed at an injection volume of 500 µL.

7. Elimination or transformation of unreliable responses

During the course of measuring the different responses of the DOE trials, it was assumed that

➢ The experiments are independent from one another
➢ The variance of the responses is constant and not dependent on the mean. In case this was not obvious in a given set, a Box-Cox transformation was applied to that set of responses. A Box-Cox transformation increases the readability of the results. In this study, the influences of the deposition parameters on PCA results were studied after using a negative log transformation on the responses.

8. Validation of the DOE model

A final experiment, ‘Experiment -1’ or ‘H9’ was conducted using the lower parameter values (one extreme) outside the parameter matrix. This was done in order to potentially discard interactions between the parameters. The experiment H9 also provided an additional point of analysis for the experimental domain.
4.3 DOE for NsARC coatings by pp-MOCVD

The parameter matrix is set up as shown in the Table 4. J. Land provided the MATLAB code for the DOE modeling and analysis.

**Table 4.4 Operational parameters for DOE NsARC films**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Susceptor temperature (°C)</th>
<th>Precursor conc. (mol %)</th>
<th>Injection Volume (μL)</th>
<th>Base pressure (Pa)</th>
<th>Number of pulses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z–A, B, C</td>
<td>500</td>
<td>4</td>
<td>500</td>
<td>100</td>
<td>750</td>
</tr>
<tr>
<td>H1</td>
<td>525</td>
<td>5</td>
<td>500</td>
<td>115</td>
<td>1000</td>
</tr>
<tr>
<td>H2</td>
<td>525</td>
<td>3</td>
<td>500</td>
<td>85</td>
<td>1000</td>
</tr>
<tr>
<td>H3</td>
<td>475</td>
<td>3</td>
<td>500</td>
<td>115</td>
<td>500</td>
</tr>
<tr>
<td>H4</td>
<td>475</td>
<td>5</td>
<td>500</td>
<td>85</td>
<td>500</td>
</tr>
<tr>
<td>H5</td>
<td>525</td>
<td>5</td>
<td>250</td>
<td>85</td>
<td>500</td>
</tr>
<tr>
<td>H6</td>
<td>525</td>
<td>3</td>
<td>250</td>
<td>115</td>
<td>500</td>
</tr>
<tr>
<td>H7</td>
<td>475</td>
<td>3</td>
<td>250</td>
<td>85</td>
<td>1000</td>
</tr>
<tr>
<td>H8</td>
<td>475</td>
<td>5</td>
<td>250</td>
<td>115</td>
<td>1000</td>
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<tr>
<td>H9</td>
<td>475</td>
<td>3</td>
<td>250</td>
<td>85</td>
<td>500</td>
</tr>
</tbody>
</table>
4.4 Influence of Operating Parameters on Responses

4.4.1 Photocatalytic Activity

The visible light PCAs of the DOE NsARC coatings were analyzed by MBD degradation tests. The test results showed that samples H2 and H4 exhibited higher PCA compared to the rest of the samples. Figure 4.4 shows the photocatalytic degradation of MBD solution exposed to the different NsARC coatings with time. The accompanying Table 4.5 is a summary of the PCA results.

![Graph showing photocatalytic degradation of MBD solution](image)

**Figure 4.4** Results of MBD solution degradation for DOE NsARC samples
Table 4.5 Visible light PCS for DOE NsARC samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>PCA $\times 10^{-4}$ $(\pm 1 \times 10^{-4} \text{ min}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z–A, B, C</td>
<td>4</td>
</tr>
<tr>
<td>H1</td>
<td>12</td>
</tr>
<tr>
<td>H2</td>
<td>48</td>
</tr>
<tr>
<td>H3</td>
<td>12</td>
</tr>
<tr>
<td>H4</td>
<td>26</td>
</tr>
<tr>
<td>H5</td>
<td>4</td>
</tr>
<tr>
<td>H6</td>
<td>0.08</td>
</tr>
<tr>
<td>H7</td>
<td>2</td>
</tr>
<tr>
<td>H8</td>
<td>9</td>
</tr>
<tr>
<td>H9</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The relative influence of the different operating parameters of the pp-MOCVD process on PCA was evaluated using the chart in Figure 4.5.

Figure 4.5 Relative influence of different parameters on the PCA of the NsARC samples
The following inferences were made using the chart in Figure 4. 5.

➢ Temperature of deposition has a slightly negative influence on the negative log(PCA) of the NsARC samples compared to the other processing parameters. This implies that higher PCA is observed in samples deposited at higher temperatures.

➢ The precursor concentration, injection volume and number of pulses have significant positive influences on the negative log(PCA) of the NsARC samples. Due to the Box-Cox transformation this shows that NsARC samples prepared with lower injection volumes and lower precursor concentration are more photoactive.

➢ The base pressure of the deposition process influences the negative log(PCA) negatively. This implies samples NsARC samples prepared with higher working base pressures are more active under visible light.

➢ The coefficient of the first ghost parameter shows that there is an interaction between some of the other operating conditions which positively impacts the photocatalytic performance of the NsARC coatings.

4.4.2 Thickness of the DOE NsARC Coatings

The thicknesses of the NsARC coatings were measured from the fracture surface SEM images samples. The Figure 4. 6 shows the fracture surface SEMs of the samples and the Table 4. 6 has the list of measured thicknesses. Enlarged images of the fracture surfaces are provided in Appendix A2.
Figure 4.6 Fracture surface views of NsARC films prepared using DOE parameter matrix
Table 4.6 Thicknesses of the DOE NsARC films on fused silica substrate

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Thickness (± 0.5 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z–A, B, C</td>
<td>8.64 ± 0.5</td>
</tr>
<tr>
<td>H1</td>
<td>16.03 ± 1.8</td>
</tr>
<tr>
<td>H2</td>
<td>8.94 ± 0.70</td>
</tr>
<tr>
<td>H3</td>
<td>4.03 ± 0.30</td>
</tr>
<tr>
<td>H4</td>
<td>7.47 ± 0.26</td>
</tr>
<tr>
<td>H5</td>
<td>5.89 ± 0.43</td>
</tr>
<tr>
<td>H6</td>
<td>2.05 ± 0.26</td>
</tr>
<tr>
<td>H7</td>
<td>6.23 ± 0.66</td>
</tr>
<tr>
<td>H8</td>
<td>10.77 ± 1.22</td>
</tr>
<tr>
<td>H9</td>
<td>2.80 ± 0.16</td>
</tr>
</tbody>
</table>

The influence of the operating parameters on coating thickness is provided in Figure 4.7.

Figure 4.7 Relative influence of different operating parameters of pp-MOCVD on NsARC coating thickness
The chart in Figure 4. 7 was used to infer the following:

➢ All five parameters have varying degrees of positive impacts on the thicknesses of the NsARC coatings prepared via DOE.

➢ Deposition temperature has a positive influence on the sample thicknesses but the influence is not as significant as the other parameters. This behavior is due to the depositions taking place in the mass-transport controlled regime of the pp-MOCVD process.

➢ The influence of precursor concentration and number of pulses is significantly higher compared to the other deposition conditions. This shows that higher precursor concentrations and higher number of pluses produce thicker NsARC samples.

➢ The injection volume positively influences the sample thickness but to a lesser degree than concentration and number of pulses. A larger injection volume leads to the deposition of thicker NsARC samples.
4.4.3 Growth-rates of DOE NsARC Coatings

The thicknesses and number pulses of the NsARC samples were used to obtain the growth-rates of the coatings. The results are in Table 4.7. The influence of the processing parameters on the growth-rates of the coatings was determined using Figure 4.8.

Table 4.7 Growth-rates of DOE NsARC samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>GR (± 1.3 nm/pulse)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z–A, B, C</td>
<td>11.5 ± 0.7</td>
</tr>
<tr>
<td>H1</td>
<td>16.0 ± 2.0</td>
</tr>
<tr>
<td>H2</td>
<td>9.0 ± 0.7</td>
</tr>
<tr>
<td>H3</td>
<td>8.0 ± 0.5</td>
</tr>
<tr>
<td>H4</td>
<td>15.0 ± 0.5</td>
</tr>
<tr>
<td>H5</td>
<td>11.8 ± 0.8</td>
</tr>
<tr>
<td>H6</td>
<td>4.1 ± 0.5</td>
</tr>
<tr>
<td>H7</td>
<td>6.2 ± 0.7</td>
</tr>
<tr>
<td>H8</td>
<td>10.8 ± 1.2</td>
</tr>
<tr>
<td>H9</td>
<td>5.6 ± 0.3</td>
</tr>
</tbody>
</table>
The inferences drawn from Figure 4. 8 are:

➢ The precursor concentration significantly impacts the growth-rates of the coatings in a positive way. Higher precursor concentration produces faster-growing NsARC samples.

➢ The injection volume has a positive influence on growth-rate but is not as significant as precursor concentration. A larger injection volume produces NsARC samples with faster growth-rates.

➢ All the other parameters have very little influence on the growth-rates of the coatings.

4.4.4 Columnar Diameter of the DOE NsARC Coatings

Plan-view SEM images of the DOE NsARC coatings were used to measure the anatase column diameter of the samples. Figure 4. 9 shows the surface SEM images of the coatings. Full size SEM images are provided in Appendix A2. The columnar diameters of the anatase samples were analyzed according to ASTM E112-circle intercept method. Table 4. 8 summarizes the columnar diameters of NsARC coatings. The influence of the pp-MOCVD processing parameters on columnar sizes of the coatings is shown in Figure 4.10.
Figure 4.9 Fracture surface views of NsARC films prepared using DOE parameter matrix.
Table 4.8: Anatase columnar diameters of NsARC Coatings.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Columnar diameter (± 50 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z–A, B, C</td>
<td>438 ± 48</td>
</tr>
<tr>
<td>H1</td>
<td>730 ± 23</td>
</tr>
<tr>
<td>H2</td>
<td>517 ± 30</td>
</tr>
<tr>
<td>H3</td>
<td>307 ± 28</td>
</tr>
<tr>
<td>H4</td>
<td>474 ± 79</td>
</tr>
<tr>
<td>H5</td>
<td>338 ± 27</td>
</tr>
<tr>
<td>H6</td>
<td>204 ± 10</td>
</tr>
<tr>
<td>H7</td>
<td>460 ± 78</td>
</tr>
<tr>
<td>H8</td>
<td>670 ± 100</td>
</tr>
<tr>
<td>H9</td>
<td>291 ± 28</td>
</tr>
</tbody>
</table>

Figure 4.10: Relative influence of different processing parameters on the columnar size of NsARC coatings.
The inferences drawn from Figure 4.10 are:

➢ The columnar diameter of the coatings is significantly influenced by precursor concentration, injection volume and pulse rate. The columnar diameter increases significantly when the precursor concentration, injection volume and pulse-rate are increased during the pp-MOCVD process.

➢ The ghost parameters show that there are no interactions between any the pre-set controlled parameters.

➢ Temperature and base pressure have little influence on the columnar diameter of the DOE NsARC coatings. The chart shows that the anatase columnar diameters decrease at higher deposition temperatures.
4.4.5 RMS Surface Roughness

The RMS surface roughness values of the NsARC coatings were used to assess the three-dimensions surface topographies of the coatings prepared via DOE. The RMS roughness values of NsARC coatings were estimated by post-processing the AFM images of the NsARC samples. Figure 4. 11 presents a list of the surface topographies of NsARC coatings. Individual 3D topographical maps of the individual coatings are provided in Appendix A2. The Figure 4. 12 shows the relative influence of the different processing parameters on the RMS values of the NsARC coatings. The figure demonstrated that the pp-MOCVD parameters do not have any significant influence on the surface roughness of the NsARC coatings. Table 4. 9 has a summary of the RMS values for the DOE NsARC coatings.
Figure 4. 11 3D topographical maps of the NsARC samples
### Table 4. 9 RMS surface roughness values of DOE NsARC coatings

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>RMS Surface Roughness (± 6.4 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z–A, B, C</td>
<td>162</td>
</tr>
<tr>
<td>H1</td>
<td>115.8</td>
</tr>
<tr>
<td>H2</td>
<td>136</td>
</tr>
<tr>
<td>H3</td>
<td>57.4</td>
</tr>
<tr>
<td>H4</td>
<td>119.1</td>
</tr>
<tr>
<td>H5</td>
<td>79.2</td>
</tr>
<tr>
<td>H6</td>
<td>45</td>
</tr>
<tr>
<td>H7</td>
<td>86.8</td>
</tr>
<tr>
<td>H8</td>
<td>116.6</td>
</tr>
<tr>
<td>H9</td>
<td>62.8</td>
</tr>
</tbody>
</table>

**Figure 4. 12 Relative influence of the pp-MOCVD processing parameters on RMS surface roughness of DOE NsARC coatings**

Figure 4. 12 showed that none of the pp-MOCVD processing parameters influence the surface topography of the NsARC coatings.
4.4.6 Water Contact Angle (WCA) Measurements

The wettability of the DOE NsARC surfaces was analyzed using water contact angle measurements. The WCA measurements were performed with assistance from Dr. Z. Yang of Cirrus Materials, NZ. The WCA images are provided in Figure 4.13 (individual WCAs are provided in Appendix A2). Figure 4.14 has a chart on the relative influence of different pp-MOCVD processing parameters on the wettability of the NsARC surfaces. Table 4.10 has the WCAs for the various surfaces.
Figure 4. 13 Water contact angles of the NsARC coatings prepared in DOE
Table 4. 10 Water contact angles for DOE NsARC films

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>WCA (± 5°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z–A, B, C</td>
<td>41 ± 4</td>
</tr>
<tr>
<td>H1</td>
<td>87 ± 4</td>
</tr>
<tr>
<td>H2</td>
<td>36 ± 2</td>
</tr>
<tr>
<td>H3</td>
<td>51 ± 10</td>
</tr>
<tr>
<td>H4</td>
<td>83 ± 5</td>
</tr>
<tr>
<td>H5</td>
<td>24 ± 6</td>
</tr>
<tr>
<td>H6</td>
<td>19 ± 3</td>
</tr>
<tr>
<td>H7</td>
<td>28 ± 6</td>
</tr>
<tr>
<td>H8</td>
<td>14 ± 1</td>
</tr>
<tr>
<td>H9</td>
<td>19 ± 2</td>
</tr>
</tbody>
</table>

Figure 4. 14 Relative influence of different processing parameters on WCA of NsARC coating surfaces
The inferences drawn from Figure 4. 14 are:

➢ Precursor concentration and injection volume have significant positive influences on the wettability of the NsARC surfaces. The surface wettability of NsARC coatings is higher for samples deposited with higher precursor concentrations and injection volumes.

➢ The ghost parameters show that interactions between the pre-set parameters also significantly influence the wettability of the coatings in a positive manner.

➢ The temperature, base pressure and pulse-rate have significantly lower influences on the NsARC wettability.
4.4.7 Anatase Texture

The XRD spectra were used to determine the anatase texture-coefficients of the NsARC films prepared using the DOE parameter matrix. Figure 4.15 provides a waterfall plot of the XRD spectra of the different coatings. Individual spectra have been provided in Appendix A2. The peaks at \( 2\theta = 70.2^\circ \) represent the (220) growth orientation of anatase crystals. The accompanying Table 4.11 provides the TCs of anatase for DOE coatings. Figure 4.16 shows the chart demonstrating the relative influence of different processing parameters on anatase texture in the NsARC coatings.

![XRD spectra showing the [220] growth texture of NsARC films prepared using DOE parameter matrix](image)

**Figure 4.15** XRD spectra showing the [220] growth texture of NsARC films prepared using DOE parameter matrix
### Table 4.11 Anatase texture coefficients for DOE NsARC coatings

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Anatase TC (±0.04)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z–A, B, C</td>
<td>4.78</td>
</tr>
<tr>
<td>H1</td>
<td>4.90</td>
</tr>
<tr>
<td>H2</td>
<td>4.90</td>
</tr>
<tr>
<td>H3</td>
<td>4.55</td>
</tr>
<tr>
<td>H4</td>
<td>4.76</td>
</tr>
<tr>
<td>H5</td>
<td>4.92</td>
</tr>
<tr>
<td>H6</td>
<td>3.13</td>
</tr>
<tr>
<td>H7</td>
<td>4.67</td>
</tr>
<tr>
<td>H8</td>
<td>4.92</td>
</tr>
<tr>
<td>H9</td>
<td>3.75</td>
</tr>
</tbody>
</table>

**Figure 4.16** Relative influence of pp-MOCVD processing parameters on texture coefficient of anatase in NsARC coatings
The inferences drawn from Figure 4.16 are:

➢ Temperature and base pressure have significant negative influences on the texture of anatase. This implies that NsARC samples deposited at higher temperatures and working base pressures would have smaller TCs for the anatase phase.

➢ The first ghost parameter shows that the interaction between temperature and pressure also significantly influences the resulting anatase texture in a negative way.

➢ The precursor concentration, injection volume and pulse rate have significant positive influence on the texture of anatase in NsARC films. Increasing the precursor volume, pulse rate and injection volume will result in NsARC films with higher anatase texture coefficients.

➢ The second ghost parameter shows that the interaction between the pre-set pp-MOCVD parameters has a significant positive influence on the texture of anatase during the deposition process.
4.4.8 Anatase-Rutile Phase Ratios

The phase ratios of the DOE NsARC coatings were analyzed using the XRD spectra collected in $\chi$. The Figure 4.15 shows the influence of various pp-MOCVD process parameters on the anatase-to-rutile phase ratios of the coatings and the Table 4.12 lists the related phase-ratios.

**Table 4.12 Anatase rutile phase ratios for DOE NsARC coatings**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>A:R phase ratio (±0.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z–A, B, C</td>
<td>2.72</td>
</tr>
<tr>
<td>H1</td>
<td>4.88</td>
</tr>
<tr>
<td>H2</td>
<td>3.10</td>
</tr>
<tr>
<td>H3</td>
<td>2.35</td>
</tr>
<tr>
<td>H4</td>
<td>2.61</td>
</tr>
<tr>
<td>H5</td>
<td>2.51</td>
</tr>
<tr>
<td>H6</td>
<td>1.41</td>
</tr>
<tr>
<td>H7</td>
<td>2.97</td>
</tr>
<tr>
<td>H8</td>
<td>2.98</td>
</tr>
<tr>
<td>H9</td>
<td>5.28</td>
</tr>
</tbody>
</table>
The inferences drawn from Figure 4.17 are:

- All the processing parameters influence the phase ratios in a positive way.
- The influences of precursor concentration, injection volume and pulse-rate are more significant compared to the other parameters.
- The chart shows that, while the level on influence is within the ±2σ range, the influences of precursor concentrations, injection volume and base pressures on the phase formation cannot be disregarded without further analysis.
4.5 Linking Performance and Characteristics to Influence of Deposition Parameters

The objective of the DOE was to determine the influence of pp-MOCVD processing parameters on the resulting performance and characteristics of NsARC coatings. Table 4.13 summarizes all the responses measured for the DOE NsARC coatings. The following sections have evaluation of the influence of the processing parameters on the response of the DOE NsARC coatings and their photocatalytic performance.
Table 4. Summary of measure responses of NsARC coatings prepared for DOE

<table>
<thead>
<tr>
<th>ID</th>
<th>PCA $\times 10^4$ ($\pm 1 \times 10^4$ min$^{-1}$)</th>
<th>Thickness ($\pm 0.5$ $\mu m$)</th>
<th>GR ($\pm 1.3$ nm/pulse)</th>
<th>Columnar diameter ($\pm 23$ nm)</th>
<th>RMS values ($\pm 6.4$ nm)</th>
<th>WCA ($\pm 5^\circ$)</th>
<th>Anatase TC ($\pm 0.04$)</th>
<th>A:R phase ratios ($\pm 0.5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>4</td>
<td>8.64 $\pm$ 0.5</td>
<td>11.5 $\pm$ 0.7</td>
<td>438 $\pm$ 48</td>
<td>162</td>
<td>41 $\pm$ 4</td>
<td>4.78</td>
<td>2.72</td>
</tr>
<tr>
<td>H1</td>
<td>12</td>
<td>16.03 $\pm$ 1.8</td>
<td>16.0 $\pm$ 2.0</td>
<td>730 $\pm$ 23</td>
<td>115.8</td>
<td>87 $\pm$ 4</td>
<td>4.90</td>
<td>4.88</td>
</tr>
<tr>
<td>H2</td>
<td>48</td>
<td>8.94 $\pm$ 0.70</td>
<td>9.0 $\pm$ 0.7</td>
<td>517 $\pm$ 30</td>
<td>136</td>
<td>36 $\pm$ 2</td>
<td>4.90</td>
<td>3.10</td>
</tr>
<tr>
<td>H3</td>
<td>12</td>
<td>4.03 $\pm$ 0.30</td>
<td>8.0 $\pm$ 0.5</td>
<td>307 $\pm$ 28</td>
<td>57.4</td>
<td>51 $\pm$ 10</td>
<td>4.55</td>
<td>2.35</td>
</tr>
<tr>
<td>H4</td>
<td>26</td>
<td>7.47 $\pm$ 0.26</td>
<td>15.0 $\pm$ 0.5</td>
<td>474 $\pm$ 79</td>
<td>119.1</td>
<td>83 $\pm$ 5</td>
<td>4.76</td>
<td>2.61</td>
</tr>
<tr>
<td>H5</td>
<td>4</td>
<td>5.89 $\pm$ 0.43</td>
<td>11.8 $\pm$ 0.8</td>
<td>338 $\pm$ 27</td>
<td>79.2</td>
<td>24 $\pm$ 6</td>
<td>4.92</td>
<td>2.51</td>
</tr>
<tr>
<td>H6</td>
<td>0.08</td>
<td>2.05 $\pm$ 0.26</td>
<td>4.1 $\pm$ 0.5</td>
<td>204 $\pm$ 10</td>
<td>45</td>
<td>19 $\pm$ 3</td>
<td>3.13</td>
<td>1.41</td>
</tr>
<tr>
<td>H7</td>
<td>2</td>
<td>6.23 $\pm$ 0.66</td>
<td>6.2 $\pm$ 0.7</td>
<td>460 $\pm$ 78</td>
<td>86.8</td>
<td>28 $\pm$ 6</td>
<td>4.67</td>
<td>2.97</td>
</tr>
<tr>
<td>H8</td>
<td>9</td>
<td>10.77 $\pm$ 1.22</td>
<td>10.8 $\pm$ 1.2</td>
<td>670 $\pm$ 100</td>
<td>116.6</td>
<td>14 $\pm$ 1</td>
<td>4.92</td>
<td>2.98</td>
</tr>
<tr>
<td>H9</td>
<td>0.08</td>
<td>2.80 $\pm$ 0.16</td>
<td>5.6 $\pm$ 0.3</td>
<td>291 $\pm$ 28</td>
<td>62.8</td>
<td>19 $\pm$ 2</td>
<td>3.75</td>
<td>5.28</td>
</tr>
</tbody>
</table>
4.5.1 Temperature

The deposition temperature was selected in the range 475 °C – 525 °C to produce NsARC coatings in the mass-transport controlled regime [3] of the pp-MOCVD process. The analysis of the DOE responses showed that the variation deposition temperature positively influences the PCA and negatively influences the anatase texture coefficients. The analysis proves that samples prepared at higher temperatures exhibit higher PCA but lower texture coefficients of anatase phase TiO₂. Background literature and previous studies have shown that highly textured anatase exhibits high PCA [4, 5]. The trend chart in Figure 4.18 was used to evaluate the variation of PCA with anatase texture coefficients. The chart shows that PCA and anatase texture have a strong and positive correlation. This leads to the deduction that the visible light-active NsARC coatings exhibit highly oriented anatase columns in the films.
Figure 4. 18 Variation of PCA with anatase texture coefficient
4.5.2 Concentration

Precursor concentration has a significant positive impact on PCA, thickness, GR, columnar diameter, WCA and anatase texture coefficients. There is little to no influence of precursor concentration on anatase-rutile phase ratios and RMS surface roughness of NsARC coatings. The DOE analysis also shows that precursor concentration does not negatively influence any of the responses of the NsARC films. High precursor concentrations imply greater availability of precursor molecules that in turn lead to thicker NsARC coatings with higher growth-rates. High growth-rates in the pp-MOCVD chamber are more likely to result in the desired nanostructured columnar morphology of the coatings. The GR studies in Chapter-3 have established that the nanostructures on NsARC coatings possess high specific surface areas, which contribute to high visible light PCA of the films. High growth-rates are also associated with larger columnar diameters.

The charts between growth-rates & PCA and columnar diameter & PCA in Figure 4. 19 were used to estimate the variation of PCA with growth-rates and columnar diameters of the DOE NsARC coatings. The charts show that the samples with highest PCA (H2 and H4) are not the ones with the highest growth-rates or columnar diameters. It appears that the highest PCA occurs at an optimum growth-rate and decreases beyond that. The chart (Figure 4. 19 b) on columnar diameter and PCA exhibits a similar trend.
Figure 4.19 Variation of (a) growth-rate with PCA; (b) columnar diameter with PCA
4.5.3 Injection Volume

The precursor injection volume positively influences all the responses of the DOE NsARC coatings. The DOE analysis shows that precursor injection volume has a similar effect to precursor concentration on the responses of the NsARC. Injection volume has significant positive influence on PCA, columnar diameter, WCA, and anatase texture. The variations of PCA with anatase texture and columnar diameter have been studied using the Figure 4. 18. Injection volume has the most significant influence on the WCA measurements of the NsARC coating surfaces.

Hydrophilic surfaces exhibit higher PCA in comparison to hydrophobic surfaces [6]. WCA measures demonstrate the hydrophilicity of the NsARC. A low WCA implies a greater wettability of the coating surface and the surface is more likely to exhibit higher PCA. Figure 4. 20 shows the variation of PCA with water contact angle measurements of the NsARC coating surfaces. The chart shows that, between the two most active samples, the sample with the smaller WCA exhibits higher PCA. However, the DOE NsARC films deviate slightly from the results reported by Banerjee et al. The samples that have low WCAs (H5, H6, H8 & H9) do not always exhibit high PCA and vice versa.
Figure 4. Variation of PCA with Water Contact Angle (WCA)

$R^2 = 0.311$
4.5.4 Base Pressure

The base pressure of pp-MOCVD process effects the growth-rates of the films prepared in the mass-transport controlled regime [3]. Previous work by Dr. Lee established that lower base pressures result in thicker films and thus high growth-rates of the coatings [7]. The DOE analysis shows that base pressure of the pp-MOCVD process has a negative influence on most of the responses of the DOE NsARC coatings. The exclusions are thicknesses and anatase-rutile phase ratios of the where the base pressure has positive influences but the level of influence is relatively insignificant compared to the other processing parameters. The most significant negative influence of base pressure is observed on PCA and anatase textures. Lower base pressure results in highly textured NsARC coatings that exhibit high visible light PCA. The variation of PCA with anatase texture has been studied using Figure 4. 18.
4.5.5 Pulse Rate

The number of pulses of the deposition process is unique to the pp-MOCVD system. The DOE analysis shows that number of pulses has a positive influence on almost all the responses of the NsARC coatings except on WCA. The influence of number of pulses on the wettability of the films is significantly lower than the other deposition parameters. The most significant influence of the number of pulses is observed on PCA, thickness, columnar diameter and anatase texture of the NsARC coatings. The influence of number of pulses on anatase-rutile phase ratios is within the ±2σ level, but it is not low enough to be discarded from the analysis. The variation of PCA with anatase texture and columnar diameters has been presented in Figure 4. 18 and Figure 4. 19 (b). Figure 4. 21 shows the variation of PCA with NsARC film thickness and anatase-to-rutile phase ratios. The variation of PCA with thickness follows a similar trend to growth-rate (Figure 4. 19 a). Figure 4. 21 (b) shows that there is no trend for the variation of PCA with phase ratio of the coatings. It is yet to be determined if PCA and phase-ratios have a non-linear relationship.
Figure 4.21 Variation of PCA with (a) film thickness; (b) anatase-rutile phase ratios
4.6 Conclusion

The influence of the pp-MOCVD deposition parameters on performance and characteristics of the NsARC coatings has been studied using the DOE methodology. The technique identified two samples, H2 and H4, that are remarkably active under visible compared to the other samples prepared using the DOE parameter matrix. The next step is to use advanced characterization techniques to determine if the nanostructures of H2 and H4 exhibit any unique features. The questions are:

- Which particular characteristics of H2 and H4 are responsible for the high PCA?
- What are the crystallographic properties of these samples?
- What is the role of carbon in the nanostructure formation of H2 and H4?
- Where is carbon located in the micro- and nanostructure of the NsARC films?
References


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Chapter 5: Mechanisms behind the PCA of NsARC

The DOE methodology in Chapter 4 was used to determine the influence of pp-MOCVD processing parameters on the performance and characteristics of NsARC composite films. The screening test performed using MBD degradation under visible light identified two samples, H2 and H4, that exhibited enhanced PCA compared to the rest of the samples in the DOE.

The current chapter methodically analyzes the samples H2 and H4 to establish if they possess the characteristics that are suspected to be responsible for their high PCA. A combination of HRTEM, XRD and Raman spectroscopy was used to determine their characteristics and properties. In the Forensic Investigative approach this step is analogous to ‘Establishing the motive(s) of the perpetrator’.

5.1 Deposition Parameters and Response Measurements for H2 and H4

The deposition parameters of the samples H2 and H4 are listed in Table 5.1

<table>
<thead>
<tr>
<th>ID</th>
<th>Deposition temperature</th>
<th>Precursor concentration</th>
<th>Injection Volume</th>
<th>Base Pressure</th>
<th>Number of pulses</th>
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<tr>
<td>H2</td>
<td>525 °C</td>
<td>3 mol%</td>
<td>500 μL</td>
<td>85 Pa</td>
<td>1000</td>
</tr>
<tr>
<td>H4</td>
<td>475 °C</td>
<td>5 mol%</td>
<td>500 μL</td>
<td>85 Pa</td>
<td>500</td>
</tr>
</tbody>
</table>

The deposition conditions are mostly different except for injection volume and working base pressure of the pp-MOCVD process. Among the other deposition parameters, the ones that significantly influence the performance are precursor concentration and number of pulses. Table 5.2 summarizes the different responses of...
H2 and H4 samples. The deposition temperatures, though different, do not influence the PCA significantly, as the process occurs in the mass-transport controlled regime for both H2 and H4. A comparative table below lists the different characteristics of H2 and H4 obtained from the various analyses performed on these samples.

**Table 5.2 Comparison of the performance and characteristics of H2 and H4**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>H2</th>
<th>H4</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCA (±1×10⁻⁴ min⁻¹)</td>
<td>4.8 × 10⁻³</td>
<td>2.6 × 10⁻³</td>
</tr>
<tr>
<td>Thickness (±0.5 μm)</td>
<td>8.94 ± 0.70</td>
<td>7.47 ± 0.26</td>
</tr>
<tr>
<td>Growth-rates (±1.3 nm/pulse)</td>
<td>9.0 ± 0.70</td>
<td>15.0 ± 0.5</td>
</tr>
<tr>
<td>Anatase Column Diameter (±23 nm)</td>
<td>517 ± 30</td>
<td>474 ± 79</td>
</tr>
<tr>
<td>RMS surface roughness (±6.4 nm)</td>
<td>136</td>
<td>119.1</td>
</tr>
<tr>
<td>Water Contact Angle (±5°)</td>
<td>36 ± 2</td>
<td>83 ± 5</td>
</tr>
<tr>
<td>Anatase Texture coefficient (±0.04)</td>
<td>4.90</td>
<td>4.76</td>
</tr>
<tr>
<td>Anatase-rutile phase ratio (±0.5)</td>
<td>3.10</td>
<td>2.61</td>
</tr>
<tr>
<td>Bandgap (±0.01 eV)</td>
<td>1.79</td>
<td>1.80</td>
</tr>
</tbody>
</table>

The PCA of H2 is higher than that of H4 despite the similar optical bandgap values for the coatings. This is possibly due to the higher number of pulses for H2, which is responsible for thicker films with larger grain diameters. The variation of PCA with film thickness and grain diameter in Chapter 4 showed that, between H2 and H4, the performance is superior for the thicker coating with larger grains. The H2 NsARC film also exhibits higher surface roughness and a smaller water contact angle showing the higher wettability of H2. This demonstrates that H2 possibly possesses higher surface energy [1, 2]. The determination of orientation of anatase and rutile crystal
columns in H2 and H4 may provide insight into the surface energies of these coatings. Finally, the texture coefficient of anatase is marginally higher for H2 than for H4, providing yet another reason for the higher PCA of H2.

Surface energy of crystalline materials is a property of the orientation and exposed facets of the crystals in the materials. The ASTAR™-ACOM phase and orientation mapping of NsARC films in Chapter 3 showed that the anatase columns are single crystals with secondary nanoscale features. The rutile columns also possess secondary nanostructures, but they are polycrystalline. The following sections describe the materials characteristics and crystallography of anatase and rutile columns in H2 and H4.

5.2 Material and Crystallographic Characterization for NsARC H2

The phase and compositional analysis of H2 are provided in Appendix A2. HRTEM images were used to analyze the crystal orientations and possible exposed facets of H2 NsARC coatings. The FFT images associated with the HRTEM images provided crystallographic information that was loaded into the crystal modelling software, VESTA [3]. The software was used to visualize the orientation of the crystal planes with respect to each other and with respect to the anatase growth orientation of A\{220\}. Rutile crystals exhibit polycrystalline behavior and hence, the crystal surfaces were modeled with respect to the naturally occurring R\{110\} facets. The raw crystal structure data files for anatase [4] and rutile [5] were obtained from the RRUFF crystallography database.
5.2.1 Structure and Phase Morphology of H2

The high-mag SEM and STEM images of H2 show typically observed crystal morphologies of NsARC with some subtle differences. The images are provided in Figure 5.1.

Figure 5.1 (a) SEM image showing the plan-view surface of H2; (b) STEM image showing the cross-sectional view of H2
The anatase columns have the appearance of pyramidal layered on the surface and the rutile columns have dendritic nanostructures. The ASTAR™ results established that rutile grows on top of anatase. The anatase columns of H2 are observed to have additional nanostructures when compared to the anatase columns in a typical NsARC coating (Figure 5. 2). The rutile structures on the other hand are observed to have smaller nanoscale dendritic features than the ones found on a typical NsARC coating. The evidence is provided in Figure 5. 3. It can be theorized that the structure of rutile on H2 is only ‘partially’ transitioned from anatase and therefore has the smaller nanoscale features. The partially transitioned surfaces could be the anatase-rutile polymorphic heterostructures. Figure 5. 4 (a) shows the SEM image of the ROI identified for HRTEM imaging. The TEM image of the FIB lamella prepared from H2 sample is shown in Figure 5. 4 (b). The rutile and anatase columns are separated into three regions for HRTEM analysis.
Figure 5.2 Plan view SEM images of anatase columns on (a) H2; (b) typical NsARC
Figure 5. 3 Plan view SEM images of rutile columns on (a) H2; (b) typical NsARC
Figure 5.4 (a) SEM image of anatase and rutile crystals of the H2 sample; (b) Corresponding HRTEM image showing the ROIs used for crystallographic analysis
5.2.2 Anatase Phase of H2

The HRTEM image of the ROI H2-A1 corresponding to a region near the top of the anatase column is given in Figure 5. 5. The FFT image of the HRTEM image provides the lattice spacing details for the highlighted ROI. The lattice spacing values from the FFT inset were identified as A{101} and A{105}. Following the A(101) and A(105) lattice planes to the extremities of the ROI, it can be deduced that these planes are the probable terminating surfaces for the tops of the anatase. The VESTA crystal model (Figure 5. 6), constructed by replicating the A(1̅01) and the A(105) planes, closely resembles the top of the anatase column in Figure 5. 4. The model also contains the lattice planes of A[110] to indicate the growth direction of the anatase column. A comparison of the lattice planes and crystals surfaces is provided in Figure 5. 6. Appendix A1 has the lattice spacing values for all the crystallographic orientations observed in the anatase crystals.
Figure 5. (a) HRTEM image of H2-Al with FFT inset; (b) VESTA crystal model showing the observed exposed facets with respect to the A[110] growth direction
**Figure 5.6** VESTA lattice plane model showing the positions of A\{101\}, A\{105\} and A\{004\} crystal surfaces with respect to the A\{110\} growth orientation for anatase

HRTEM image of the ROI closer to the center of the anatase crystal column is shown in Figure 5. 7. The FFT inset in the figure provides the lattice spacing information for this ROI. The diffraction pattern shows that the ROI in Figure 5. 5 and Figure 5. 7 exhibit the same zone axis of A\{010\}. The HRTEM image in Figure 5. 7 (a) exhibits well-defined lattice planes for A\{101\}. The image also exhibits clear lattice planes for A\{004\}. The VESTA crystal model has been provided only to reference the relative positions of the A(101) and A(004) lattice planes with respect to the growth orientation of the anatase crystal.
Figure 5. 7 (a) HRTEM image of H2-A2 (anatase core) with FFT inset; (b) VESTA crystal model showing the observed lattice planes with respect to the A[110] growth direction.
Figure 5. 8 shows the HRTEM image for a single plate tip observed on an anatase crystal of the H2 sample. The image in Figure 5. 8 (a) shows well defined lattice planes for A{101}. The A{112} lattice planes are not immediately evident but can be observed on a close inspection of the lattice planes at the tip of the plate. From this image it is deduced that the tips are terminated by the A{112} planes at the corners while the A{101} lattice planes dominate most of the HRTEM image.
Figure 5.8 (a) HRTEM image of H2-A2 (anatase plate-tip) with FFT inset; (b) VESTA crystal model showing the observed exposed facets with respect to the A{110} growth direction
The crystal columns are indistinguishable from each other at the film-substrate interface as evidenced from Figure 5. 4. The HRTEM in Figure 5. 9 shows clear evidence of randomly oriented lattice planes at the interface. The FFT inset shows the H2 film at the interface exhibits a polycrystalline behavior with dominant A(101) lattice planes. This means that as the deposition time progresses, certain facets of anatase TiO$_2$ compete with others lead to the formation of the well-defined crystal columns observed at lower magnifications.
Figure 5. 9 (a) HRTEM image of H2-A3 (film-substrate interface) with FFT inset. The dotted circle indicates the ring pattern for polycrystalline A(101); (b) VESTA crystal model showing the A(101) lattice planes with respect to the A[110] growth direction.
5.2.3 Rutile Phase of H2

The subtle differences in the surface morphology of rutile crystals in H2 and typical NsARC coatings have been shown in Figure 5.3. The H2 rutile crystals have smaller nanoscale dendrites. The HRTEM image in Figure 5.10 shows the lattice spacing for R{101} and R{111}. A comparison of the VESTA crystal model with the surface topography of an H2 rutile crystal is provided in Figure 5.11. When a composite model is constructed by layering the single crystal from Figure 5.10 (b), the illustration closely resembles the 2D rendering of the top of a rutile crystal. The orientation of rutile phase is not yet determined; hence, the rutile crystal models have been constructed with reference to its most stable R[110] lattice planes.
Figure 5. 10 (a) HRTEM image of H2-R1 (rutile-top) with FFT inset; (b) VESTA crystal model showing the predicted exposed facets with respect to the direction of R[110] planes.
Figure 5.11 VESTA crystal model showing the positions of R\{101\}, R\{111\} crystal surfaces with respect to the R\{110\} lattice plane direction for rutile.

Figure 5.12 shows the HRTEM image of the H2 rutile crystal close to the center of the column. The FFT inset shows that the lattice planes for R\{110\} are clearly evident. A closer inspection of the HRTEM image also shows the presence of R\{100\} lattice planes. The VESTA crystal model in Figure 5.12 (b) shows the relative positions of the R\{110\} and R\{100\} planes with respect to the direction of R\{110\} lattice planes.
Figure 5. 12 (a) HRTEM image of H2-R2 (rutile-core) with FFT inset; (b) VESTA crystal model showing the location of the R {110} and R{100} planes with respect to the direction of R[110] planes.
The HRTEM image of the ROI on the tip of a rutile dendrite for H2 is shown in Figure 5. 13 (a). The lattice spacing values analyzed from the FFT inset are concurrent with the values for R\{110\} and R\{310\} surfaces of rutile phase TiO₂. The tip of the plate is observed to be composed of R\{310\} at the end closer to the primary core of the crystal column which are terminated by the R\{110\} crystal facets. The VESTA crystal model in Figure 5. 13 (b) shows the relative positions of the R\{110\} and R\{310\} crystals with respect to the direction of R[110] lattice planes.
Figure 5.13 (a) HRTEM image of H2-R2 (rutile dendrite-tip) with FFT inset. The dotted red line highlights a single rutile dendrite; (b) VESTA crystal model showing the location of the R{110} and R{310} planes with respect to the direction of R[110] planes.
The HRTEM image in Figure 5. 14 (a) shows the bottom of the rutile crystal at interface of the H2 film and the fused silica substrate. It is observed that the crystals at the interface are not immediately distinguishable. The FFT inset is observed to be a circular diffraction pattern similar to that of a polycrystalline material. The analysis of the diffraction pattern shows that the ROI H2-R3 exhibits polycrystalline anatase signature. This is further evidence of the fact that TiO$_2$ nucleates in its anatase during the early stages of the deposition process and transitions into rutile as the deposition time progresses.
Figure 5.14 (a) HRTEM image of H2-R3 (film-substrate interface) with FFT inset; (b) VESTA crystal model showing the location of the A{101} planes with respect to the growth direction of A[110] planes.
5.2.4 Summary of Crystallographic Orientations Observed in H2

The Figure 5.15 shows illustrations of anatase and rutile columns of H2 NsARC coatings with the exposed facets and crystallographic orientations at the four main ROIs. The HRTEM analyses showed that the rutile crystals grow out of anatase nucleation sites. At this stage, the exact location of the interface between anatase and rutile phases in the crystal column has not been observed.
Figure 5.15 Summary of HRTEM results for H2 – (a) anatase crystal column; (b) rutile crystal column
5.3 Material and Crystallographic Characterization for NsARC H4

The phase and compositional analysis of H2 are provided in Appendix A2. HRTEM images were used to analyze the crystal orientations and possible exposed facets of H4 NsARC coatings. The FFT images associated with the HRTEM images provided crystallographic information that was loaded into the crystal modelling software, VESTA. The visual models of the crystal facets and lattice planes were constructed in the same manner as for H2.

5.3.1 Structure and Phase Morphology of H4

The Figure 5.16 shows the plan-view and cross-sectional SEM images for the H4 NsARC sample. The anatase crystals on the H4 sample look similar to the ones observed in H2. They exhibit a rougher topography as compared to the typical NsARC coatings prepared by pp-MOCVD. The comparison is provided in Figure 5.17. The rutile columns on the H4 sample resemble the ones on a typical NsARC coating and exhibit well-defined nanoscale dendrites unlike the columns on H2. A comparison of a single rutile column on H4 with a column on typical NsARC is provided in Figure 5.18. The SEM image of the ROI identified for sample preparation is shown in Figure 5.19 (a) and the TEM image of the FIB cross-section is provided in Figure 5.19 (b). The figure also shows the ROIs used in HRTEM analysis for the anatase and rutile columns of the H4 NsARC sample.
Figure 5. 16 (a) SEM image showing the plan-view surface of H4; (b) STEM image showing the cross-sectional view of H4
Figure 5. Plan view SEM images of anatase columns on (a) H4; (b) typical NsARC
Figure 5. Plan view SEM images of rutile columns on (a) H4; (b) typical NsARC
Figure 5. 19 (a) SEM image of anatase and rutile crystals of the H4 sample; (b) Corresponding HRTEM image showing the ROIs used for crystallographic analysis.
5.3.2 Anatase Phase of H4

The HRTEM image in Figure 5.20 shows the top of an anatase crystal on H4 sample with the region of interest identified for reference. The FFT inset in Figure 5.21 was used to determine the lattice planes observed in the HRTEM image as A\{101\} and A\{103\}. The VESTA crystal model in Figure 5.21 (b) was constructed to show the relative positions of the A\{101\} and A\{103\} at the top surface of the anatase crystal. The direction of the A[110] lattice planes has been provided to indicate the growth-direction of the anatase crystal columns. A different VESTA model was constructed using the A[1\bar{0}1] and A(103) planes to visualize the orientation of the observed surfaces in comparison to the top of the H4 anatase crystal. The Figure 5.22 shows the most probable locations of the A\{101\} and A\{103\} facets on the H4 anatase crystal.
Figure 5. 20 TEM image of the top of a H4 anatase crystal. The ROI for HRTEM is highlighted in the red square.
Figure 5. 21 (a) HRTEM image of H4-A1 with FFT inset; (b) VESTA crystal model showing the observed exposed facets with respect to the A[110] growth direction.
Figure 5. 22 VESTA lattice plane model showing the positions of A\{101\}, A\{103\} and A\{004\} crystal surfaces with respect to the A[110] growth orientation for Anatase.

HRTEM image of the center of the anatase column on H4 is shown in Figure 5. 23. The image clearly shows the A\{112\} and A\{101\} lattice planes. The VESTA crystal model in Figure 5. 23 (b) shows the position of the aforementioned lattice planes with respect to the A[110] growth orientation. There are no exposed facets at this particular ROI in the H4 anatase crystal column.
Figure 5. 23 (a) HRTEM image of H4-A2 (anatase core) with FFT inset; (b) VESTA crystal model showing the observed lattice planes with respect to the A[110] growth direction.
Figure 5. 24 shows the HRTEM image of an anatase plate tip observed on the H4 sample. The image clearly shows the A\{101\} and A\{112\} lattice planes at the edge of the tip. The A\{112\} lattice planes are along the long edge of the plate while the short edge of the plate tip is terminated by the A\{101\} lattice planes.
Figure 5. 24 (a) HRTEM image of H4-A2 (anatase plate-tip) with FFT inset; (b) VESTA crystal model showing the observed exposed facets with respect to the A[110] growth direction.
The crystal columns at the interface of the H4 coating and the FS substrate exhibit similar crystallographic characteristics as the H2 samples. The H4 coating has indistinguishable crystal columns at the substrate interface with the A(101) planes clearly evident in the HRTEM image provided in Figure 5. The crystal model in Figure 5 (b) is solely to provide insight into the position of the A{101} lattice planes with respect to the A[110] growth direction.
Figure 5.25 (a) HRTEM image of H4-A3 (film-substrate interface) with FFT inset; (b) VESTA crystal model showing the A(101) lattice planes with respect to the A[110] growth direction
5.3.3 Rutile Phase of H4

The similarities between the surface morphology of H4 rutile columns and the rutile columns of a typical NsARC coating have been shown in Figure 5. 18. The HRTEM image in Figure 5. 26 shows the top of a H4-rutile column. The lattice spacing and orientation of the R{220} planes have been derived from the FFT inset. These planes are not immediately evident in the provided image. A composite model created by layering the VESTA model from Figure 5. 26 (b) is compared to the plane view SEM image of the H4 rutile column. The Figure 5. 27 compares the crystal facets from the model with the nanoscale features on the physical column. The model also demonstrates that the nanoscale features on the H4 rutile columns are terminated by the R{101} planes and the R{211} planes at the top of the columns.
Figure 5. 26 (a) HRTEM image of H2-R1 (rutile-top) with FFT inset; (b) VESTA crystal model showing the predicted exposed facets with respect to the direction of R[110] planes.
**Figure 5.** 27 VESTA crystal model showing the positions of $R\{101\}$ and $R\{211\}$ crystal surfaces for H4 with respect to the $R\{110\}$ lattice plane direction for rutile.

The HRTEM image of the center of the rutile column for H4 is provided in Figure 5. 28. The FFT inset and the lattice planes exhibit anatase phase crystallographic signature. The A$[110]$ planes are perpendicular to the substrate surface and this result is concurrent with the growth texture analyzed from XRD. The VESTA crystal model in Figure 5. 28 (b) shows the relative positions of the A$\{112\}$ and A$\{101\}$ planes with respect to the A$[110]$ lattice planes.
**Figure 5.** 28 (a) HRTEM image of H4-R2 (rutile-core) with FFT inset; (b) VESTA crystal model showing the location of the A{211} and A{101} lattice planes with respect to the direction of A{110} planes.
Figure 5. 29 shows the HRTEM image of four rutile nanoscale dendrites. The analysis of the lattice spacing values from the FFT inset show that the plates are composed of the R\{200\} and R\{110\} crystal planes. The R\{200\} planes are not as evident as the R\{110\} planes and can only be observed on the edge of the plate. The R\{110\} planes terminate the R\{200\} plates and form the corner of the dendritic features observed on the rutile columns of H4.
Figure 5.29 (a) HRTEM image of H4-R2 (rutile dendrite-tip) with FFT inset; (b) VESTA crystal model showing the location of the R\{110\} and R\{100\} planes with respect to the direction of R[110] planes.
The Figure 5. 30 shows the HRTEM image for the interface of the rutile crystal with the FS substrate. It is concurrent with all the other HRTEM images obtained at the film-substrate interface and shows that the ROI H4-R3 exhibits polycrystalline signature for anatase phase TiO$_2$. 
Figure 5. 30 (a) HRTEM image of H4-R3 (film-substrate interface) with FFT inset; (b) VESTA crystal model showing the location of the A[101] planes with respect to the growth direction of A[110] planes.
5.3.4 Summary of Crystallographic Orientations Observed in H4

The Figure 5.31 shows illustrations of anatase and rutile columns of H2 NsARC coatings with the exposed facets and crystallographic orientations at the four main ROIs. The HRTEM analyses showed that the rutile crystals grow out of anatase nucleation sites. The rutile crystal in H4 also exhibited anatase signature at the center of the crystal (ROI H4-R2).
Figure 5. 31 Summary of HRTEM results for H4 – (a) anatase crystal column; (b) rutile crystal column
5.4 Discussion

The PCA results showed that the H2 sample is almost twice as active as H4. This is due to the \{105\} facets exposed on H2 and the \{103\} facets exposed on H4. The sample preparation for HRTEM imaging involves capping the ROIs with a Pt layer. This step makes it challenging to image the tops surfaces of the anatase and rutile columns edge on. Thus, the arrangement of the \{101\} and \{103/5\} lattice planes and the observed zone axis in the line of view was used to deduce that the anatase crystals of NsARC have exposed \{101\} and \{105\} facets (l>1). Chen et al. reported that the \{10l\} (l>1) family of planes or the high index facets of the [010] zone axis exhibited superior photocatalytic abilities. The \{103\} facets in H4 and \{105\} facets in H2 possess high-density atomic steps which theoretically resemble the step-edges described by the authors [1]. DFT calculations by Jiang et al. showed that the \{105\} facets possess higher surface energies than \{103\} crystal facets [6]. This explains the higher PCA observed for the H2 NsARC sample in the DOE sample set. Jiang et al. also observed that the formation of the \{105\} faceted crystal was time-dependent. They reported that as the deposition time progressed, the \{101\} facets transitioned to \{105\} facets at high processing temperatures [6]. For the sample H2, both the processing temperature and the duration of deposition are higher than H4 providing ideal conditions for the formation of the \{105\} facets. The lower deposition time and processing temperature for H4 results in the formation of the lower energy \{103\} crystals.

The feather-like nanostructures on the anatase columns for H2 and H4 are composed of \{101\} and \{112\} crystal planes. Oliver et al. and Sushko et al. reported that the \{112\} crystal facets possess higher surface energies than the naturally occurring \{101\} facets [7, 8]. Sushko et al. reported that the exposure of \{112\}
crystal facets leads to highly oriented 3D crystal structures that are potential photocatalytic materials.

H2 and H4 NsARC coatings exhibited the presence of rutile columns that have anatase nucleation sites. Rutile has been reported to nucleate on the A{112} surfaces of anatase crystals in the absence of impurities and dopants [9]. As both H2 and H4 possess exposed A{112} facets, it is can be deduced that the exposed A{112} facets have transitioned into the rutile phase when the deposition conditions are suitable [10]. The cause for selective transition of anatase to rutile is not yet determined.

5.5 Conclusion
The exposed high-energy facets for H2 and H4 have been determined and their role in enhancing the visible light PCA of these samples has been established. The high-energy A{103}, A{105} and A{112} facets are also unstable. The next step is to establish the reasons for the appearance and stability of these high-energy facets. In forensic investigative approach, the next chapter is a continuation of the step – ‘Establishing the motive(s) of the Perpetrator’.

References


Chapter 6: Role of Carbon in Inducing Nanostructures on TiO$_2$

The previous chapter described the different facets of anatase and rutile crystals in NsARC coatings by analyzing the two most active samples (H2 & H4) prepared using the DOE parameter matrix. The stabilization of the high-energy exposed facets was attributed to the co-deposition of pyrolytic carbon during the pp-MOCVD process. Raman spectroscopy conducted during the preliminary investigations showed that NsARC coatings deposited with temperatures $\geq 450 \, ^\circ C$ were composites of TiO$_2$ and amorphous carbon. The black color of the coatings provided visual proof of the presence of carbon, but the distribution of carbon has not yet been determined.

In this chapter, EELS spectroscopy was used to determine the location of carbon in the H2-NsARC coating. The results were used to deduce the role of carbon co-deposition in the nanostructuring of the TiO$_2$ composite coatings prepared by pp-MOCVD.
6.1 Electron Energy Loss Spectroscopy of NsARC

The EELS analysis was performed on the two most active samples identified from the NsARC sample set prepared for DOE. The deposition conditions of H2 are recapped in Table 6.1.

Table 6.1 Deposition parameters of samples H2

<table>
<thead>
<tr>
<th>ID</th>
<th>Deposition temperature</th>
<th>Precursor concentration</th>
<th>Injection Volume</th>
<th>Base Pressure</th>
<th>Number of pulses</th>
</tr>
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<tr>
<td>H2</td>
<td>525 °C</td>
<td>3 mol%</td>
<td>500 μL</td>
<td>85 Pa</td>
<td>1000</td>
</tr>
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</table>

The qualitative analysis of carbon content in the H2 NsARC coatings was performed using Raman Spectroscopy. The Raman spectrum for H2 is shown in Figure 6.1. The obtained spectrum was deconvoluted using a Gaussian fitting to obtain the peak information for compositional analysis. The spectrum exhibits the peaks for anatase, rutile and amorphous carbon. The spectrum also shows that the amorphous carbon does not dope or alter the chemical composition of TiO₂ in the H2-NsARC coating in any manner. The peak information from the deconvolution is provided in Appendix A1.
Figure 6. 1 Representative Raman spectrum for H2-NsARC coating.
The STEM image in Figure 6.2 shows the cross-section of H2 on fused silica substrate. Three ROIs (highlighted in red) were selected in the FIB lamella where anatase and rutile columns were evident. A detailed STEM image of the highlighted ROIs is shown in Figure 6.3.

*Figure 6.2 STEM image showing the cross-section of H2-NsARC films on FS substrate with the ROI highlighted in red.*
Figure 6. 3 STEM image of the ROI of H2 showing the anatase and rutile columns.
The sample for EELS analysis was obtained by preparing a FIB lamella from the H2 sample. EELS was performed using a JEOL Grand-ARM 300CF equipped with a GIF Quantum Summit spectrometer. The spectra were collected in the low-loss region and the core-loss region. The spectra were accumulated with a resolution of 2048×2048 pixels and 2048 channels for one data set. The experimental energy dispersion was set at 0.25 eV/channel. The obtained spectra were post-processed using the GMS 3 (Gatan Inc.).

Figure 6. 4 provides the representative ZLP and core-loss spectra for the H2-NsARC film. Figure 6. 4 (b) shows the ionization edges of C_K (284.1 eV), Ti_L (456.1 eV) and O_K (532 eV). The ionization edges of the spectra were identified using the EELS database [1-3]. The results showed that NsARC coatings are composed of stoichiometric TiO₂ and co-deposited amorphous carbon.
Figure 6. 4 EELS (a) Zero-loss spectrum & (b) core-loss spectrum showing the presence of C, Ti and O in the H2-NsARC sample.
Multiple EELS spectra were obtained from the The accumulated EELS spectra were used to prepare composite spectral maps showing the relative location of the different elements in the corresponding STEM image. Figure 6. 5 shows the EELS spectral maps obtained for Ti and O in the H2-NsARC sample. The spectral map for carbon is shown in Figure 6. 6.

The spectral maps for Ti and O appear identical to the STEM image of the selected ROI. The spectral map for C shows that the amorphous is distributed in the nanostructure of the NsARC coating.
Figure 6.5 STEM image and corresponding EELS spectral maps for Ti and O.
Figure 6. STEM image and corresponding EELS spectral maps showing C distribution in H2NsARC
The distribution of carbon around anatase and rutile columns was evaluated by preparing a mosaic plot of the EELS spectral map for C. EELS spectral maps provided the information for areal density and percentage composition of the distribution of C in the NsARC films. The mosaic plot of the C\textsubscript{k} EELS spectral map is provided in Figure 6. The mosaic plot of the ROI was generated by dividing the anatase and rutile columns into 30 100 nm × 100 nm regions each. Table 6.2 provides the carbon atomic % around anatase and rutile. The atomic percentage evaluation does not show a significant difference in the values for carbon distribution around anatase and rutile.
Figure 6. Mosaic plot of the ROI on H2 used to determine the distribution of C around anatase (Green Boxes) and rutile (white boxes).

Table 6.2 Atomic percentage of carbon around anatase and rutile

<table>
<thead>
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<th>Phase</th>
<th>Carbon at. %</th>
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<tr>
<td>Rutile (white boxes)</td>
<td>2.30 ± 0.16</td>
</tr>
<tr>
<td>Anatase (green boxes)</td>
<td>2.02 ± 0.40</td>
</tr>
</tbody>
</table>
6.2 Affinity of Carbon to High-Energy Exposed Facets

The HRTEM analysis in Chapter 5 provided evidence through deductions that the exposed facets in H2 and H4 possess high surface energies. The deposition of carbon on these exposed facets is a likely contribution to their stability during the extreme deposition conditions of pp-MOCVD. Calatayud et al. report using oleic acid to selectively tailor the morphology of anatase nanoparticles. The authors reported that the ligands of oleic acid preferentially attach to the high-energy surfaces of anatase crystals promote their stability during the synthesis process [4]. Chen et al., report using carbonate ions as capping agents to stabilize and expose the high-energy facets of anatase crystals [5]. Similar phenomenon has been described by other research groups. The commonality in these experimental studies is the stabilization of the [001] facets using carbon-based chemicals. There are fewer studies on the stability of high-energy facets of rutile, however the PCA of rutile R{111} surfaces has been studied under visible light. Zhang et al. report that rutile R{111} exhibits superior visible light and UV PCA because of its lower charge recombination rates [6].

Based on the results of HRTEM and EELS analysis coupled with the background literature, it can be asserted that NsARC samples possess high-energy exposed anatase and rutile facets that are stabilized by amorphous carbon co-deposition. The location of carbon between the nanoscale features on the anatase and rutile columns leads to the deduction that carbon co-deposition occurs with every pulse during the pp-MOCVD deposition process.
References


Chapter 7: Discussion & Conclusion

The thesis was aimed at elucidating the factors that were responsible for the high visible light PCA of NsARC coatings deposited by the pp-MOCVD system. Three different studies were performed to determine the applicability of NsARC coatings on antimicrobial touch surfaces. The evidence obtained at different stages of this doctoral research is reconstructed to deduce the crystal structures that would be involved in the PCA of NsARC coatings. The research work was carried out in four stages. The characteristics of NsARC coatings responsible for high PCA have been deduced by answering the following research questions:

1. What is NsARC and is it feasible coating for antimicrobial touch-surfaces?
2. How do the pp-MOCVD deposition parameters influence the growth of the NsARC films?
3. What are the reasons for the high PCA of certain variants of the coatings prepared by pp-MOCVD?
4. What influence does carbon have on the nanostructures observed in the NsARC coatings?

7.1 Characteristics and Performance of NsARC Coatings

NsARC films deposited in the mass-transport controlled regime exhibit high growth-rates and conformality [1]. The growth-rate studies were performed with coatings deposited at 525 °C.

Three samples with different thicknesses (0.50 μm – 11.50 μm) were investigated to determine the growth-rates of samples deposited at high temperatures. All three samples exhibited mixed-phase composition and co-deposited amorphous carbon. The samples also exhibited a remarkable texture in the A[220] direction. The XRD results
showed that the texture coefficient of the anatase phase of the NsARC coatings increased with increasing film thickness. Highly textured materials have been reported to exhibit higher photocatalytic activity than their un-textured or nanoparticle counterparts. This is supported by the work of Hou et al. The authors report that TiO$_2$ films oriented in the A<101> direction exhibit a higher rate of 4-chlorophenol degradation than TiO$_2$ nanoparticles [2]. Byun et al published similar results where they report enhanced photocatalytic performance of TiO$_2$ with a preferential orientation in the A[112] direction [3].

The focus of the thesis was now narrowed down to highly-textured NsARC samples deposited at 500 ± 25 °C. The SEM images showed that 11.5 μm NsARC sample exhibited two distinct morphological characteristics of TiO$_2$ crystals. The ASTAR™ results showed that the pyramidal plated columns were anatase single crystals and the dendritic columns were rutile. The anatase and rutile columns exhibited nanostructured features along the length of the columns. The enhancement of SSA was studied using methylene blue dye adsorption tests. Antimicrobial tests performed using the ISO standard test showed that the NsARC samples were capable of reducing viable bacterial cell count by 99.99% after four hours of exposure to visible and UV light sources.

The AMA of the films is due to the production of ROS by NsARC crystal surfaces that generate electron and hole pairs upon photonic irradiation. The photoactivity of TiO$_2$ under UV is a well-known phenomenon. The visible light absorption of the NsARC is explained by presence of a layer pyrolytic carbon on the crystal surfaces. The interesting behavior of the NsARC coatings was observed when the samples exhibited a 2log reduction of bacterial cell count in the dark. The postulate for killing in the dark is that the surface morphology of the NsARC coatings is proving
to be unfavorable to bacterial colonization. The reviews by Bandara et al. and Lin et al. support this postulate. The authors report the efficiency of nanostructured and nanopatterned surfaces in bacterial cell-membrane distortion [4, 5]. It is also possible that the NsARC coatings are capable of modifying the zeta-potential of the bacteria cell-membranes [6]. The modification of zeta-potential leads to cell-wall distortion in turn causing the death of the bacterial cells.

**7.2 Influence of the pp-MOCVD Operation Parameters on NsARC performance**

Preliminary investigations into the performance and characteristics of NsARC coatings provided the ranges of pp-MOCVD operating parameters in which the visible light activated materials could be deposited. The operating parameters that produce the highest AMA NsARC are required in order to reliably manufacture NsARC coatings. The commercialization of pp-MOCVD system necessitates a thorough understanding of the influence of the various operating parameters on the NsARC coatings.

The pp-MOCVD process has five deposition parameters that influence the structure and composition of the resultant NsARC coatings. A novel approach based on the principles of ‘Forensic Science’ was used evaluate the that factors that influence the PCA of NsARC coatings. The Design of Experiments approach was used to statistically determine the significant influences of the various operating parameters on the resultant films.

The results of the DOE identified two NsARC samples that exhibited high visible light PAC. The results of the DOE showed that the responses that were significantly influenced by all the parameters (negative or positively) were the PCA and the anatase texture. The other responses that were being influenced by one or more
Deposition parameters were the thicknesses of the coatings, columnar diameters and surface wettability. The current range of pp-MOCVD operating parameters did not influence the surface roughness measurements and the phase ratios of the coatings.

The variation of PCA with the growth texture of anatase showed that the visible light-active NsARC coatings possess highly oriented anatase crystals but the converse is not true. The variation of PCA of the NsARC films with growth-rates and columnar diameters exhibit similar trends. The PCA of the films was observed to increase with the growth-rates and columnar diameters up to a certain point beyond which the PCA drops significantly. This can be explained by the available SSA on the NsARC crystal columns.

Nanostructured features on crystal surfaces with dimensions approximately 15 nm have been reported to exhibit superior PCA due to reduced recombination of electrons and holes [7, 8]. The nanoscale features on the samples that exhibit higher growth-rates and larger columnar diameters are measured to be greater than 15 nm mitigating the electron-hole pair migration to the surface of the NsARC films. The absence of observable nanostructures on the samples with slower growth-rates is evident from the plan-view SEMs and this shows that NsARC coatings without sufficiently dimensioned nanoscale features are not capable of exhibiting visible light PCA.

An interesting observation in the DOE NsARC samples is their characteristic surface roughness and surface-wettability. The DOE analysis shows that surface roughness of the coatings is not significantly influenced by the pp-MOCVD deposition parameters. The variation of surface roughness with PCA also shows a weak trend. It
can concluded that surface roughness values do not affect the performance of the NsARC coatings prepared in the current DOE parameter range.

Water contact angles of DOE NsARC surfaces are significantly influenced by the precursor injection volume and the precursor concentration. High precursor concentration and injection volumes deposit films with a higher WCAs. High WCAs on the surface imply that the surface possesses a lower surface energy [9]. The review by Fujishima et al. on TiO$_2$ photocatalysis reports that efficiency of photocatalysis is directly proportional to the surface energy of the semiconductor [10]. However, the DOE NsRAC samples deviate from this reported behavior. The most active samples exhibit hydrophilic surface properties. The lowest WCA was measured on a sample that is five times less active than the most active sample. The low activity can be attributed to the higher charge recombination rate in the sample that exhibits low PCA.

The only common deposition parameters for the most active samples in the DOE set are the injection volume and the working base pressure of the pp-MOCVD system. The influence of the deposition temperature shows that the sample deposited at the lower operating temperature of 475 °C exhibits lower PCA than the one deposited at 525 °C. The results also showed that, within the frame of the pp-MOCVD operating parameters set for DOE, the samples with higher precursor concentration and higher number of pulses exhibit higher PCA. The number of pulses positively influences the anatase growth-texture and the resulting orientation. At this stage of the Forensic Approach to materials design, I postulate that the crystallographic orientation of the nanoscale features on the visible light active samples are responsible for the high PCA exhibited by these samples.
7.3 Determination of the Crystal Facets on Visible Light-Active NsARC

HRTEM imaging was used to analyze the crystallography of the NsARC samples that exhibit high visible light PCA. The analysis of the film and substrate interfaces showed that at early stages of deposition the NsARC films nucleate in the anatase phase. The HRTEM images of the interfaces also showed that the anatase exhibits polycrystalline behavior in the early stages of film growth. Similar behavior of NsARC thin films was reported by Gardecka et al. [11]. As the deposition progresses, competitive growth of crystals causes the anatase phase to orient in the A[220] growth direction. At the end of the deposition, the fully grown anatase columns possess exposed A{101} facets and A{103/5} facets. The sample that exhibits higher PCA possesses exposed A{105} facets [12].

The appearance of rutile in the films is not completely understood at this stage. HRTEM results have shown that certain anatase columns transition to rutile at sufficiently high temperatures and growth-rates [13]. Literature reviews have theoretically demonstrated that in the absence of impurities and dopants the A{112} facets of anatase transform into rutile. The visible light active NsARC films exhibit the presence of A{112} facets at the tips of nanostructures. The A{112} facets are normally unstable when they are formed but they could be stabilized by means of carbon capping during the deposition process [14]. I postulate that the amorphous carbon co-deposition has a role in the selective transition of certain anatase columns to rutile. It can be deduced that when the A{112} are not capped by carbon due to competitive growth and crystal shadowing effects in the deposition chamber they transform into the more stable rutile phase of TiO₂.
7.4 Role of Carbon

In this stage of the Forensic approach, NsARC samples were studied using atomic-resolution EELS. The EELS analysis of the coatings showed that the amorphous carbon is distributed uniformly in the nanostructures of the NsARC samples. These results support the theory that carbon capping during the deposition process stabilized the exposed high-energy A\{112\} facets. However, the carbon content is uniform along the lengths of both anatase and rutile columns. The results show that carbon capping is a continuous process during the deposition. I postulate that the shadowed crystals transitioned to rutile during a certain pulse cycle. Once the transition has taken place, as long as the deposition process is progressing the carbon capping will occur with every pulse. This phenomenon could explain the appearance of the nanoscale dendrites on rutile columns.
7.5 Conclusion and Future Work

The ‘Forensic Approach’ to materials design was aimed at answering the following research questions:

1. What is NsARC and is it feasible coating for antimicrobial touch-surfaces?

Nanostructured Anatase Rutile Carbon Composite coating is a visible light activated photocatalytic material that can be deposited on a range of surfaces for self-cleaning and antimicrobial applications. The durability tests indicate that NsARC is a robust coating for high-touch applications.

2. How do the pp-MOCVD deposition parameters influence the growth of the NsARC films?

This study demonstrated that the nanostructures on the NsARC films are induced by the pp-MOCVD deposition process. The five deposition parameters influenced the films growth to varying extents. In the mass-transport controlled regime the most significant influence on the performance and characteristics of the NsARC coatings was due to the variation in the precursor concentration and the pulse-rate.

3. What are the reasons for the high PCA of certain variants of the coatings prepared by pp-MOCVD?

The most active NsARC samples exhibit the presence of exposed high-energy facets on the crystal surfaces. The high visible light PCA is also attributed to the accumulation of carbon on the crystal surfaces. Carbon is capable of absorbing the low energy photonic-radiation and extending the bandgap of the NsARC coatings to the visible spectrum.
4. What influence does carbon have on the nanostructures observed in the NsARC coatings?

The co-deposition of pyrolytic carbon with every pulse was deduced to be the reason for the nanostructures formed on the anatase and rutile columns of the NsARC coatings. It was postulated that the absence of carbon co-deposition on certain high energy anatase facets facilitated these facets to transition into the rutile phase. The quantitative analysis of carbon content in the NsARC films requires further investigation. The future work would entail using atomic-resolution ASTAR™ phase mapping to determine the location of anatase-to-rutile transformation sites in the NsARC coatings.

References


Appendix-A1: Lattice Spacing Values for Anatase & Rutile and Raman Peak IDs

Table A1.1 Miller indices and corresponding $2\theta$ values for anatase and rutile lattice planes

<table>
<thead>
<tr>
<th>Phase</th>
<th>$2\theta$ (Degrees)</th>
<th>Miller indices (hkl)</th>
<th>$d_{hkl}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A(101)</td>
<td>3.52</td>
</tr>
<tr>
<td></td>
<td>25.3</td>
<td>A(103)</td>
<td>2.43</td>
</tr>
<tr>
<td></td>
<td>36.9</td>
<td>A(004)</td>
<td>2.38</td>
</tr>
<tr>
<td></td>
<td>37.8</td>
<td>A(112)</td>
<td>2.33</td>
</tr>
<tr>
<td></td>
<td>53.9</td>
<td>A(105)</td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>55.1</td>
<td>A(211)</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td>70.3</td>
<td>A(220)</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>82.14</td>
<td>A(224)</td>
<td>1.17</td>
</tr>
<tr>
<td>Anatase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.5</td>
<td>R(110)</td>
<td>3.25</td>
</tr>
<tr>
<td></td>
<td>36.1</td>
<td>R(101)</td>
<td>2.49</td>
</tr>
<tr>
<td></td>
<td>39.2</td>
<td>R(200)</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>41.2</td>
<td>R(111)</td>
<td>2.19</td>
</tr>
<tr>
<td></td>
<td>44.1</td>
<td>R(210)</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>54.3</td>
<td>R(211)</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td>64.08</td>
<td>R(310)</td>
<td>1.45</td>
</tr>
<tr>
<td>Rutile</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table A1. 2 Raman shift peak IDs for anatase, rutile and amorphous carbon

<table>
<thead>
<tr>
<th>Raman Shift (cm(^{-1}))</th>
<th>Chemical Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>145 (A(_1))</td>
<td>Anatase TiO(_2)</td>
</tr>
<tr>
<td>196 (A(_2))</td>
<td></td>
</tr>
<tr>
<td>399 (A(_3))</td>
<td></td>
</tr>
<tr>
<td>517 (A(_4))</td>
<td></td>
</tr>
<tr>
<td>638 (A(_5))</td>
<td></td>
</tr>
<tr>
<td>445 (R(_1))</td>
<td>Rutile TiO(_2)</td>
</tr>
<tr>
<td>1396 (D(_1))</td>
<td>Carboxylate</td>
</tr>
<tr>
<td>1436 (D(_2))</td>
<td>CH(_2) (weak polymeric chain)</td>
</tr>
<tr>
<td>1469 (D(_3))</td>
<td>Aromatic ring</td>
</tr>
<tr>
<td>1509 (D(_4))</td>
<td>Aromatic ring</td>
</tr>
<tr>
<td>1598 (G(_1))</td>
<td>Aromatic/hetero ring</td>
</tr>
<tr>
<td>1624 (G(_2))</td>
<td>C=C (sp(^2) bond)</td>
</tr>
</tbody>
</table>
Appendix-A2: DOE NsARC Images and Characterization Results

Experiment Zero – ZA, ZB, ZC

Photocatalytic Activity (PCA)

\[
\text{PCA} = 4.0 \times 10^{-4} \text{ min}^{-1}
\]
Optical Bandgap from Tauc plot

Bandgap of Z = 1.80 eV
Plan-View Surface SEM

Anatase columnar diameter = 438 ± 48 nm
Surface Topography

RMS value = 162 nm

Water Contact Angle

WCA = 41±4°
X-ray Diffraction

Anatase TC for A[220] = 4.78

Anatase-to-rutile phase ratio = 2.72
Raman Spectrum
Experiment – H1

Photocatalytic Activity (PCA)

\[ \text{PCA} = 1.2 \times 10^{-3} \text{ min}^{-1} \]
Optical Bandgap from Tauc Plot

Bandgap = 1.80 eV
Plan-View Surface SEM

Anatase columnar diameter = 730 ± 23 nm
Surface Topography

RMS value = 115.8 nm

Water Contact Angle

WCA = 87 ± 4°
X-ray Diffraction

Anatase TC = 4.90

Anatase-to-rutile phase ratio = 4.88
Raman Spectrum
Experiment – H2

Photocatalytic Activity (PCA)

\[ \text{PCA} = 4.8 \times 10^{-3} \text{ min}^{-1} \]
Optical Bandgap from Tauc Plot

Bandgap = 1.79 eV
Anatase columnar diameter = 517 ± 30 nm
Surface Topography

RMS value = 136 nm

Water Contact Angle

WCA = 36 ± 2°
X-ray Diffraction

Anatase TC = 4.90

Anatase-to-rutile phase ratio = 3.10
Raman Spectrum
Experiment – H3

Photocatalytic Activity (PCA)

\[ PCA = 1.2 \times 10^{-3} \text{ min}^{-1} \]
Optical Bandgap from Tauc Plot

Bandgap = 1.79 eV
Plan-View Surface SEM

Anatase columnar diameter = 307 ± 28 nm
Surface Topography

RMS value = 57.4 nm

Water Contact Angle

WCA = 51 ± 10°
X-ray Diffraction

Anatase TC = 4.55

Anatase-to-rutile phase ratio = 2.35
Raman Spectrum
Experiment – H4

Photocatalytic Activity (PCA)

\[ \text{PCA} = 2.6 \times 10^{-3} \text{ min}^{-1} \]
Optical Bandgap from Tauc plot

Bandgap = 1.80 eV
Anatase columnar diameter = 474 ± 79 nm
Surface Topography

RMS value = 119.1 nm

Water Contact Angle

WCA = 83 ± 5°
X-ray Diffraction

Anatase TC = 4.76

Anatase-to-rutile phase ratio = 2.61
Raman Spectrum
Experiment – H5

Photocatalytic Activity (PCA)

\[ \text{PCA} = 4.0 \times 10^{-4} \text{ min}^{-1} \]
Optical Bandgap from Tauc Plot

Bandgap = 1.79 eV
Anatase columnar diameter = 338 ± 27 nm
Surface Topography

RMS value = 79.2 nm

Water Contact Angle

WCA = 24 ± 6°
X-ray Diffraction

Anatase TC = 4.92

Anatase-to-rutile phase ratio = 2.51
Raman Spectrum
Experiment – H6

Photocatalytic Activity (PCA)

\[ PCA = 8.0 \times 10^{-6} \text{ min}^{-1} \]
Optical Bandgap from Tauc Plot

Bandgap = 1.78
Plan-View Surface SEM

Anatase columnar diameter = 204 ± 10 nm
Surface Topography

RMS value = 45 nm

Water Contact Angle

WCA = 19 ± 3°
X-ray Diffraction

Anatase $TC = 3.13$

Anatase-to-rutile phase ratio $= 1.41$
Raman Spectrum
Experiment – H7

Photocatalytic Activity (PCA)

\[ PCA = 2 \times 10^{-4} \text{ min}^{-1} \]
Optical Bandgap from Tauc Plot

Bandgap = 1.80 eV
Plan-View Surface SEM

Anatase columnar diameter = 460 ± 78 nm
Surface Topography

RMS value = 86.8 nm

Water Contact Angle

WCA = 28 ± 6°
X-ray Diffraction

Anatase TC = 4.67

Anatase-to-rutile phase ratio = 2.97
Raman Spectrum
Experiment – H8

Photocatalytic Activity (PCA)

\[ \text{PCA} = 9 \times 10^{-4} \text{ min}^{-1} \]
Optical Bandgap from Tauc Plot

Bandgap = 1.81 eV
Anatase columnar diameter = 670 ± 100 nm
Surface Topography

RMS value = 116.6 nm

Water Contact Angle

WCA = 14 ± 1°
X-ray Diffraction

Anatase $\text{TC} = 4.92$

Anatase-to-rutile phase ratio $= 2.98$
Raman Spectrum
Experiment – H9 (‘-1’)

Photocatalytic Activity (PCA)

\[ PCA = 8.0 \times 10^{-6} \text{ min}^{-1} \]
Optical Bandgap from Tauc Plot

Bandgap = 1.80 eV
Plan-View Surface SEM

Anatase columnar diameter = 291 ± 28 nm
Surface Topography

RMS value = 62.8 nm

Water Contact Angle

WCA = 19 ± 2°
X-ray Diffraction

Anatase TC = 3.75

Anatase-to-rutile phase ratio = 5.28
Raman Spectrum