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Study of Nanostructured Semiconductor Metal Oxide as Visible-Light Photocatalyst

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Statement of Originality

I hereby certified that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other university or institution.

Date

Tan Pei Yun

Summary

Since the discovery of the “Fujishima-Honda” effect almost five decades ago, research on photocatalyst effect has been extensive and wide applications have been developed. These include water-splitting, removal of volatile-organic-compounds (VOCs), as well as disinfection for improved air and water quality. In recent years, there have been increasing global awareness to adopt more environmental-friendly approaches. Therefore, photocatalytic oxidation (PCO) process provides a clean alternative for disinfection and removal of environment pollutants and industrial wastes. The current market leader, titanium dioxide (TiO_2) is limited by its large bandgap of 3.2 eV to be efficient only under UV light.

In this research project, a low-cost and simple process which allows large-scale preparation of nitrogen-doped TiO_2 was firstly explored and presented. By oxidizing nano-sized titanium nitride (TiN) powder, mixed phase TiO_2 with visible-light absorption up to 525 nm was obtained. The powder oxidized at 500 °C demonstrated good Rhodamine B and gaseous toluene removal; in addition to *E. Coli* killing under the illumination of fluorescent light with $\lambda > 435$ nm. High-resolution X-ray photoelectron spectroscopy (XPS) was used to investigate the binding states of the nitrogen dopants and their effects on the overall photocatalytic performance. The charge separation efficiency was also studied through the powders’ surface photovoltage spectra and enhanced separation was observed at higher annealing temperature.

Next, this project explored a new, potential candidate for visible-light active semiconductor photocatalyst with tailorable bandgap; in the form of strontium titanate

ferrite ($\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$). Based on previous successful work by our research group on high energy ball-milled $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ nanopowder, the project aim was to develop a fabrication process for $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films using sol-gel approach. Using a modified sol-gel based on Pechini's method of polymerizable metal complex, $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films for the whole range of $0 \leq x \leq 1$ had been successfully fabricated and characterized for its potential as visible-light photocatalyst.

The devised fabrication protocol had produced uniformly coated thin films with good adhesion. The thin films had nanoporous surfaces which are beneficial for applications which require large surface-to-volume ratio. Optical study revealed bandgap reduction from 3.46 eV to 1.10 eV with increasing iron content. However, evaluation of their photocatalytic potential using Rhodamine B, bis-phenol A and stearic acid did not show obvious photocatalytic reaction despite their bandgaps which are in the visible-light range. Further investigation using XPS study showed the formation of oxygen vacancies needed to maintain charge balance. These defects can act as electron traps which prevented charge transfer to the film surface. Furthermore, the electronic conductivity of the films also increased with iron content. As a result, the films were unable to retain charge carriers long enough on their surfaces for meaningful redox reactions. These were supported by the surface photovoltage spectra where the magnitude of contact potential difference due to light illumination decreased with iron content and decayed quickly.

More investigations and diverse characterizations need to be explored to overcome these issues. For example, co-doping of non-metals and noble metals could help to overcome the charge imbalance due to substitution of Ti^{4+} with Fe^{3+} ; thereby reducing the formation of oxygen vacancies. Another method could be restricting the amount of iron

content to lower doping levels to limit the formation of oxygen vacancies while still extending the bandgap sufficiently into the visible-light range. Lastly, to increase surface area, other visible-light active photocatalyst can be embedded into the nanoporous structure of the films, which serves as holding matrix.

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List of Symbols

AO8	: Acid orange 8
CPD	: Contact potential difference
EHP	: Electron-hole pairs
PCO	: Photocatalytic oxidation
PVP	: Poly-vinylpyrrolidone
$\text{SrFeO}_{3-\delta}$	: Strontium ferrite with non-stoichiometric oxygen
$\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$	: Strontium titanate ferrite
STF01	: $\text{Sr}(\text{Ti}_{0.9}\text{Fe}_{0.1})\text{O}_{3-\delta}$
STF02	: $\text{Sr}(\text{Ti}_{0.8}\text{Fe}_{0.2})\text{O}_{3-\delta}$
SrTiO_3	: Strontium titanate
SPV	: Surface photovoltage spectra
TiN	: Titanium nitride
TiO_2	: Titanium dioxide
VOC	: Volatile organic compounds

CHAPTER 1. INTRODUCTION

1.1 Project Background

A photocatalyst is a substance that is activated by the absorption of a photon and acts as a catalyst to accelerate a reaction, while the catalyst itself remains unchanged and unconsumed at the end of the reaction [1, 2]. When light with appropriate wavelength is illuminated on a photocatalyst, electron-hole pairs (EHPs) are generated by absorption of the light. These charge carriers can then diffuse to the photocatalyst surface, where reactive species such as hydroxyl radicals and hydrogen peroxide can be created from adsorbed oxygen and water molecules via a series of redox processes. These radicals are capable of decomposing other surface absorbed organic pollutants or even breakdown bacteria cell walls for disinfection purposes. Usually, these redox processes will produce safe final products such as water and carbon dioxide.

The “Fujishima-Honda” experiment, where photolysis of water molecules was demonstrated in a photo-electrochemical cell with a semiconductor TiO_2 electrode is widely acknowledged as one of the earliest and most significant works on photocatalytic reaction [3]. For the past five decades since their discovery, this work has inspired continuous research on photocatalytic reactions. Research efforts have extended from the initial water splitting study to other applications such as pollutants and volatile organic compounds (VOC) removal, as well as disinfections; both in air and aqueous solutions. [4-9]. Based on these studies, self-cleaning products such as roof tiles, walls and tunnel surfaces have been successfully developed and commercialized [10, 11]. In recent years, there have been increasing global awareness to adopt more environmental-friendly approaches. Therefore, photocatalytic oxidation (PCO) process provides a clean

alternative for disinfection and removal of environmental pollutants and industrial wastes; compared to ozonation, chlorination, and using UV lamps.

For cleaning and disinfection applications, a good photocatalyst should generally have the following attributes:

- Non-toxic and safe to use;
- Good stability during the photocatalytic redox reaction;
- Has suitable bandgap to absorb a large spectrum from the irradiation source;
- High quantum yield and conversion efficiency;
- Low cost.

After light absorption and EHP formation, the positive hole, h^+ serves as oxidizing agent, while the negative electron, e^- is captured by surface adsorbed species for reduction process. This series of redox processes lead to the formation of active super oxide anions and hydrogen peroxide from surrounding oxygen and water. Nevertheless, as with all semiconductor materials, EHP generation is a reversible process. Recombination can occur over time and this is one of the main reasons behind the limited efficiency of most photocatalytic reactions. However, in the presence of electron and hole scavengers such as oxygen and water, recombination can be suppressed and the photocatalytic performance can be improved.

Based on the aforementioned attributes, semiconductor titanium dioxide (TiO_2) has remained the major material of interest for researchers working in the field of photocatalyst. This is because TiO_2 is stable, chemically and biologically inert, inexpensive and currently has the highest photocatalytic efficiency under UV light

illumination. Moreover, TiO_2 has been used as a source for white pigment in paints, paper, and cosmetics since ancient times.

In modern research history, early works on TiO_2 have focused mainly on its photoelectrochemical reactions. During the oil crisis in 1970s, research on alternative energy was of great interest; and the idea of using only light to achieve water-splitting was seen to possess great potential [12]. After years of research to establish fundamental understanding of light-assisted water splitting, scientists moved on to powdered TiO_2 in the form of aqueous suspension to achieve large surface area reactions. By late 70s, the strong oxidizing power of TiO_2 was proven by Frank and Bard for poisonous cyanide ion destruction [13, 14]. In 1980s, Matsunaga and his co-workers reported for the first time, the anti-bactericidal effect of TiO_2 [7]. Towards the end of 1980s, to achieve more convenient waste handling and final products separation, TiO_2 was immobilized on fixed supports such as glass, plastic, mesh or fiber to further widen its industrial applications.

The three common crystalline phases for TiO_2 are anatase, rutile and brookite. At room temperature, anatase and rutile are the more common phases. Studies by many research groups have found that by mixing both phases in optimum ratio, the photoactivity will be better than that of anatase alone [15, 16]. A good demonstration of this is the current market leader for commercial TiO_2 powder, P25 by Degussa. It is a mixed phase TiO_2 with 70% anatase and 30% rutile phase with large BET surface area ($55 \pm 15 \text{ m}^2/\text{g}$) and comparably-sized anatase and rutile crystallites of 30 nm which form aggregates of $0.1 \text{ }\mu\text{m}$ [17].

1.2 Project Motivation

The bandgap of TiO_2 ranges from 3.0 eV to 3.2 eV, which explains its good UV light absorbance but mostly inactivity under visible light illumination. This is manifested in its white colour appearance as well. This stability under visible light also translates to limited efficiency and restricts its usefulness to outdoor applications, especially for self-cleaning purposes using natural sunlight which consists of only 4-7% UV. For indoor applications, due to weak UV intensity, EHP generation is insufficient to produce significant photocatalytic reactions. For decades, there have been relentless efforts in the search for a novel visible-light active photocatalyst, as well as shifting the TiO_2 light absorption towards visible light, to better utilize this largest component of solar light spectrum [11]. These include exploring and evaluating other small bandgap materials (CdS , Cu_2O , Fe_2O_3 , and WO_3) [18], doping TiO_2 with transition metals (Cr, Fe, or Ni) [19, 20] and non-metals (N, S or C) [21-24].

Doping with non-metals appeared to be more effective so far. For example, substitutional nitrogen doping had been found to induce significant red shift in TiO_2 absorption up to 500 nm [21]. The methods used to produce N-doped TiO_2 include sol-gel [25-27], sputtering [21, 28, 29], ion-implantation [30], chemical vapour deposition [31-33], direct amination [34] or by annealing TiO_2 in N_2 or NH_3 [35-37]. With these methods, the doping level rarely goes beyond 2% [38]. Apart from the process limits, when the doping level is too high, the visible light response was found to be lower due to increased recombination rate [29].

Meanwhile, refractory titanium nitride (TiN) has been used for many decades in various applications to achieve mechanical, functional or decorative purposes [39]. Pure titanium nitride oxidizes easily in air with few nanometers of surface oxide [40]. With high temperature annealing, it can be completely oxidized to TiO₂ [41]. Partially oxidized TiN, or oxynitride (TiN_xO_y) has garnered considerable interest due to its properties dependence on the N:O ratio [42-45]. Various forms of TiN_xO_y films were prepared using pulsed-laser deposition [46], magnetron sputtering [47, 48] and plasma enhanced chemical vapour deposition [49]. Thus, direct oxidation of TiN can provide an easy and low-cost method to prepare nitrogen-doped TiO₂. Compared to conventional nitrogen doping methods where nitrogen is often introduced into TiO₂ starting materials, this method may be able to achieve higher nitrogen doping with good control of oxidation process. Upon successful process optimization, the simplicity of this process would allow large volume production, which translates to lower production costs for commercialization purposes.

Besides TiO₂, non-TiO₂ materials have also been explored as potential visible-light photocatalyst, such as perovskite-structured ferroelectric materials. Owing to their high dielectric constants, these materials are traditionally used for DRAM and microwave applications [50-52]. In 1980, the photocatalytic property of SrTiO₃ oxide was first discovered [53-55]. Since SrTiO₃ also has large bandgap similar to TiO₂, doping of SrTiO₃ was widely investigated to extend its usefulness to visible light range [55-58]. On the other hand, SrFeO_{3-δ}, was found to possess redox behaviour [59] and gas sensing properties [60, 61]. As early as 1979, a brownmillerite-like Sr₂Fe₂O₅ compound, which has a perovskite structure with randomly distributed oxygen vacancies had demonstrated

remarkable nitrous oxide (NO) thermal decomposition [62]. More recently, nanostructured SrFeO_3 powder has been reported by our group to be efficient in decolorizing a common industry waste dye, Methylene Blue under visible-light illumination [63].

SrTiO_3 and SrFeO_3 can form a continuous solid state solution in the form of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$. It has been reported that the bandgap of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ system is iron content-dependent and can be reduced from 3.17 eV for SrTiO_3 to that of 2.0 eV for SrFeO_3 [64-66]. Therefore, based on the reported photocatalytic property of SrTiO_3 and small bandgap of SrFeO_3 , $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ appears to be a promising candidate for new visible-light active photocatalyst with tailorable bandgap for indoor photocatalytic applications. Based on the nano-sized visible-light active SrFeO_3 photocatalyst successfully synthesized by our group for methylene blue removal [63], the work in this project will be focused on the development and characterization of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films via sol-gel method followed by the evaluation of its potential as visible-light photocatalyst.

To the best of our knowledge, there is no reported work on the preparation of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films using sol-gel fabrication. Using other methods such as pulsed-laser-deposition, electrospinning and electrospraying, the reported x values for iron content have not exceeded 0.4, and large area coating will be difficult in terms of uniformity and processing time [67, 68]. Thus, a thin film fabrication process that encompasses both solution preparation and thin film coating will be devised with the aim of developing a protocol that can be applied to all x values. This means that $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films with variable bandgap from 3.17 eV (SrTiO_3) to 2.0 eV ($\text{SrFeO}_{3-\delta}$) can be prepared, and its suitability as visible-light driven photocatalyst can be investigated. Finally, the use of

thin films will open up the possibility of using this material for indoor self-cleaning surfaces in common places such as schools, offices and critical amenities such as hospitals and research centres.

1.3 Objectives

The objectives and scope of work for this project are mainly divided into two main parts. The first objective was to prepare and study visible-light photocatalyst in the form of oxidized titanium nitride (TiN) nanoparticles. Under this study, the following works have been carried out:

a) Thermal oxidation of nano-sized commercial titanium nitride powder

Commercially available TiN nano-sized powder was oxidized in air at different annealing temperatures to obtain TiO₂ with varied amount of nitrogen still remaining on the powder surface to form visible-light active nitrogen-doped TiO₂.

b) Characterizations of oxidized powders

The oxidized powders were characterized to understand the oxidation properties and mechanism, and to determine the optimum process parameters. Of all, the binding state of the remaining nitrogen species was studied using high resolution X-ray photoelectron spectroscopy (XPS) since this is believed to be the main factor determining the final photocatalytic performance. The charge separation efficiency was also investigated using a surface photovoltage study to better explain the powders' performance.

c) Evaluation of visible-light photocatalytic performance

The obtained powders were finally tested for the removal of Rhodamine B, a common industrial waste dye, as well as gaseous pollutant, toluene under visible-light illumination. Finally, their anti-bacterial effect on *E.Coli* was also investigated.

The second part of this project makes up a major part of this thesis. This part is aimed at developing a sol-gel based fabrication process for $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films with $0 \leq x \leq 1.0$. This is followed by thin films characterizations and evaluation of their suitability for visible-light photocatalytic applications. To achieve this, systematic works were conducted in the following sequence:

a) Sol-gel study for $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films preparation

Extensive efforts were put into developing a solution preparation route that can achieve the entire spectrum of x values. Conventional sol-gel route based on hydrolysis of metal alkoxide precursors was first adopted and its suitability was compared against the Pechini's method, which is based on polymerizable complex route. Careful studies and modifications on the processing parameters were conducted to optimize the solution preparation process and thin film fabrication methods to obtain uniformly coated, and stoichiometric $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films. The difference in their sol-gel chemistry was investigated and compared.

b) Characterizations of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films

With the optimized preparation process, the films were characterized across $0 \leq x \leq 1$ to investigate how parameters such as crystal phase, lattice constants, optical bandgap, oxygen vacancies, and surface morphology change with iron content. Lastly, the possibility of using these films as visible-light active photocatalyst was explored using Rhodamine B, bis-phenol A and stearic acid. The potential of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films as visible-light active photocatalyst was evaluated and discussed based on its conductivity behavior studied using inter-digitated electrodes IV and surface photovoltage measurements.

1.4 Major Contribution of Thesis

Based on the objectives and scope of work lined-up, the following results have been achieved for this project:

- a) In the study of thermal oxidized titanium nitride, a simple, one-step oxidation in muffled furnace has successfully produced nano-sized nitrogen-doped TiO_2 with large BET surface area of $30 \text{ m}^2/\text{g}$. The oxidized nanopowders were composed of rutile/anatase mixed phase TiO_2 with different nitrogen contents while annealing in the temperature range between 400°C and 550°C for 2 hours. Bulk and surface stoichiometric studies using energy-dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS) revealed that most nitrogen dopants remained on the powder's sub-surface layer while diffuse reflectance spectra showed a visible-light absorption which extended up to 525 nm due to presence of nitrogen dopants.

- b) The effect of annealing temperature on the visible light-driven photocatalytic performance of the powders was studied. The powders were tested for the removal of cationic dye, Rhodamine B and anionic dye, Acid Orange 8 (AO8) under 40W indoor fluorescent light illumination with $\lambda \geq 435$ nm. Of all, the sample annealed at 500 °C could remove 96% of Rhodamine B dye after 22 hours of illumination. However, only weak physical absorption was observed for AO8. This was consistent with the Zeta-Potential measurements which indicated that the powders had a negative surface charge. The powders were further tested for their visible-light anti-bacterial properties using *Escherichia Coli* (*E. Coli*) and the bacteria population was reduced by more than half after only 5 hours of visible-light illumination with the 500 °C annealed sample. In addition, when spray-coated, this sample also proved to have the best performance for decontamination of gaseous phase toluene based on the CO₂ evolution.
- c) The thermal evolution of the TiN to nitrogen-doped TiO₂ was studied and the visible-light photocatalytic mechanism was investigated. The formation of mixed phase TiO₂ was observed to start from an amorphous oxynitride overcoat surrounding well-crystallized TiN core that formed into well-crystallized TiO₂ upon annealing. Of particular importance are the studies of the nitrogen binding states using XPS and charge-separation efficiency using surface photovoltage (SPV) spectra. The analysis of N 1s core spectra revealed that the remaining nitrogen dopants existed in residual TiN phase, interstitial nitrogen and adsorbed N₂ molecules. Furthermore, the surface photovoltage magnitude was observed to increase with the amount of interstitial nitrogen species, signifying its importance

for the good photocatalytic performance observed for sample annealed at 500 °C. Finally, the surface photovoltage decay was slower at higher annealing temperatures, due to increased surface resistivity and improved charge separation upon formation of rutile phase in favourable ratio with anatase phase. This helped in the prevention of charge recombination for improved photocatalytic performance.

- d) This thesis reports for the first time in literature, a complete synthesis of nano-structured, single phase cubic perovskite $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films for the full range of x values. Two main synthesis routes were compared, namely the conventional sol-gel method based on reactive hydrolysis of metal alkoxides and a modified and improved method based on Pechini's polymerizable complex mechanism. The thermal evolution of the films was studied using differential thermogravimetric analysis (DTA). Using the conventional sol-gel method, the range of x value is limited to $x < 0.5$. However, based on the polymerization of metal complexes, a single formation mechanism can be applied for $0 \leq x \leq 1$ to obtain single phase $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$. Moreover, the inherent wettability problem associated with this method had been solved successfully by applying UV ozone treatment on the substrates prior to coating, and by adding the stress-relieving agent, poly-vinylpyrrolidone (PVP) into the solution. With these approaches, the solution preparation and coating method devised can be suitable for large area and uniform coating over various substrates for extended applications. The processing parameters were further optimized in terms of the precursor content and pH value

to obtain well-crystallized films and at the same time better solution stability for prolonged storage.

- e) Based on the optimized synthesis method, $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films ranging from SrTiO_3 to $\text{SrFeO}_{3-\delta}$ were fabricated for systematic characterizations. For all films, a single phase with cubic perovskite structure could be obtained from a low temperature of 500 °C to 700 °C. At higher annealing temperature, phase change to tetragonal and brownmillerite phases associated with the rearranging of oxygen vacancies was observed. FE-SEM observations revealed uniform, nanoporous thin films with porosity that increased with iron content. Furthermore, good adhesion to substrate and thickness control was achieved. The thickness of 3 layers of thin films obtained varied from 250 – 280 nm on platinum surface.
- f) The potential of using these films as visible-light active photocatalyst was first investigated by their optical bandgap study. Based on their transmission curves, the visible-light absorbance was observed to increase with iron content. Bandgap estimation using Tauc Plot showed continuous bandgap reduction from 3.46 eV for SrTiO_3 to 1.1 eV for $\text{Sr}(\text{Ti}_{0.2}\text{Fe}_{0.8})\text{O}_{3-\delta}$. This due to the formation of the Fe 3d energy band above the O 2p valence band, as indicated by their low energy X-ray photoelectron spectra. However, evaluation of their photocatalytic properties using Rhodamine B indicated reduced decolouration rate with increasing iron content. With bis-phenol A and stearic acid tests, no obvious photocatalytic reaction could be observed. Based on the detailed XPS study of the films, increasing oxygen vacancy which acted as electron trap was believed to be the reason for the lack of photoreactivity. Furthermore, the films showed increased electronic conductivity

with iron content, therefore making it difficult for charge retention on the film surface before photocatalytic reaction can occur. This is supported by the visible-light surface photovoltage study whereby contact potential difference was observed, but with increasing iron content, the recombination rate also increased. Therefore the films could not sustain the surface charge sufficiently long for photocatalytic reactions.

1.5 Organization of Thesis

In Chapter 1, an introduction to photocatalyst and its current state of research are presented. Next, the motivation of this project, as well as the objectives is outlined. This is followed by the scope of work laid out, and the experimental results and findings were summarized as the major contributions of this thesis.

Next, in Chapter 2, a literature review on the background knowledge and topics related to this project are discussed. The history of photocatalyst, research, achievements and limitations of TiO_2 -based photocatalyst are presented. This is followed by understanding the properties of SrTiO_3 , $\text{SrFeO}_{3-\delta}$ as well as $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$. The advantages and disadvantages of the various preparation methods are compared to justify the sol-gel method chosen for this project.

Chapter 3 outlines the experimental methods and materials used in this project. Both preparation and characterizations of thermal oxidized TiN and $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films are described. Then, various setups for the evaluation of photocatalytic performance using dyes, anti-bacterial, stearic acid and gaseous toluene are presented.

In Chapter 4, the main findings for the study of thermally oxidized TiN are presented in details. The effects of annealing temperature on the phase transition, the surface area, surface charge, stoichiometry, optical absorption, chemical states, and charge separation efficiency of the mixed-phase TiO₂ are presented. Next, the test results for Rhodamine B, Acid Orange 8, and toluene removal, as well as *E. Coli* killing efficiency are compared to find the optimum annealing temperature.

Chapter 5 follows the development of a fabrication process for Sr(Ti_{1-x}Fe_x)O_{3-δ} thin films via sol-gel and spin-coating method. Two sol-gel routes, namely the conventional and modified sol-gel routes are compared and improvised to devise a stable solution preparation method which can be applied for the entire range of the x value for the iron content. The optimization of the solution for enhanced crystallization and longer stability are also reported. Finally, an efficient method to improvise the solution wettability and film uniformity on various surfaces is presented.

Next, in Chapter 6, results of systematic characterizations done on the Sr(Ti_{1-x}Fe_x)O_{3-δ} thin films are reported and discussed in details. Furthermore, the evaluation of the possibility of using these films as visible-light active photocatalyst is presented by means of Rhodamine B, bisphenol-A and stearic acid degradation tests.

Finally, Chapter 7 concludes the works reported in this thesis, together with a few proposed ideas for future work.

CHAPTER 2. LITERATURE REVIEW

2.1 Introduction

Figure 2-1. Schematics of electron-hole pair generation in a photocatalyst particle and the mechanisms involved, as depicted by de Lasa [69].

The mechanism involved in photocatalytic oxidative degradation of organic pollutants is outlined by Legrini et al. and depicted in Figure 2-1 [69, 70]. When a photon with energy larger than the bandgap (E_g) of a photocatalyst reaches its surface, excitation occurs and electron-hole pairs (EHP) are generated. Electrons from the valence band are excited to the higher energy conduction band, leaving behind holes in the valence band (equation 2-1).

The generated electrons will be used for reduction processes, whereas the holes will be scavenged for oxidation process if there are suitable species present on the photocatalyst surface; for example oxygen and water molecules. However, the reverse process of equation 2-1 can also occur, i.e. recombination. Hence, a major challenge for

efficient photocatalytic reaction is to prevent recombination, and to increase reaction efficiency.

In the redox reactions that follow EHP generation, holes, h^+ react with the adsorbed substrate (RX_{ad}), water (H_2O_{ad}) or hydroxide ions (OH_{ad}) ions.

In general, equation 2-4 is most likely to occur, due to the high concentration of OH_{ad}^- from water dissociation. On the other hand, oxygen molecules act as the scavenger for the photogenerated electrons, by accepting the electrons to form super-oxide anions, O_2^- .

The formation of super-oxide anions subsequently brings about more reactions to generate hydroxyl radicals, OH_{ad}^* and hydrogen peroxide, H_2O_2 as shown in equations 2-6 and 2-7. The hydrogen peroxide produced can also absorb photons to produce even more hydroxyl radicals directly (equation 2-8).

These reactive hydroxyl radicals can oxidize organic pollutants that are adsorbed onto the photocatalyst surface into non-harmful materials, such as carbon dioxide and water, as shown in equation 2-9.

For photodegradation of volatile-organic-compounds (VOC), the formation of intermediates has been determined [71, 72]. During the degradation reactions, these intermediates will occupy the active sites on the photocatalyst surface, hence their accumulation will decrease the reaction rates. Nonetheless, photodegradation of VOCs has proven to be an efficient method and has found wide applications in the field of air quality control, water treatment, disinfections and self-cleaning surfaces.

2.2 Titanium Dioxide (TiO₂) Photocatalyst

The most studied semiconductor photocatalyst, TiO₂ can be found in three different phases: anatase, rutile and brookite phase. Figure 2-2 shows the crystal structures of the more commonly found anatase and rutile phases [73]. Generally, pure anatase (bandgap 3.2 eV) has a significantly higher photocatalytic activity than pure rutile (3.0 eV), whereas brookite does not exist in normal temperature range [12, 74]. Ironically, anatase has a larger bandgap compared to rutile. One common explanation for this is the higher reduction potential of the photogenerated electrons in anatase, since the conduction band of anatase is 0.1 V more negative than rutile [75]. Another possible reason is that anatase can form a greater number of reduced Ti³⁺ site due to the capturing of photogenerated electrons. With this, recombination rate is reduced, leaving more holes free for subsequent photooxidation reactions [76, 77]. Furthermore, based on the study of

photo-induced hydrophilicity dependence on crystal structure, the hydroxyl groups formed on rutile crystal are said to be more stable, and thus they cannot be involved easily in oxidizing reactions [78-80].

Figure 2-2. Crystal structure of (top) rutile and (bottom) anatase phase of TiO_2 [73].

Nevertheless, compared to single phase TiO_2 , mixed phase TiO_2 shows enhanced photocatalytic performance. Bickley et al. [81] and Bacsá et al. [15] explained that rutile phase, although less active due to its high rate of recombination has electron sinking property. When mixed in close proximity with anatase, the electrons generated in the smaller bandgap anatase can transfer to the neighboring rutile crystallite; therefore separating the electron-hole pairs in two different phases to prevent recombination and improve the overall performance. However, an inversed mechanism was proposed by

Hurum et al. [16], whereby electron transfer takes place from rutile to the lower energy site in anatase. Nevertheless, P25, a commercial TiO_2 nanopowder by Degussa is the current market leader and widely used as benchmark for research TiO_2 photocatalyst. It is an efficient photocatalyst under UV light, comprising of 70% anatase and 30% rutile phase with large BET surface area ($55 \pm 15 \text{ m}^2/\text{g}$) [17].

2.2.1 History and Applications of TiO_2 Photocatalyst

In modern history, scientific study on TiO_2 was first reported in 1938, where photobleaching of dye was carried out under UV light, under aerobic and anaerobic conditions [82]. However, it was not until the UV light-induced water-splitting experiment of Fujishima and Honda in 1972 that active scientific research on TiO_2 took place [3]. In the 1980s, instead of photochemical cell, TiO_2 in the form of powder suspension was also investigated for water-splitting [19]. For the past three decades, vast environmental applications for pollutant and volatile organic compounds (VOCs) removal were studied and developed for TiO_2 [4, 5, 13, 14, 71, 72, 76, 83]. To ease post-processing separation, supported TiO_2 on various surfaces were also developed [6, 78, 84-87].

In addition to VOC destructions, TiO_2 has also shown good photocatalytic performance for anti-microbial applications [9, 88-91]. Another important discovery is its photo-induced superhydrophilicity [10, 92]. This useful attribute has been employed for development of self-cleaning surfaces on building exterior and window glasses. The water contact angle on UV-illuminated TiO_2 film can go down to almost 0° , achieving close to 100% wettability such that water can wash off any decomposed organic contaminants and

dust on the surface, hence keeping the surface clean. In Japan, this technology has been successfully commercialized on rooftops, car windows, walls and tunnels, as shown in an example in Figure 2-3.

Figure 2-3. Self-cleaning (A) and ordinary (B) tiles developed commercially in Japan [10].

2.2.2 Photocatalytic Mechanism of TiO_2

The general mechanism of heterogeneous photocatalytic process on TiO_2 surface was proposed by Hoffman and illustrated in Figure 2-4 [17]. In process (1), when photons, with energy $h\nu$ that matches or exceeds the bandgap of TiO_2 , arrive on its surface, they will be absorbed by TiO_2 such that electrons, e^- from its O 2p valence band, can be promoted to the Ti 3d conduction band, leaving a hole, h^+ behind.

Figure 2-4. Processes involved in a photoelectrochemical mechanism [17].

Thereafter, these photogenerated e^- and h^+ pairs (EHP) can follow three paths. Firstly, they can recombine while dissipating the input photon energy as heat, as indicated by process (2). Secondly, they might get trapped in metastable surface states such as surface dangling Ti^{4+} bond or titanol group, shown by processes (6) and (7). Finally, in an ideal situation, they will react with electron donors (indicated as Red in diagram) and electron acceptors (O_x) adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. This redox process will cause further thermal and photocatalytic reactions to mineralize target pollutants as seen in process (5).

The valence band holes are powerful oxidizing agents, while the conduction band electrons are good reducing agents. Thus, without any electron and hole scavengers, recombination will occur within a few nanoseconds and energy is dissipated as heat. Suitable scavenger or surface defect state can trap the electron or hole to prevent recombination, leading to subsequent redox reactions.

2.2.3 Towards Visible Light Photocatalyst : Alternative Materials and Modified TiO₂

The sunlight consists of ultraviolet, visible and infrared with energy distribution of approximately 4-5 % UV, 44-45% visible light and 51% infrared light [20, 38]. As discussed previously, TiO₂ has a large bandgap of 3.2 eV, therefore only UV photons can generate electron-hole-pairs for photocatalytic reactions. This has severely restricted its major applications to reactors with UV light source, and self-cleaning surfaces in the outdoor, where sufficient UV light can be obtained from the sunlight. It is thus the interest of researchers to move the absorption spectra of TiO₂ towards the visible light region, to better utilize the solar energy. A few major approaches are summarized as follow:

- ***Doping TiO₂ with Transition Metals***

Doping with transition metals such as Chromium (Cr) [19], Iron (Fe) [74, 93, 94], Copper, (Cu) [95] and Nickel (Ni) creates a new local energy band within the bandgap of the host semiconductor [20]. The energy gap from this local band to the conduction band edge lies in the visible light spectra. Theoretically, it is proposed that the electrons from the introduced impurity state will absorb visible light photons and generate free radicals on the photocatalyst surface for chemical reactions. However, by creating the metal ion energy band nearer to the conduction band edge, recombination can also occur in the reverse direction if there is no efficient charge separation mechanism. Thus, the performance of transition metal doped photocatalyst is highly dependent on the preparation method and binding states of the dopants.

- ***Doping TiO₂ with Non-Metals***

Other than transition metals, non-metals such as Nitrogen (N), Sulfur (S) and Carbon (C) are also used as dopants [21-23, 96, 97]. Among them, nitrogen-doped-TiO₂ gave better visible-light photoactivity and received the most research attention. A widely quoted work by Asahi on substitutional nitrogen doping found isolated, narrow N 2p band above the valence band which allowed visible-light absorption up to 500nm [21]. The common synthesis methods of N-doped TiO₂ are chemical sol-gel [25-27], sputtering [21, 28, 29], ion-implantation [30], chemical vapour deposition [31-33], direct amination [34], and annealing TiO₂ in N₂ or NH₃ [35, 98]. However, the energy states introduced by the dopants usually exist in the form discrete levels or narrow band, putting restriction on holes' mobility and photocatalytic performance. Therefore, for both metal and non-metal doping, the introduced energy level must be broad enough for sufficient overlapping and integration with the O 2p valence band for efficient bandgap narrowing. In addition, good charge separation mechanism is also essential since with narrowed bandgap, recombination can occur more easily.

- ***Physical and chemical modifications of TiO₂***

Attempts have also been made to create oxygen vacancies in the lattice to serve as electron traps and therefore preventing radiative recombination [24, 99]. As early as 1959, Cronemeyer [100] proposed, based on experimental data, that oxygen vacancy states in a reduced anatase TiO₂ lie between 0.75 – 1.18 eV below the valence band. This lowered the bandgap from 3.2 eV to 2.02 eV, allowing visible-

light absorption up to 614 nm, as illustrated in Figure 2-5 [99]. Besides TiO_2 reduction, oxygen vacancies can also be obtained via preparation methods such as plasma treatment magnetron sputtering [101-103].

Figure 2-5. Band structure of anatase TiO_2 with oxygen vacancies, proposed by Nakamura et al. [99].

○ *Searching for alternative Materials*

Table 2-1 lists and compares TiO_2 with a few other materials studied as photocatalyst [69]. Besides TiO_2 , ZnO is another widely studied semiconductor photocatalyst with similar bandgap and good efficiency. However, studies on ZnO have found that ZnO is unstable with respect to incongruous dissolution. This forms $\text{Zn}(\text{OH})_2$ on the ZnO particle surface, and prevents further photoactivity over time [104, 105]. Other smaller bandgap materials show limited photoactivity even though they have smaller bandgaps. For example, using $\text{In}_{1-x}\text{Ta}_x\text{O}_4$ with bandgap of 2.6 eV which falls in the visible-light region, Zou et al. [18]

demonstrated water-splitting in visible light, but the efficiency is less than 1%. These small bandgap materials also face the issue of chemical instability during photocatalytic reactions. When used as electrodes for photoelectrolysis of water, the photogenerated holes will oxidize the catalyst themselves.

Table 2-1. Bandgaps of various materials studied as photocatalyst [69].

Semiconductor	Bandgap Energy (eV)	Wavelength (nm)
TiO ₂ (rutile)	3.0	413
TiO ₂ (anatase)	3.2	388
ZnO	3.2	388
ZnS	3.6	335
CdS	2.4	516
Fe ₂ O ₃	2.3	539
WO ₃	2.8	443

2.3 Strontium Titanate (SrTiO₃) as Photocatalyst

As early as 1976, researchers have shown that photo-assisted electrolytic water-splitting is not a unique attribute of TiO₂. Using single crystal SrTiO₃, Watanabe et al. [106] first demonstrated this and showed that the quantum efficiency is comparable to TiO₂. On top of that, the SrTiO₃ photoelectrode remained stable and insoluble throughout the process. Their work was soon confirmed by Mavroides et al. [107], where ten-fold improvement in quantum efficiency was observed with SrTiO₃ as compared to TiO₂. This

was attributed to its smaller electron affinity, giving a 0.2 eV larger band-bending when put in contact with the electrolyte; and hence better electron-hole pair separation. Wrighton et al. [108] further observed that sustained water-splitting could be achieved in a photoelectrochemical cell without external bias (in aqueous alkaline solution) when the SrTiO_3 electrode was irradiated with wavelength shorter than 390 nm.

The observation that light-assisted water-splitting can be achieved using Pt/ SrTiO_3 electrodes without external voltage application suggests that the reaction can take place on the same surface. Wrighton et al. [109] studied water electrolysis at the interface of platinized SrTiO_3 crystal and basic electrolyte upon UV illumination. However, due to the large bandgap and the insufficiently negative conduction band position, the obtained efficiency was not satisfactory. Wagner et al. [53] compared photoelectrochemical and photocatalytic water splitting of SrTiO_3 by the volume of hydrogen evolved. They observed a high dependence of photocatalytic rate on the hydroxyl concentration. These hydroxyl groups are important hole scavengers which can help to prevent recombination. A high hydroxyl ion concentration allows constant dehydroxylation of the catalyst surface, giving sustained photocatalytic reaction.

The mineralization of phenol using sol-gel derived SrTiO_3 nanocrystals with high surface area in H_2O_2 and NaClO_3 were demonstrated by Ahuja [54]. In their works, defects in the form of strontium and oxygen vacancies, as shown in Figure 2-6 are believed to prevent recombinations and allow charge transfer to the crystal surface for oxidation reactions. The bandgap of SrTiO_3 is widely reported to be 3.2 - 3.3 eV, which is similar to TiO_2 [110, 111]. Therefore, various doping and co-doping of transition metals,

noble metals, and non-metals elements was also investigated on SrTiO₃ to achieve visible-light response.

Figure 2-6. Energy levels for native point defects in cubic perovskite SrTiO₃ energy band diagram [54].

For example, chromium-doped SrTiO₃ nanopowders showed red-shift in its light absorption to degrade Methylene Blue under visible-light illumination [112], while iron-doped SrTiO₃ showed enhanced Rhodamine B degradation [113]. Doping with noble metal ions such as rhodium shifted the absorption the wavelength response to 580 nm without the formation recombination centres which can sacrifice photocatalytic performance [2]. 20 wt% nitrogen-doped SrTiO₃ also showed three-fold improvement in nitrogen monoxide (NO) removal under visible-light and near-UV illumination [114].

Although in pure SrTiO₃, oxygen vacancies have been reported to be beneficial charge traps, it is ironically found to act as charge recombination centre in the case of doped-SrTiO₃. By trapping the electrons in the oxygen vacancies without fast transfer to the photocatalyst surface, recombination can occur with the holes left in the acceptor energy level formed by the dopants above the SrTiO₃ valence band. Therefore quantum

efficiency will be reduced and longer induction period is needed for photocatalytic reactions. The formation of oxygen vacancies is more obvious when transition metals are used as dopant, due to their ability to switch between oxidation states easily [56]. To suppress the formation of oxygen vacancies due to charge imbalance caused by a single dopant, co-doping is another commonly used method to modify SrTiO₃. A summary of co-doped SrTiO₃ for photolysis applications is presented in Table 2-2.

Table 2-2. Co-doped SrTiO₃ and their optical/photocatalytic properties.

Dopants	Visible-light Absorption	Photoactivity	Reference
Antimony, Sb Chromium, Cr	Up to 520nm $\approx$ 2.4 eV	H ₂ evolution from aqueous methanol Incident light > 420nm	[115]
Tantalum, Ta Chromium, Cr	Up to 700nm $\approx$ 1.8 eV	H ₂ evolution from aqueous methanol Incident light > 440nm	[55]
Nitrogen, N Lanthanum, La	Up to 500nm $\approx$ 2.5 eV	Acetone evolution from gaseous 2- propanol Incident light : (410-500nm)	[57]
Sulphur, S Carbon, C	Up to 606nm $\approx$ 2.05 eV	Acetone evolution from aqueous 2-propanol Incident light > 500 nm	[58]

For example, when antimony or tantalum is co-doped with chromium into SrTiO_3 , H_2 evolution from aqueous methanol was observed under visible-light illumination [55, 115]. The main transition metal, Cr and non-metal, N dopants form discrete donor levels above valence band. When illuminated with visible-light, electrons and holes would be generated in the conduction band and donor levels. Due to the non-continuous nature of the donor level, the holes are not capable of evolving O_2 from water, but can only cause simple oxidation reactions, such as methanol oxidation. Without the co-dopant, the low-mobility holes will eventually recombine with electrons, giving poor photocatalytic efficiency. Co-dopants serve to maintain charge balance and avoid the formation of Cr^{6+} and oxygen vacancies, which are non-desirable, recombination sites, so that the holes would be able to induce simple oxidation process.

2.4 Strontium Ferrite as Photocatalyst

Strontium ferrite is an inherently non-stoichiometric ferromagnetic material. Oxygen deficiency is needed to maintain charge balance. The difficulty in achieving stoichiometric SrFeO_3 is due to the instability of the iron oxidation state at +4 oxidation state. Therefore, with some iron existing as Fe^{3+} , oxygen deficiency is needed to maintain charge balance. This non-stoichiometry is usually denoted as $\text{SrFeO}_{3-\delta}$ or $\text{SrFeO}_{2.5+x}$.

In addition, depending on the oxygen content and temperature, strontium ferrite exists in different phases [116]. Using the $\text{SrFeO}_{2.5+x}$ notation, the four phases identified are orthorhombic-brownmillerite (BR, $x = 0$), orthorhombic-perovskite (OP, $x = 0.23$), tetragonal-perovskite (TP, $x = 0.36$), and cubic perovskite (CP, $x = 0.4-0.5$). This non-stoichiometry and composition-temperature dependence is manifested as measurable

physical and chemical changes, which have been exploited for sensing applications [117-120]. At high temperature (700 – 950 °C) and high oxygen partial pressure ($p_{O_2} > 10^{-4}$ atm), it has mixed conductivity behaviour with both oxygen vacancy and electron-hole as the carrier. The electron-hole conduction in the brownmillerite structure is governed by the bandgap of 2.0 eV, as shown in Figure 2-7 [65].

Figure 2-7. Density of states, $N(E)$ for $SrFeO_{2.5+\delta}$ as δ changes from 0 to 0.5 and oxygen vacancy increases [65].

Compared to its application as chemical sensor, strontium ferrite is much less studied for catalytic reactions and pollutant removal. For catalytic application, the brownmillerite-like compound $Sr_2Fe_2O_5$ showed remarkable thermal decomposition of nitrogen oxide (NO) to N_2 and O_2 at 700 – 900 °C by transforming to vacancy disordered perovskite structure [62]. Perovskite-type $SrFeO_{3-\delta}$ and chlorine-doped $SrFeO_{3-\delta}$ were also tested for oxidative dehydrogenation of ethane with good selectivity [121]. However,

there is no reported work of strontium ferrite for photocatalytic applications until a recent finding by our group, in which ball-milled $\text{SrFeO}_{3-\delta}$ nanopowder has showed good performance in the degradation of methylene blue under visible-light [63].

2.5 Strontium Titanate Ferrite ($\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$) as Potential Visible-Light

Photocatalyst

Strontium Titanate Ferrite, $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ is a continuous solid state solution between the two end members, strontium titanate, SrTiO_3 and strontium ferrite, SrFeO_3 [66, 122]. Figure 2-8 shows the cubic perovskite unit cell for SrTiO_3 . In $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$, iron atoms substitute for titanium atom. Due to the difference in their preferential oxidation states (+4 for Ti and +3 for Fe), oxygen vacancies are formed to maintain charge balance in the system.

Figure 2-8. Unit cell of SrTiO_3 , exhibiting the cubic perovskite structure [57].

The transition at $T = 830\text{ }^\circ\text{C}$ from vacancy disordered perovskite (SrFeO_3) to ordered brownmillerite ($\text{Sr}_2\text{Fe}_2\text{O}_5$) has made it unstable in many high temperature applications [116, 123]. Thus, the substitution of Ti into Fe site was believed to stabilize the perovskite structure [124, 125], with short-range ordering of oxygen vacancy about

the Fe site [126, 127] as compared to the long-range ordering observed in SrFeO₃. The system exists as a single phase cubic structure at low iron concentration, whereby the lattice parameter, a_0 and bandgap, E_g decrease with increasing Fe. The changes in these values are shown in Table 2-3. [124].

Table 2-3. Changes of lattice parameter (a_0), oxygen vacancy (y), bandgap (E_g) and enthalpy of annihilation of oxygen vacancy, ΔH_a as a function of x in Sr(Ti_{1-x}Fe_x)O_{3- δ} [124].

x	$a_0 \pm 0.001(\text{\AA})$	$y = 3 - (x/2)$	$E_g \pm 0.1(\text{eV})$	$\Delta H_a \pm 0.2(\text{eV})$
0	3.907	3	3.2	2.0
0.1	3.907	2.95	2.8	1.0
0.2	3.906	2.90	2.6	0.5
0.4	3.900	2.80	2.2	0.1
0.5	3.896	2.75	2.1	0.0
0.6	3.890	2.70	2.2	0.0
0.8	3.878	2.60	2.1	-0.2

The solid solution system of Sr(Ti_{1-x}Fe_x)O_{3- δ} has gained a lot of interest in the field of gas sensor, especially in lean engine due to its negligible sensitivity towards temperature [66, 128]. Rothschild et al. [128] proposed the energy band structure of Sr(Ti_{1-x}Fe_x)O_{3- δ} system based on the gas sensing properties and conductivity behaviours. From the measured values of SrTiO₃, SrFeO₃, SrTi_{0.65}Fe_{0.35}O_{3- δ} , and SrTi_{0.5}Fe_{0.5}O_{3- δ} , the bandgap relation with x was proposed to follow second order polynomial $E_g(x) = 3.26 - 1.93x + 0.54x^2$ eV, as shown in Figure 2-9. From the proposed bandgap equation, the energy diagram was further illustrated in Figure 2-10 versus oxygen partial pressure. The Fermi energy level, E_F decreases with increased oxygen pressure. With increasing iron concentration, the acceptor level (Fe⁺³/Fe⁺⁴) broadens, effectively narrowing the bandgap and moving the Fermi level closer to the valence band.

Figure 2-9. Bandgap of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ as a function of iron content, x [128].

Figure 2-10. Proposed energy diagram for $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ at (a) low (e.g. 1%), (b) intermediate (e.g. 35%) and (c) high (e.g. 50%) iron concentration [128].

2.5.1 Synthesis Methods

Besides oxygen sensing [124, 129], $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ has also found vast applications in hydrocarbon sensor [130], fuel cell [124, 131], oxygen separation membranes [125] and phase shifters in communication systems [132]. Most works currently focus on oxygen sensing and ionic conduction applications and do not provide much direct insight on the potential of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ as visible-light photocatalyst, except for the work by Rothschild et al. [128], which proposed the continuous reduction in bandgap with increased iron content.

Depending on the application, many synthesis methods have been used to prepare $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ in the form of macro and nano-sized powders, as well as thick and thin films. The pros and cons of these methods will be discussed in this section.

a) Conventional Ceramic Route for Powder and Thick Films

In conventional ceramic route, the metal oxides powders are physically mixed together, usually by ball-milling or hand grinding. For $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$, the starting materials commonly used are SrCO_3 , SrO , TiO_2 and Fe_2O_3 . After mixing, a calcination process is needed to drive the diffusion controlled solid-state-reaction at high temperatures. The temperatures employed are usually at least 1000 °C, and the calcination lasts at least 10 hours. Single phase cubic perovskite $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ can be obtained consistently with this method and the produced macro-sized powders can be made into compacts, pellets and targets. Micron-thick films can then be fabricated using screen-printing [133-135]. $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ powders in various form have been successfully fabricated by various research groups [66, 125, 128, 130, 136].

Another variation of this method uses high-purity SrCO_3 , TiO_2 and $\text{FeC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ as starting materials. In addition, a thermal process is used to decompose the metal salts into stoichiometric mixture of oxides, followed by calcination at high temperatures for more than 30 hours. In between, regrinding was repeated to ensure homogeneous mixture of the different powders [137, 138]. Another technique to achieve good mixing homogeneity is to use a liquid medium, usually alcohol, water or acid to dissolve the powders and mix them evenly before high-temperature calcination. The liquid mixtures prepared are usually strontium carbonate, ammonium ferric citrate, and titanium citrate solutions. Powders obtained from this method have been pressed into tablet for defect structure studies [124, 139].

b) Sol-precipitation or Wet Chemical Route for Fine Powder

Due to the high calcination temperature and long hours involved, the above-mentioned routes inevitably produced macro-sized powders. In the application of sensors and catalyst, a high surface-to-volume ratio is desirable to maximize reaction rate. Using a wet chemical route, nanosized-powders have been fabricated. A sol is prepared using $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ and titanium isopropoxide, dissolved in glacial acetic acid and water. The precipitation can be initiated by adding NaOH in the continuously stirred sol. The obtained nano-powder is then calcined at 850°C for 3 hours [68, 133].

c) Coatings for Thin Films

The preparation of bulk $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ powder requires high temperature and long processing time to drive the solid state reactions. As opposed to the bulk powder preparation, $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films fabrication does not only reduce the processing

time and temperatures, but will also widen its potential for commercialization purpose, as in the case of TiO_2 . For this project, the development of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin film allows the study of its potential for self-cleaning via photocatalytic reactions. Synthesis of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin film and coating preparations in the literature are limited to pulsed-laser-deposition (PLD) [67, 134], electrospinning and electrospraying [68, 133]. In these methods, the processing temperature could be reduced to 700 °C. Thin film sensors fabricated by electrospinning and electrospraying method have been shown to have improved sensor functionality.

d) Proposed Method – Sol-gel Processing

PLD is by far the only reported method for $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ dense, thin film deposition which is limited by high system setup cost, small deposition area and uniformity issue. To overcome these limitations, sol-gel processing will be used for this project. Sol-gel processing was firstly used to prepare decorative and constructional materials in history. Today sol-gel methods are reaching their full potentials, enabling the preparation of new generation of advanced materials under mild, low energy conditions. Sol-gel can be broadly defined as the preparation of ceramic materials by preparation of a sol, gelation of the sol, and removal of the solvent [140]. These processes are generally termed as hydrolysis and condensation, gelation, ageing, drying and densification. The starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds such as metal alkoxides.

In a typical sol-gel process, the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension, commonly known as the sol.

Further processing of the sol enables one to make ceramic materials in different forms as shown in Figure 2-11. Thin films can be produced on a piece of substrate by spin-coating or dip-coating. When the sol is cast into a mold, a wet gel will form. With further drying and heat-treatment, the gel is converted into dense ceramic or glass articles. If the liquid in a wet gel is removed under a supercritical condition, a highly porous and extremely low density material called aerogel is obtained.

Figure 2-11. Summary of sol-gel technologies and products [141].

When the viscosity of a sol is adjusted into a proper viscosity range, ceramic fibers can be drawn from the sol. Ultra-fine and uniform ceramic powders are formed by precipitation, spray pyrolysis, or emulsion techniques. As compared to the high temperature solid-state reactions, sol-gel is a relatively simple process at low processing temperature. This approach provides possibilities to control a number of the determining parameters of the final product such as homogeneity, purity, doping, microstructure (pore size and surface area) with high precision, and sintering temperature. Therefore, it enables

production of sophisticated structures such as thin film, fiber, monoliths, porous membranes for wide area of applications. Lastly, sol-gel is a well-understood process that is compatible to the semiconductor process technology.

Thin film (normally $< 1\mu\text{m}$ in thickness) can be formed using sol-gel approach by dipping, spin-coating, or spraying. Compared to conventional thin film processes such as CVD, evaporation, or sputtering, sol-gel film formation requires considerably less equipment and is potentially less expensive. More importantly, it enables precise control of the microstructure of the deposited film. Spin coating is adopted for the thin film formation in this project. The advantage of spin coating is that a film of liquid tends to become uniform in thickness during spin-off and, once uniform, tends to remain so provided that the viscosity is not shear dependent and does not vary over the substrate [140].

CHAPTER 3. EXPERIMENTAL SETUP

3.1 Synthesis of Nitrogen-doped TiO₂ Powders

Amongst all the non-metals used in TiO₂ doping, nitrogen was found to be most effective, with significant visible-light absorption up to 500 nm observed [21]. Methods used to dope nitrogen into TiO₂ include sol-gel [25-27], sputtering [21, 28, 29], ion-implantation [30], chemical vapour deposition [31-33], direct amination [34], and annealing TiO₂ in N₂ or NH₃ [35, 98]. Direct oxidation of titanium nitride (TiN) in air is a simple, low-cost and mass producible method to prepare nitrogen-doped TiO₂. Instead of introducing nitrogen into TiO₂, TiN is used as the starting material and high temperature annealing is used to convert TiN to anatase TiO₂ [142, 143]. Compared to other methods, this method is less studied for visible-light photocatalytic application, especially with regards to the relationship between the binding states of the nitrogen and the photocatalytic performance [144, 145]. In addition, increasing annealing temperature also led to formation of mixed phase TiO₂ because some anatase phase would transform to rutile. This close proximity of nano-sized rutile and anatase may play an important role in charge separation to enhance the overall photocatalytic performance by improving charge separation efficiency [15, 16]. It is therefore useful to investigate the binding states of the remaining nitrogen dopants and the charge separation efficiency, as well as their collective effects on photocatalytic performance.

Titanium nitride nanopowder (97%, Oxygen<1.0%) with an average particle size of 20 nm from Hefei Kaier, China was used as the starting material. To ensure consistency, each oxidation was carried out using a 9 cm alumina boat from Coorstek, and loaded with

2.0 g of titanium nitride. The powder was annealed in a Thermolyne 62700 furnace under ambient air for 2 hours at the temperature range from 350 °C to 600 °C respectively. The temperature was ramped up at 10 °C/min, and allowed to cool naturally overnight to room temperature.

3.2 Sr(Ti_{1-x}Fe_x)O_{3-δ} Thin Film Preparation

3.2.1 Preparation of Sol-Gel Solution

The solutions used for thin film spin coating in this project were prepared by two major methods. The first method shown in Figure 3-1 is based on conventional sol-gel method, namely via the hydrolysis reaction of metal alkoxides. The metal precursors used were strontium acetate, Sr(CH₃COO)₂·1/2H₂O (Nacalai Tesque), titanium butoxide Ti(OC₄H₉)₄ (97%, Sigma-Aldrich), and iron nitrate, Fe(NO₃)₃·9H₂O (99%, Merck). Glacial acetic acid (Best Chemical) and acetylacetone, C₅H₇OOH (Fisher Scientific) were used as chelating agents to stabilize the precursor ions before mixing them together. Finally, to adjust the concentration, anhydrous 2-methoxy-ethanol (99.8%, Sigma-Aldrich) was chosen as solvent. Another variation of this method was also explored, whereby the chelating agent for iron nitrate was switched to acetylacetone. A detailed discussion will be presented in Chapter 5.

Figure 3-1. Flowchart of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ solution preparation using conventional sol-gel route.

The second solution preparation is a modified route based on Pechini's method. This is the first time that this method is being used for the preparation of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films. It is a polymerizable complex method based on the esterification reaction between a multi-functional organic acid and a diol. The organic acid can also serve as a strong chelating agent, while the diol can function as solvent. This sol-gel route is widely used to prepare multi-metal oxides, especially in cases where the alkoxides of these metals may not be easily available, as in our case for iron. The solution preparation route is presented in Figure 3-2. The metal precursors used were Strontium Nitrate, $\text{Sr}(\text{NO}_3)_2$ (99%, Sigma Aldrich), Titanium Isopropoxide, $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (97% Sigma Aldrich) and iron nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%, Merck). Citric acid, $\text{C}_3\text{H}_4\text{OH}(\text{COOH})_3$ (99.5+% Sigma

Aldrich) was used as chelating agent, while ethylene glycol anhydrous, $C_2H_4(OH)_2$ (99.8%, Sigma Aldrich) was the diol which served in the polyesterification reaction.

Figure 3-2. Flowchart of $Sr(Ti_{1-x}Fe_x)O_{3-\delta}$ solution preparation using polymerizable complex method.

3.2.2 Fabrication of Thin Film

The thin films were fabricated using spin-coating technique. The spinning speed was fixed at 3000 rpm for duration of 30 seconds. After each layer of coating, two soft bakes were carried out at 150 °C and 300 °C for 5 minutes each. Depending on the characterizations that followed, 3-5 layers of thin films were coated on various substrates such as thermal oxidized silicon wafer, platinum coated silicon wafer, alumina, or fused quartz. The spin coated films were amorphous after the low temperature soft bakes. Hence, thermal annealing was carried out in a Lindberg quartz tube furnace, under simulated air atmosphere ($O_2 : N_2 = 1 : 4$) for 1 hour to achieve film crystallization. The temperature ramp-up and cooling rates were fixed at 10 °C per minute.

3.3 Material Characterization Techniques

3.3.1 Thermogravimetric and Differential Thermal Analysis

In this project, a Shimadzu DTG-60H system was employed for DTG measurements. Data were collected in air ambient with a flow rate of 20 ml/min; while the heating and cooling rates were fixed at 2 °C/min and 10 °C/min, respectively. The heating was performed from 30 °C to 900 °C. To prepare the DTG samples, 25 ml of $Sr(Ti_{1-x}Fe_x)O_{3-\delta}$ solution was dried in a crystallizing dish by heating it on a hotplate at 80 °C for 3 days in continuous air flow. The obtained gel or powder was then placed in alumina crucible, alongside a reference sample. For solutions prepared using conventional sol-gel, the heating process resulted in non-uniformly coloured compact powder; while monolithic, clear, and uniform gel was formed from solutions prepared by Pechini's method. Therefore, the non-uniform powder had to be ground with agate mortar and pestle before

40 mg of them were used for DTG measurement. Although the gel could be used straight from the crystallizing dish, due to its large volume expansion which varied with iron content during DTG measurement, the amount of gel used was varied from 15 mg to 30 mg. Nonetheless, in all cases, a 1 : 1 sample weight ratio to alumina powder was maintained.

3.3.2 X-Ray Diffraction (XRD) Analysis

Figure 3-3. Illustration of X-Ray diffraction from a crystal plane according to Bragg's Law [7].

The X-ray diffraction phenomenon is illustrated in Figure 3-3, and is governed by the Bragg's Law. When two monochromatic X-rays (λ_1 and λ_2) hit a crystallized sample surface and are diffracted at two lattice planes spaced at a distance, d away, a phase difference would form between the two diffracted rays, λ_1' and λ_2' . Based on geometrical analysis, if the additional path ($2d \sin \theta$) travelled by λ_2 is a multiple of λ , the two diffracted waves would be in phase and constructive interference occurs to produce a larger signal. This angle θ could be obtained by Bragg's Law in equation 3-1.

$$2d \sin \theta = n \lambda, \text{ where } (n = 1, 2, 3 \dots) \quad (3-1)$$

From the equation, there will be several angles at which strong diffraction signals can be detected which represent the crystallographic orientation of the sample. From the diffraction peaks detected, the grain size could be calculated via Scherrer's formula shown in equation 3-2.

$$\text{Grain Size} = K\lambda / (\beta \cos \theta) \quad (3-2)$$

Here, K is the Scherrer constant that falls in the range 0.70 - 1.70, but usually fixed at 0.9; while β is the full width half maximum (FWHM) of the diffraction peak detected at 2θ . Scherrer equation usually under-estimates the grain size of the crystal because it assumes zero broadening of peaks due to the instrumental error and micro-strain inside the grain.

The Siemens D5008 X-ray diffractometer was used to test the phase change of TiN nanopowder and $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin film samples. The Cu K-alpha radiation X-ray with a wavelength of $\lambda = 1.5406 \text{ \AA}$ operating at 40 kV and 40 mA was used as the source. For thin films, the XRD spectra were collected using the glancing incidence mode, with incident angle fixed at 1° , and 2-theta collected from 20° to 80° in step size of 0.01° . Similar setting was used for the powder XRD scan, except the scanning mode used was lock coupled, whereby the incident angle was varied from 10° to 40° to impinge the X-ray on a larger volume of bulk powder.

3.3.3 Electron Microscope Observation

Scanning electron microscopy (SEM) is a commonly used technique in thin film and coating characterization work to study nano-scale morphological features unobservable by normal light microscope. During observation, a high energy electron beam (acceleration voltage from a few keV to 30 keV) is impinged onto a sample surface and interacts with the surface volume with a depth up to 3 μm . Depending on the depth of interaction; different types of electrons will be reflected off the surface, such as secondary electrons, backscattered electrons, and Auger electrons; each type can be detected with designated detector. The surface morphology can be mapped according to the electron counts collected.

Two commonly used modes in SEM observation are the secondary electron imaging (SEI) and backscattered electron (BSE) modes. As the names suggest, the former mode detects electrons reflected from sub-surface depth, less than 10 $\text{\AA}$, hence giving useful information on surface morphology. On the other hand, the counts of backscattered electron detected are very much dependent on the size of the atom deflecting it. Larger atoms produce larger deflection angle, hence appeared brighter in the mapped image. Therefore, this imaging mode is useful to obtain the compositional distribution on sample surface.

Jeol JSM-6340F and Leo Gemini field emission-SEM (FE-SEM) were used in this project to study the morphology of thin films and nanoparticles. Compared to conventional SEM, FE-SEM produces finer and brighter electron beam; therefore it is able to achieve higher resolution. This is important for non-conductive samples, as in our

case, to observe the nano-structured morphology of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films. Meanwhile, in transmission electron microscopy (TEM), highly focused electron beam can penetrate a thin sample, usually less than 200 nm to give high spatial resolution. In this project, high resolution TEM observations and selected-area electron diffraction (SAED) were performed using JEOL TEM-2010F to identify the morphology and crystal structure of oxidized TiN nanoparticles.

3.3.4 UV-Vis Spectrometer – Optical Study

In UV-Vis spectrometer, two light beams are passed through a reference sample and the sample of interest. The reference sample is usually one with little or no absorption within the wavelength range of the light beams. By comparing the intensity of these two light beams, the absorption of the sample can be observed. When the energy of the light beam is above the bandgap of the sample, a large absorption will occur. Therefore, the absorption edge can give a rough indication of the bandgap of a material. If the intensities of the incident and transmitted light beams are given by “ I_o ” and “ I ” respectively, the transmittance of the sample can be given by equation 3-3.

$$\text{Transmittance, } T (\%) = 100 (I/I_o) \quad (3-3)$$

Another way to express this sample interaction with light is by its absorbance, which is related to transmission according to equation 3-4.

$$\text{Absorbance, } A = \log (I_o/I), = \log (1/T) \quad (3-4)$$

The transmission (T) spectra of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ films were obtained by a Shimadzu UV-2450 spectrometer to study their optical absorbance ($A = -\log T$). For this,

the films were coated on quartz substrate and annealed at 600 °C. The optical bandgaps were further estimated using Tauc plot, $(\alpha h\nu)^{1/2}$ versus eV for indirect allowed transition [58, 146-148].

For oxidized TiN powders, their light absorption characteristics were studied using diffuse-reflectance mode with the powders compacted into a standard sample holder. This is because the rough surface of the nano-sized powders will cause light scattering in all directions, and the integrating sphere can help to collect the average reflected light rays over all angles of measurement. From the reflectance data, a Kubelka-Munk (KM) transformation [149] was performed using the UV Probe software to obtain their absorbance versus wavelength profiles.

3.3.5 X-Ray Photoelectron Spectroscopy (XPS) – Surface Chemical Study

XPS is a powerful characterization tool based on the ejection of photoelectron from a sample surface upon X-ray bombardment. By measuring the kinetic energy, E_k of the photoelectrons, the binding energy, BE of the electrons can then be calculated. The basic equation that governs the XPS characterization is the conservation of energy.

$$\text{Kinetic Energy, } E_k = E_{ph} - BE \quad (3-5)$$

E_{ph} represents the energy of the photoelectrons, which can be obtained directly from the wavelength, λ of the radiation source by using Planck's constant, h and speed of light, c .

$$E_{ph} = h\nu = hc/\lambda \quad (3-6)$$

By plotting the electron counts versus BE , and comparing the spectra against the standard binding energy of elements, useful information such as the elements present, their relative quantities, their oxidation state, as well as the depth composition profile can be obtained. XPS is surface-sensitive up to 1-10 nm. The detection limits is around 0.2 – 1.0 atm%.

For the XPS analysis of oxidized TiN nanopowders and $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films, the Kratos AXIS spectrometer with monochromatic Al $K\alpha$ (1486.71 eV) X-ray radiation was used. The survey spectra in the range of 0-1200 eV were recorded in 1 eV step for each sample, followed by high-resolution spectra over different element peaks in 0.1 eV steps, from which the detailed compositions were calculated. Curve fitting was performed after a Shirley background subtraction using a Lorentzian-Gaussian method. Surface element atomic concentration (%) was also calculated with the following equations :

$$\% n_i = 100 \left[\frac{\frac{I_{ij}}{\sigma_{ij} E^{0.7}}}{\sum \frac{I_{ij}}{\sigma_{ij} E^{0.7}}} \right] \quad (3-7)$$

$$I_{ij} = K \cdot T(E) \cdot L_{ij}(\gamma) \cdot \sigma_{ij} \cdot n_i \cdot \lambda(E) \cdot \cos(\theta) \quad (3-8)$$

where

- n : atomic quantity;
- I_{ij} : area peak j from element i;
- K : instrumental constant;
- $T(E)$: transmission function of analyzer;
- $L_{ij}(\lambda)$: angular asymmetric factor of orbital j of element i;
- σ_{ij} : photoionization cross-section of peak j from element i;

- E : kinetic energy of the emitted electron;
- $\lambda(E)$: inelastic mean free path;
- θ : take-off angle of the photoelectrons measured with respect to surface normal.

Before the XPS scans, the powders were all pressed into compact 1-mm thin pellets with a diameter of 6 mm for ease of handling and vacuuming the XPS chamber.

3.3.6 Surface Photovoltage (SPV) Study with Kelvin Probe

Surface photovoltage (SPV) method based on Kelvin Probe was employed to study light-induced changes in the surface contact potential (V_{CPD}) of oxidized TiN nanopowder and $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films. It is a useful, non-contact and non-destructive method to study the interaction of surfaces with light photons. Figure 3-4 shows the working principle of the Kelvin Probe [150]. In the energy diagram of a metal, the Fermi level, ϵ_F is defined as the highest occupied energy level. The energy required to remove an electron from the level to the vacuum is known as the Work Function, ϕ of the metal.

Figure 3-4. Working principles of the Kelvin Probe [150]. A : before contact, B : after contact, C : after contact with external bias, V_b .

Figure 3-4 (A) compares the Fermi-levels of the Kelvin Probe's metal tip (left) and the sample (right) before they are brought into contact. When they are brought into contact via an external electrical circuit, the Fermi-levels equalize, resulting in a flow of charges which produces a potential gradient, as depicted in Figure 3-4 (B). This potential gradient is termed as the contact potential or V_{CPD} . Under this condition, the surfaces have equal, but opposite charges. If a variable backing potential, V_b is applied, the tip or sample can be biased to change the contact potential. When the value of V_b is equal to $-V_{CPD}$, the surface charges become zero, as illustrated in Figure 3-4 (C). If the tip is vibrated, the Kelvin Probe system can return a null output signal at this position.

If the sample measured is a semiconductor, its surface Fermi-level shifts with illumination, and therefore the contact potential will change accordingly. The surface photovoltage (SPV) is defined as the change in the surface potential as a result of illumination [151]. In the 1940s, Brattain et al. [152] first studied the effect of light illumination on semiconductor surfaces, through the generation of charge carriers due to band-to-band electron transition [153]. Then, the minority carrier diffusion length and lifetime was further studied using this method around 1960s [154, 155]. Gatos et al. developed a way to characterize the surface states using sub-bandgap illumination [156]. In the 1990s, SPV related techniques were widely developed for application in the semiconductor industry; for example in the detection of metal contamination or surface defects [157], as well as in the study of semiconductor heterojunctions [158, 159].

For the past decade, the usefulness of SPV measurement has been extended for photocatalytic research. This method is useful for the study of light-induced charge generation, separation, recombination and transfer to surface states [160]. The sign of the

SPV signal upon superband gap illumination can also provide information on the carrier type of the semiconductor [161, 162]. In general, higher SPV signal shows that the photogenerated electron-pairs have better charge separation and slow recombination rate [163, 164].

In this project, SPV measurement was performed using a UHV Kelvin probe system (KP Technology Ltd.) incorporated with an optical monochromatic illumination system through a quartz window, as shown in Figure 3-5 [165]. The optical system is made up of an ASB-XE-175 Xenon fiber optic light source from Spectral Products and a monochromator with $340 \text{ nm} \leq \lambda \leq 700 \text{ nm}$, coupled by Oriel VIS liquid light guides. In addition, to enhance the SPV signal, a high-power LED light source with switchable wavelengths in the range of $365 \text{ nm} \leq \lambda \leq 850 \text{ nm}$ from Mightex was also incorporated. The emission spectra for both light sources are shown in Figure 3-6.

Figure 3-5. Overview of the Kelvin Probe system used in surface photovoltage (SPV) study.

(a) Xenon (ASB-XE-175) fiber optic light source.

(b) High-power LED light source with switchable wavelengths.

Figure 3-6. Light sources used in the Kelvin Probe-based surface photovoltage (SPV) measurement system.

For SPV study of oxidized TiN, the samples were prepared by coating the powders onto conductive FTO glass via doctor blade method followed by annealing at 450 °C for 1 hour. The paste was prepared by sonicating oxidized TiN powders in ethanol followed by addition of terpineol as solvent, and then added into ethyl cellulose in ethanol. Then, the

SPV of the powders were collected in vacuum by observing the change in their contact potential difference (Δ CPDs) in dark and upon illumination by the 10.8 mW/cm² high-intensity blue LED set at $\lambda = 455$ nm, as shown in Figure 3-6 (b). This specific wavelength is chosen to study the charge separation efficiency under sub-bandgap, visible-light illumination so that the effects of nitrogen-dopants can be investigated, in accordance to the absorption tails observed in Figure 4-11.

Meanwhile, the SPV study of Sr(Ti_{1-x}Fe_x)O_{3- δ} was conducted by coating the thin films on a layer of platinum which was sputtered onto standard silicon wafer. The platinum serves as the bottom contact for the surface potential measurement and all data were collected under normal air condition. Similarly, the contact potential difference (CPD) in the dark was first established by storing the samples in dark. Thereafter, a high-intensity 200W Xenon lamp ($340 \text{ nm} \leq \lambda \leq 700 \text{ nm}$) was turned on for 15 minutes to observe the change in CPD. The emission spectrum of this Xenon lamp is shown in Figure 3-6 (a). Then, the CPD was allowed to return slowly to its dark equilibrium and the rate of decay was observed.

Xenon light is chosen for the thin films because in contrast to oxidized TiN, the visible-light absorption is caused by overall bandgap reduction when Fe⁺³/Fe⁺⁴ energy band overlaps with O 2p valence band, and not narrow dopant levels as with the case of oxidized TiN. So the charge separation efficiency studied is for electron-hole pairs generated by band-to-band absorption. Furthermore, the visible-light response of the thin films are much weaker compared to the films, therefore the use of Xenon light can produce more appreciable SPV signal.

For both powders and thin films, the contact potential difference (CPD) of a SPV measurement is given by:

$$e \cdot CPD = \phi_s - \phi_m \quad (3-9)$$

where ϕ_s is the sample surface work function, while ϕ_m is the work function of the Kelvin Probe, which was firstly calibrated on Au surface and remained unchanged under illumination. Therefore, the CPD change due to light illumination can be obtained by the following equation:

$$e \cdot \Delta CPD = CPD (Light) - CPD (Dark) = \Delta \phi_s = -e \cdot \Delta V_s = -e \cdot SPV \quad (3-10)$$

where ΔV_s is the potential change on the sample surface. Before illumination, the CPD in dark condition was obtained by storing the sample in dark vacuum chamber (pumped to 10^{-6} Torr) for more than 16 hours, while the CPD in light condition was obtained when the samples were illuminated by either the Xenon or LED light.

3.3.7 Current-voltage Characteristics of $Sr(Ti_{1-x}Fe_x)O_{3-\delta}$ thin films

The I-V measurements for $Sr(Ti_{1-x}Fe_x)O_{3-\delta}$ thin films were conducted with help from Dr. Chow Chee Lap using a home-designed gas sensor characterization system (GSCS). Due to the relatively high resistivity of the films, they were deposited on interdigitated microelectrodes with width of 25 μm , and spacing of 25 μm to ensure stable electrical measurement signal. Figure 3-7 shows photo images of the e-beam evaporated gold interdigitated microelectrodes on Si/SiO₂ wafer and $Sr(Ti_{1-x}Fe_x)O_{3-\delta}$ spin-coated on the microelectrodes, ready for I-V measurements.

Figure 3-7. Photo images of (a) gold interdigitated microelectrodes on Si/SiO₂ wafer and (b) Sr(Ti_{1-x}Fe_x)O_{3-δ} thin film deposited on a pair of electrode, ready for I-V measurement.

The direct current-voltage (I-V) measurement was performed with a Keithley 236 source measurement unit, which is part of the GSCS as reported in Dr. Chow's earlier work [166]. The sample was kept in air and supplied with a constant voltage continuously, and the current was measured at temperatures ranging from 27 °C to 500 °C.

3.4 Photocatalytic Test

3.4.1 Dye Removal Test for Powder and Film

Figure 3-8. Experimental procedure and setup for dye removal test for powder (left) and thin film sample (right).

Figure 3-8 above illustrates the experimental procedure and setup for dye removal test. For the oxidized TiN nanopowders, the dye decolouration tests were carried out under 40 W of fluorescent light (Hitachi F8T5, 5 tubes, 8 W each, warm white with

intensity of ~ 1700 Lux) with a UV filter that removed any wavelength below 435 nm.

Figure 3-9 shows the emission spectrum of this light source with and without the UV filter.

Figure 3-9. Top: the emission spectrum of fluorescent light used for dye decolouration test with oxidized TiN nanopowders. Bottom: with UV filter added.

The powder loading used was 1.0 g/L, dispersed in 50 ml DI water by continuous stirring. Then, either Rhodamine B or Acid Orange 8 was added into the powder suspension to achieve a final concentration of 15 $\mu\text{mol/L}$. Before the lights were turned on, the powder suspension in dye solution was allowed to achieve absorption equilibrium for 2 hours in the dark. Prolonged experiments in the dark were also conducted to serve as reference. The amount of dye remaining was quantified using a Shimadzu UV-Vis spectrometer by considering the absorption of the peak at 554 nm and 487 nm for Rhodamine B and Acid Orange 8, respectively. Before measurement, the dispersion was centrifuged at 13 krpm for 5 minutes to remove the powders.

The setup to evaluate the photocatalytic dye removal of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films was relatively simple. The test was conducted by dipping the thin film samples coated on 2'' x 2'' quartz into 20 ml of Rhodamine B solution in a crystallizing dish. The concentration of Rhodamine B used was 10 $\mu\text{mol/L}$. Prior to illumination, the samples were dipped in the dark for 30 minutes to achieve absorption equilibrium. Since the reaction rate is expected to be low due to the small surface area, the light source used was a high intensity LED light (350 mW) from Prizmatix. The intensity of the light for this case was measured to be 250 kLux without any light filter and the emission spectrum is given in Figure 3-10. Using a Melles Griot broadband power/energy meter (Model : 13PEM001), the average emission power over the range of 200 nm to 20 μm is 27 mW/cm^2 . The Rhodamine B was sampled at different intervals directly without the need for centrifugation.

Figure 3-10. Emission spectrum of 350 mW, high intensity LED light source use for dye decolouration by $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films.

The molecular structure and basic decolorization mechanisms for both Rhodamine B and Acid Orange 8 will be discussed in section 4.4.1 and 4.4.2 to facilitate the discussions on the photocatalytic tests results of oxidized TiN powders.

3.4.2 Anti-bacteria Test for Powder

Figure 3-11 summarizes the anti-bacteria test protocol for oxidized TiN powder. The *Escherichia coli* (*E. coli*) used was genetically modified from the MG1655 strain to enable fluorescence observation [167].

Figure 3-11. Anti-bacteria test protocol for oxidized TiN powder with *E. Coli* as target bacteria.

A single *E. Coli* colony was inoculated in 5 ml of LB (Lygsogeny broth) media for 16 hours. The concentration of the bacteria suspension in de-ionized water was adjusted to 2×10^7 CFU/ml by controlling the optical density (OD) at 600 nm to 0.02. 100 μ l of adjusted bacteria suspension was added into 20 ml of powder suspension (2.0 g/L) to achieve a final bacteria concentration of about 1×10^5 CFU/ml. The prepared suspensions

were illuminated in the same light box depicted in Figure 3-5 with constant stirring by magnetic stirrers. They were illuminated under high intensity discharge Xenon lamp (Philips HPI-T Plus, 250 W) and fluorescent light bulbs (Hitachi F8T5, 5 bulbs, 8W each, warm white). The light intensities under Xenon lamp and fluorescent were measured to be approximately 20,000 Lux and 1,700 Lux, respectively. The emission spectrum of Xenon lamp is shown in Figure 3-12 while that of the fluorescent light is shown in Figure 3-9. Similarly, a UV filter was used to block photons with wavelengths below 435 nm. 100 μ l bacteria suspension were sampled each time at scheduled intervals to determine the bacteria survival using standard plate count method. The sampled suspension was diluted twice and each dilution was plated on agar plate with two duplicates. The plated agars were incubated at 37 °C for 16 hours to allow bacteria growth followed by counting of colony forming unit (CFU).

Figure 3-12. Emission spectra of high-intensity-discharge Xenon lamp used for anti-bacterial test.

3.4.3 Gaseous Toluene Removal Test for Coated Powder

In Chapter 4, oxidized titanium nitride powders were spray-coated on polyester filters, and tested for the oxidation of toluene. Their performances were evaluated via the formation of CO₂ using an in-house custom-built test system by Ms. Zhang Li, as shown in Figure 3-13. The photocatalytic test system is designed and setup according to the latest international standards for the characterization of photocatalyst (ISO 22197-1:2007 [168], JIS R 1701-2: 2008 [169] and JIS R 1701-3:2008 [170]). Some modifications have been done to fit in with existing analytical instruments.

Figure 3-13. Schematic diagram (courtesy of Ms. Zhang Li) of an in-house custom-built test system for the photocatalytic oxidation of gaseous toluene by planar film samples.

Gaseous toluene removal test was conducted for Toluene liquid from Fisher (99.9%) was used for this experiment. It was first infused into the heating chamber (HC1) with a syringe pump (SP1) at a rate of 2.65 mL/hour. The heating chamber was set at 60 °C to vaporize the liquid toluene. At the same time, compressed dry air (CDA) was passed through a zero air generator (ZAG) from Peak Scientific Instrument (ZA300) with a rate of 4.99 standard litre per minute (slm) fixed by a mass flow controller (MFC5). The zero air was needed to dilute the vaporized toluene to 2000 ppm and carry it to subsequent chambers. A second dilution took place in the mixing chamber (MIX) by homogenizing the 2000 ppm vaporized toluene with humidified zero air. The mixing chamber is fitted with temperature, humidity and pressure probes. By setting MFC7 to 9 slm and MFC 6 to 1 slm, the final concentration of the toluene gas was 200 ppm. Another syringe pump (SP2) set the relative humidity of the gas stream by controlling the water infusion rate. This diluted toluene carried by the humidified air was then passed through three photoreactors (PR1, PR2 and PR3) at flow rates of 50 standard centimetre cubic per minute (sccm), 100 sccm and 300 sccm; controlled by MFC1, MFC2 and MFC3 respectively.

The three photoreactors contained different photocatalytic test pieces to compare their performance. Seven fluorescent light tubes from Osram with a power rating of 13W each were used as the irradiation source, with their emission spectrum shown in Figure 3-14. The output gas stream from the photoreactors was fed into a gas chromatography (GC) system (Perkin Elmer, Clarus 600) through a six port-sampling/injection valve. Thereafter, a flame ionization detector (FID) in the GC can detect and analyze the peaks of toluene and other intermediate gaseous products formed.

Figure 3-14. Emission spectrum of fluorescent lamps used in the photocatalytic gas test system.

3.4.4 Stearic Acid Test for Film

Stearic acid test was conducted for $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin film samples under the same fluorescent light illumination. Prior to the test, all samples sized 1" by 1" were activated under the light condition for 3 hours. Fourier Transform Infrared (FT-IR) background of the activated samples was collected from 400 to 3000 cm^{-1} with a Perkin Elmer FT-IR system. Using a pipette, 15 μL of stearic acid solution (100 μM in ethanol) was carefully dripped to fully cover the sample surfaces and baked dry at 60°C for 5 minutes. Time zero absorbance was then measured from 2000 to 3000 cm^{-1} . All samples were then illuminated in the light box and changes in absorbance were determined over various sampling time points. Quantification of stearic acid was done by estimating the area under the absorbance spectrum ($\text{A}\cdot\text{cm}^{-1}$) from wavenumber 2800 – 2945 cm^{-1} , as

shown in Figure 3-15. The obtained absorption areas were normalized to time zero values, to better represent the percentage change in concentration over UV illumination time.

Figure 3-15. FT-IR absorbance spectrum for stearic acid.

CHAPTER 4. THERMAL OXIDATION AND PHOTOCATALYTIC PROPERTIES OF TITANIUM NITRIDE

This chapter details systematic study of nitrogen-doped TiO₂, prepared by thermal oxidation of TiN. Its thermal evolution from TiN to mixed phase TiO₂ was studied by XRD, EDX and TEM observations. Next, a detailed study on its surface chemistry change with respect to annealing temperature was performed using high-resolution XPS. Particularly, the binding states of the remaining nitrogen dopants were revealed and their effects on the overall photocatalytic performance were discussed. The visible-light absorption of the powders was characterized using diffuse reflectance spectra. The photocatalytic performance was evaluated by the removal of Rhodamine B and gaseous toluene under visible-light illumination. In addition, the anti-bacterial property of the powders was demonstrated using *E. Coli* as a sample bacterium. Finally, the charge separation efficiency was studied by SPV and related to the surface resistivity and mixed phase formed at higher annealing temperatures.

4.1 Thermal Evolution from Titanium Nitride to Titanium Dioxide

The XRD spectra in Figure 4-1 illustrate how the nano-sized titanium nitride (TiN) powders were oxidized into titanium dioxide (TiO₂) after annealing at temperatures ranging from 350 °C to 600 °C in air. Each annealing process lasted for 2 hours. As can be seen from the figure, the as-purchased TiN powder had a NaCl-type, face-centred cubic crystal structure (Fm3m space group). This phase was maintained up to 350 °C. When the annealing temperature was raised further to 400 °C, anatase TiO₂ became the main phase but some trace of TiN cubic structure can still be observed. The TiN phase can no longer

be detected by XRD when the annealing temperature reached 450 °C. However, a few weak diffraction peaks of rutile TiO₂ appeared, due to the transition of some anatase phase to rutile structure, thereby forming a mixed-phase TiO₂. As expected, when the annealing temperature was further increased, more anatase transformed to rutile, as shown by the increased diffraction intensity of the rutile peaks.

Figure 4-1. XRD spectra of titanium nitride nanopowders at various annealing temperatures.

Based on the above observations, to form nitrogen-doped TiO₂ from TiN by direct oxidation in air, the minimum annealing temperature should be 450 °C. Furthermore, based on the XRD spectra, the weight fractions for anatase (w_A) and rutile (w_R) phases in the oxidized powders can be calculated according to the diffraction peak intensities, I_A and I_R using equation 4-1 [171] :

$$w_A = \frac{1}{1 + \frac{1}{K} \frac{I_R}{I_A}} \quad (4-1)$$

In this case, K is a constant fixed at 0.79 for $w_A > 0.2$. Assuming the samples were fully crystallized into either anatase or rutile phase, the weight fraction of rutile phase is therefore given by:

$$w_R = 1 - w_A \quad (4-2)$$

The calculated weight ratios are presented in Table 4-1 where it can be seen that the weight ratio of rutile TiO_2 increased from 0.16 at 450 °C to 0.44 at 600 °C. Next, Scherrer's equation was employed to calculate the volume averaged grain sizes based on the strongest peaks of anatase (101) at 25.3° and rutile (110) at 27.5°. Evidently, the crystal grains grew with annealing temperature, with the grain size of rutile phase being slightly larger than that of anatase phase for all cases. The specific surface areas were also determined using an adsorption analyzer (TriStar II 3020) from Micromeritics Instrument and the obtained values are also shown in Table 4-1. From the data, annealing the powder between 450 °C to 550 °C did not reduce the surface area significantly. At these temperatures, the specific surface areas reduced slightly from 33.0 to 29.8 m²/g. However, a significant reduction to 22 m²/g was observed at 600 °C due to fast particle sintering at elevated temperature.

Table 4-1. Weight fraction, grain size and BET surface area of annealed TiN powders.

Annealing Temperature (°C)	Anatase		Rutile		BET (m²/g)
	Weight fraction, w_A	Grain size (nm)	Weight fraction, w_R	Grain size (nm)	
450	0.84	9.7	0.16	10.9	33.0
500	0.78	11.2	0.22	12.5	32.4
550	0.71	11.6	0.29	12.4	29.8
600	0.56	13.5	0.44	14.0	22.0

The HR-TEM images in Figure 4-2 compare the particle sizes and crystallinity of the powder as-purchased and after annealing at 500 °C. It can be seen from Figure 4-2 (a) that TiN nanoparticles have uniformly distributed particle size of less than 50 nm. High magnification image in Figure 4-2 (b) further revealed a thin amorphous overcoat surrounding the well-crystallized TiN phase in the core. This amorphous phase is believed to be oxynitride phase, TiN_xO_y formed after TiN exposure to air. It has been observed by Jung et al. that titanium oxynitride phase transformed from sputtered TiN thin film was amorphous with TiN crystallites remaining inside [48]. Next, comparison of Figure 4-2 (a) to Figure 4-2 (c) showed that the particle size did not grow significantly after annealing at 500 °C, which agrees well with the BET surface area measurements. Meanwhile, the amorphous outer layer had reduced significantly, and well-crystallized grains can be observed at higher magnification in Figure 4-2 (d). However, particle growth took place, which explained the slight reduction in BET surface area obtained.

Figure 4-2. HR-TEM images for (a)-(b) titanium nitride; and (c)-(d) titanium nitride oxidized at 500 °C.

The bulk stoichiometry of the powders annealed at different temperatures was investigated using energy dispersive X-ray (EDX) attached to a JEOL JSM-5600LV SEM from Oxford Instruments, and the results are summarized in Table 4-2. After eliminating only surface adventitious carbon, the ratio of Ti:O was found to be 1:2 for all samples, suggesting that the oxidized powders were in stoichiometric composition. The EDX spectrum of the powders annealed at 450 °C is shown in Figure 4-3. There was no presence of nitrogen detected due to its relatively low content. Therefore, the amount of nitrogen remaining in the bulk of the powders was expected to be quite low, and thus

undetectable by the EDX due to its low minimum detection limit (MDL). There are two factors contributing to this poor minimum detection limit (MDL). Firstly, N has low atomic number. Secondly, high background count and peak overlapping with O due to the close proximity of binding energies for N and O can reduce MDL significantly to 1-2 wt% only, even under best experimental condition [7]. Next, surface sensitive X-ray photoelectron spectroscopy, or XPS was employed to investigate the nitrogen doping content on the powder surface, and to give insight on their binding states.

Table 4-2. Bulk atomic percent of annealed nano-sized TiN powder determined by EDX.

Temperature (°C)	Ti	O	C	Ti : O
450	33.27	66.55	0.18	2.0
500	33.24	66.48	0.29	2.0
550	33.26	66.52	0.21	2.0
600	33.12	66.25	0.63	2.0

Figure 4-3. EDX spectra of titanium nitride powder annealed at 450 °C.

4.2 Chemical States and Surface Stoichiometry Study with XPS

Figure 4-4 shows how the Ti 2p core level spectra of the samples changed with annealing temperature. The Ti 2p spectra consisted of doublet pairs due to inherent orbital splitting. From these spectra, three different pairs of doublet peaks can be identified. The peak with the highest intensity in all cases was centred at 458.6 ± 0.2 eV and it can be attributed to O-Ti-O bonds while the least intense peak centred at 455.4 ± 0.1 eV is due to N-Ti-N bonds from bulk titanium nitride species [172-174]. For the middle peak (456.9 ± 0.1 eV) between the two binding states of O-Ti-O and N-Ti-N, there are two explanations in the literature about its origin. Firstly, it has been widely attributed to Ti-N-O bonds from the oxynitride species which formed due to residue oxygen after the TiN preparation process, or due to slow oxidation when TiN is exposed to air [46, 175, 176]. Another explanation is that this peak is the shake-up satellite peaks due to interband transitions such as those observed by Strydom et. al [177] using electron energy loss spectroscopy (EELS).

Prior to Strydom's observation, Porte et. al [178] have studied the effects of vacancies on the shake-up signals of non-stoichiometric TiN, denoted as TiN_x , and strong satellite peak was observed for $x > 0.8$. Therefore, by adopting both shake-up and oxynitride explanations for this peak, the method used by Milosev [172] for quantitative analysis is employed for our current analysis. In his study, a pristine, sputter-cleaned and stoichiometric titanium nitride was used as a reference such that there was no oxynitride species formed on the surface, and the area ratio of shake-up peak to nitride peak was found to be 0.6. Thus, after deducting the contribution from the shake-up peak, the remaining area from the middle peak can be assigned to the oxynitride species.

Figure 4-4. Ti 2p XPS spectra of titanium nitride at different annealing temperatures.

From Figure 4-4 (a), all three peaks were detected for the as purchased TiN. The O-Ti-O oxide bond (458.7 eV) was expected, since titanium nitride is known to oxidize easily in air up to a few nanometers, which falls into the sensitivity range of XPS [40]. This oxide peak was due to thin, surface oxide layer and not bulk TiO₂ species since no trace of this phase was seen in XRD and EDX analyses earlier. The shake-up/oxy-nitride peak (457.0 eV) was very pronounced for this sample as well, with almost the same intensity as the nitride peak (455.5 eV). When the powder was annealed, both the shake-up/oxy-nitride and nitride peaks diminished. From 400 °C onwards, only the main oxide peak remained. In addition, this peak had also shifted slightly to higher binding energy and became symmetrical. These observations agreed well with the XRD spectra in Figure 4-1 whereby the powder transformed into anatase TiO₂ at 400 °C. Similarly, TiN was the main crystal phase at 350 °C based on XRD results without any trace of TiO₂. Therefore, the O-Ti-O species at 350 °C and below should originate from surface sub-oxide species, rather than anatase TiO₂.

The O 1s spectra consolidated in Figure 4-5 agreed well with the above discussion. Broadening of the high energy shoulder was observed in as-purchased TiN and powders annealed up to 350 °C. This was due to the middle peak at 531.1 eV, which can be assigned to Ti-N-O bond in oxynitride phase [46, 47, 175]. At higher temperatures, this broadening was not obvious and the O 1s profiles became similar for all samples up to 600 °C. The O-Ti-O bonds at 530 eV was symmetrical and well-defined due to formation of bulk TiO₂. Meanwhile, surface adventitious species such as hydrocarbon (C-H), carbonate species (C-O, C=O) and adsorbed water (OH_{ads}) bonds (532 eV) can also be observed due to contamination from environment during characterization.

Figure 4-5. O 1s XPS spectra of titanium nitride at different annealing temperatures.

On the other hand, the N 1s peak intensity decreased gradually with annealing temperature but diminished quickly above 350°C, as shown in Figure 4-6. This observation can be expected since the oxidation of TiN at low temperature follows a logarithmic model and at high temperature, the oxidation rate is parabolic [40, 142]. The lower oxidation rate at lower temperature is explained by slower oxygen diffusion, which is manifested by a temperature-dependent initiation time for oxygen to diffuse into grain boundaries [143]. For the as-purchased TiN and sample annealed at 250 °C shown in Figure 4-6 (a) and (b), the main peak at 397.3 eV is attributed to nitrogen in titanium nitride environment (N^{3-}), forming N-Ti-N bonds [47, 173-175]. For a chemically well-defined titanium nitride, the N 1s peak will be Gaussian, centred at 397 – 398 eV with FWHM of 1.6-1.9 eV [173]. In our case, the peaks were not Gaussian, and significant broadening was observed at lower binding energy side. This shoulder at lower energy is reported as oxynitride phase, represented by the N-Ti-O peak centred at 396.2 eV [174, 179]. The presence of this peak confirmed the earlier observation whereby an oxynitride peak was observed for Ti 2p. The amount of nitrogen in oxynitride phase increased with annealing temperature and at 350 °C, this peak overtook the nitride peak as the main peak, as can be seen from Figure 4-6 (c). Thereafter, at 400 °C and above, the intensities of both peaks reduced significantly due to fast oxidation process. Besides these two main peaks, there were two other small peaks detected at higher binding energy, centred at 399.0 eV and 401.7 eV. These are reported to be chemisorbed N_2 , also denoted as γ - N_2 , released during the oxidation of TiN and trapped underneath the oxynitride layers [41, 142, 172]. The difference between the two peaks lies with the screening effect, with the peak at 399.0 eV being well-screened γ - N_2 , and at 401.7 eV, poorly screened γ - N_2 [41].

Figure 4-6. N 1s XPS spectra of titanium nitride at different annealing temperatures.

From 400 °C to 550 °C, mainly TiO₂ with very little nitrogen was detected on the samples. The N 1s spectra in Figure 4-6 (d) had different profiles compared to the samples at lower temperatures. Only weak N 1s peaks appeared in all samples except the sample annealed at 600 °C where no nitrogen could be detected. In addition, a new peak centred between 399.7 – 400.0 eV was detected for samples annealed from 400 °C to 550 °C. This peak is commonly observed in N-doped TiO₂ and is believed to originate from interstitially-doped nitrogen atoms in TiO₂ environment, denoted in Figure 4-6 (d) as N_{interstitial} [33, 38, 180, 181] which contribute to the formation of localized mid-bandgap N 2p energy states. Since anatase TiO₂ was only formed at 400 °C and above, it therefore made sense that this interstitial nitrogen species was only detected at this temperature range. Despite this, some N-Ti-N and N-Ti-O bonds can still be observed due to a small amount of residual, incompletely oxidized TiN phase. Also visible in these spectra is the γ -N₂ peak, due to continuous release of N₂ from fast oxidation at elevated temperatures.

While confirmation on the existence of interstitial N may be a bit ambitious based on the weak XPS signals, the confirmation of N doping is corroborated by further studies such as diffuse-reflectance spectra, surface photovoltage study, as well as the various photocatalytic tests which point to visible-light response which must be brought about by the existence of nitrogen dopants in TiO₂. Furthermore, the colour changes in the samples from dark blue for 400 °C, then gray (450 °C), yellow (500 °C), pale yellow (550 °C) and almost white for 600 °C are also quite obvious to the naked eyes, as can be seen from Figure 4-7. The detailed results of these studies will be discussed in subsequent sections.

Figure 4-7. Observable colour changes of TiN powder oxidized at temperatures ranging from 350 °C to 600 °C (right to left).

Finally, the C 1s peaks are compared in Figure 4-8 for as purchased TiN and oxidized TiN for the annealing temperature of 600 °C. It can be seen that the C 1s spectra remained almost the same, since the peaks detected were mainly due to surface carbon contamination. Table 4-3 summarized the XPS observations for all elements. The Ti:O atomic ratios obtained were almost 1:2 at higher annealing temperatures, signifying successful formation of N-doped TiO₂. However, some oxygen deficiency was observed on the surface of the samples annealed at 450 °C.

Figure 4-8. C 1s XPS spectra for titanium nitride (a) before and (b) after annealing at 600 °C.

Finally, Table 4-3 and Table 4-4 summarize the peaks from the XPS observations and their concentrations. To calculate the stoichiometry changes from TiN to TiO₂ during the annealing process, all C 1s peaks and OH_{ads} will be omitted since they are surface adventitious species. The atomic concentrations for Ti, O and N with respect to annealing temperature is tabulated in the tables and depicted in Figure 4-9. It was observed that TiN surface was already oxygen-rich before annealing. This is due to its prolonged exposure to air and ease of oxidation. The surface stoichiometry remained almost the same even after annealing at 250 °C. Beyond that, oxidation process proceeded quickly with sharp drop in nitrogen content from 350 °C to 400 °C. Nitrogen concentration dropped sharply from 21.5% at 250 °C to 1.89% at 400 °C. At 450 °C, 500 °C and 550 °C, the nitrogen content are 1.43%, 1.34% and 0.52%, respectively. Finally, for the TiO₂ phase formed at 400 °C and beyond, the O/Ti atomic ratio changed from non-stoichiometric 1.87 (400 °C) and 1.90 (450 °C) to near stoichiometric values of 1.99 (500 °C), 2.00 (550 °C) and 1.99 (600 °C), as the oxygen vacancies were suppressed by the fast oxidation process and diminished nitrogen content.

Figure 4-9. Atomic concentration of oxidized TiN at different annealing temperatures.

Table 4-3. Summary of binding energy and atomic concentration of TiN powder annealed at different temperatures (250 °C to 400 °C).

Elements	TiN		250 °C		350 °C		400 °C	
Ti 2p	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %
N-Ti-N	455.4	3.52	455.4	2.55	455.5	0.94	-	-
N-Ti-O	456.8	4.11	456.9	4.04	457.0	2.67	-	-
Shake-up	456.8	2.11	456.9	1.53	457.0	0.56	-	-
O-Ti-O	458.7	13.35	458.8	12.58	458.8	17.08	458.7	20.79
O 1s	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %
O-Ti-O	530.0	21.73	530.1	20.64	530.1	30.97	530.0	38.81
N-Ti-O/C-O	531.3	10.68	531.3	7.42	531.2	10.33	531.3	8.51
O-H _{ads}	532.64	0.90	532.5	4.38	532.7	0.54	-	-
N 1s	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %
N-Ti-N	397.4	8.17	397.5	5.82	397.1	1.84	-	-
N-Ti-O	396.2	5.10	396.3	5.53	396.1	2.99	396.3	0.28
γ-N ₂	398.9	2.31	399.1	2.01	402.1	1.44	403.3	0.59
γ-N ₂	401.1		401.9					
N _{interstitial}	-	-	-	-	-	-	399.9	0.28
C 1s	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %
C-H	285.0	20.27	285.0	23.23	285.0	24.95	285.0	24.93
C-O	286.3	5.78	286.2	8.42	286.3	4.42	286.1	4.17
C=O	288.9	1.96	289.1	1.85	288.9	1.41	288.8	1.63
Total	99.99		100.00		100.02		100.00	
Atomic concentration based on TiN _x O _y								
Ti (Atm%)	32.48		33.32		30.46		34.22	
O (Atm%)	45.60		45.17		60.32		63.88	
N (Atm%)	21.92		21.51		9.22		1.89	

Table 4-4. Summary of binding energy and atomic concentration of TiN powder annealed at different temperatures (450 °C to 600 °C).

Elements	450 °C		500 °C		550 °C		600 °C	
Ti 2p	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %
N-Ti-N	-	-	-	-	-	-	-	-
N-Ti-O	-	-	-	-	-	-	-	-
O-Ti-O	458.7	21.66	458.7	21.43	458.7	21.52	458.7	21.79
O 1s	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %
O-Ti-O	530.0	41.17	529.9	42.71	529.9	42.97	529.9	43.32
N-Ti-O/C-O	531.3	8.58	531.4	8.15	531.4	8.12	531.3	8.01
N 1s	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %
N-Ti-N	397.3	0.20	-	-	-	-	-	-
N-Ti-O	-	-	396.9	0.19	-	-	-	-
γ-N ₂	403.4	0.38	403.4	0.25	403.5	0.13	-	-
N _{interstitial}	399.7	0.33	400.0	0.43	400.0	0.21	-	-
C 1s	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %	BE (eV)	Atm %
C-H	285.0	21.51	285.0	21.39	285.0	21.18	285.0	22.14
C-O	286.2	4.33	286.2	3.70	286.2	3.95	286.3	3.06
C=O	288.8	1.84	288.8	1.76	288.8	1.90	288.9	1.67
Total	99.99		100.00		100.02		100.00	
Atomic concentration based on TiN _x O _y								
Ti (Atm%)	33.98		32.96		33.19		33.47	
O (Atm%)	64.59		65.70		66.28		66.53	
N (Atm%)	1.43		1.34		0.52		0	

4.3 Light Absorption Properties

The UV-Vis spectrometer can be operated under reflectance mode to collect the diffuse reflectance spectra of the oxidized powders. This can give an overview of how their light absorption properties change with annealing temperature. The collected spectra are compared in Figure 4-10 for incident wavelengths ranging from 250 – 700 nm. The reflectance spectra for as purchased TiN and sample annealed at 350 °C are indistinguishable. There was no obvious fundamental absorption edge, which is a characteristic of semiconductor materials when electron-hole pairs are generated. This is because TiN is a material of mixed covalent, ionic and metallic bond [182] and at 350 °C, the powder was still in TiN phase, consistent with the XRD observations. The absorption edge was only obvious when annealing temperature was 400 °C and above. A Kubelka-Munk (KM) transformation [149] was carried out to obtain the absorption profiles for samples annealed at higher temperatures, which are shown in Figure 4-11 and discussed as follows.

Figure 4-10. Diffuse reflectance spectra of TiN powders annealed at different temperatures.

Figure 4-11. Effect of annealing temperature on the light absorption of TiN powders.

The TiN powders at these high annealing temperatures had already formed TiO_2 with trace of nitrogen on their surface and sub-surface layers. The fundamental absorption edge of TiO_2 is determined by the electron transition from O 2p to Ti 3d level. By increasing annealing temperature, the onset of this absorption edge for samples annealed at 450 °C, 500 °C and 550 °C were similar, and could be extrapolated to approximately 400 nm. There was a more obvious red shift found for the sample annealed at 600 °C. Since there was no nitrogen detected in the 600 °C annealed sample by XPS, this shift may be related to the formation of rutile phase which has a narrower bandgap of 3.05 eV, compared to 3.20 eV for anatase [12, 38]. The corresponding wavelength of 407 nm for 3.05 eV agreed well with the absorption onset observed.

Apart from this fundamental absorption, absorption tails extending up to 525 nm were observed for all samples with absorbance values that decreased with annealing temperature. From the XPS data, the nitrogen content decreased with temperature in the same manner. Hence, these absorption tails could be attributed to both light absorption from mid-bandgap N 2p states formed above O 2p

states introduced by the interstitial nitrogen dopants (399.8 eV) [28, 35], as well as residual TiN phase (397.1 eV).

Finally, an increasing absorption tail in the visible-light region of 525 - 800 nm was only observed at 450 °C. This is most possibly due to residual TiN, since most of the remaining nitrogen in this sample was found to remain in this state from XPS analysis. In addition, oxygen vacancies, which increased with nitrogen content to maintain charge stability, could also contribute to this absorption tail at longer wavelengths [183, 184]. It has been reported that nitrogen doping favored the formation of oxygen vacancies in TiO₂ by lowering its formation energy [185, 186] and based on the XPS analysis, the Ti : O ratio obtained for this sample was 1 : 1.90, therefore verifying the presence of oxygen vacancies. The presence of oxygen vacancies leads to defect states in the form of F-type colour centre, which is an electron pair left behind in the cavity due to loss of an O atom [187]. This colour centre can trap holes to become single electron defect (F⁺) or completely electron deficient (F⁺⁺), as well as interact with Ti⁴⁺ atoms in adjacent lattice sites to form Ti³⁺. From both experimental and theoretical studies, the energy state of the F centre lies below the conduction band, while for F⁺ centre, the energy level is closer to valence band [188]. Kuznetsov and Serpone compared the light absorption of various visible-light-active TiO₂ and proposed that absorption at 590 – 729 nm can be assigned to electron transition from the ground state to excited state of these F-type colour centres [187, 189].

The variation in the absorption spectra was manifested as obvious colour change when the powders were annealed as shown in Figure 4-7 earlier.

4.4 Photocatalytic Properties

The mechanism for photocatalytic reaction on semiconductors such as TiO_2 has been described in sections 2.1 and 2.2.2 earlier. In essence, electrons and holes absorbed by the semiconductor migrate to its surface and react with surface adsorbed molecules such as O_2 and H_2O to produce reactive oxygen species such as O_2^- and radicals such as OH^* and HO_2^* which will oxidize and mineralize pollutants (equations 2-2 to 2-8). This process can be seen as a direct photocatalytic process.

In contrast, when a coloured dye is present as the target pollutant in a semiconductor suspension, the oxidation and mineralization can be initiated by the dye. The chromophore of the dye can absorb photons of suitable wavelengths, and get excited to singlet or triplet states. If the dye is absorbed onto the surface of the semiconductor, the excited dye will then inject the electrons into the conduction band of the semiconductor, leaving behind oxidized dye radicals [190, 191]. The surface adsorbed oxygen will be a critical electron scavengers which prevent recombination between the electrons and dye radicals, i.e. regeneration of dye. In the presence of oxygen, the oxidized dye can then undergo further reactions and get mineralized. This process is therefore a sensitized photocatalytic process, also known as photosensitization in short. For a dye- TiO_2 mixture, the reactions involved are shown by equations 4-1 to 4-5 [192].

Therefore, if the illumination source consists of both UV and visible-light, e.g. a solar-simulating lamp, both direct and sensitized photocatalytic processes can happen via absorption of UV by TiO₂ and visible-light by dye to fully harness the light energy of the source. Figure 4-12 shows both processes happening concurrently when Acid Orange 7 (AO7) is mixed with TiO₂ under illumination of a solar-simulating Xenon lamp [193]. From equation 4-3, it can be seen that the injected electrons undergo similar fate to electrons generated by TiO₂ itself and therefore interfacial electron transfer from dye to TiO₂ is critical for sensitized photocatalytic process [194]. For the sake of clarity, the term “photocatalytic” will refer to the conventional, direct photocatalytic process, while “photosensitization” will refer to the latter, sensitized photocatalytic process in the ensuing discussions.

Figure 4-12. A schematic diagram by Styliadi et al. [193], illustrating both direct and sensitized photocatalytic processes when a dye-semiconductor suspension is illuminated by solar light.

4.4.1 Rhodamine B Removal Test

Figure 4-13 compares the Rhodamine B degradation tests for oxidized TiN powders. Fluorescent light with UV filter that cuts off wavelength below 435 nm was used as

illumination source (Figure 3-9). All samples were kept in the dark for two hours to achieve physical adsorption-desorption equilibrium. Thereafter light was turned on with its intensity maintained at 1,700 Lux. Experiments under completely dark condition were also conducted to verify that the observed dye degradation was due to light-driven reactions. Similar test was also carried out for P25 to serve as comparison. From Figure 4-13 (a), in a control sample of Rhodamine B solution (pH = 5.5) illuminated without any powder, the concentration remained almost the same up to 24 hours. This shows that Rhodamine B cannot self-compose under such weak visible-light irradiation. Similarly for non-semiconductor TiN, there was not much difference between light and dark reactions. In all other cases, the reaction rates under light were significantly faster than the dark condition, as expected. It can be seen that with increasing annealing temperature, the difference between the light and dark experiments became more significant, with the fastest overall degradation rate achieved by sample annealed at 500 °C. With this powder suspension, 95% of the initial Rhodamine B concentration was removed after 22 hours of visible-light illumination. However, the sample annealed at 600 °C could also degrade the dye, despite having the least visible-light absorption (Figure 4-11) due to the absence of nitrogen dopants. The same could be observed for P25; although its rutile phase has a bandgap of 3.05 eV and it should have little visible light absorption. Therefore, a major part of the Rhodamine B photodegradation observed was due to photosensitization process.

Figure 4-13. Rhodamine B degradation tests for P25 and oxidized TiN powders under dark and light conditions. Light was turned on after 2 hours.

An anomaly can be observed in Figure 4-13 (c). In most of the data obtained, the characteristics of this sample annealed at 400 °C appeared to be a transition point from lower temperature, TiN-rich powder to high temperature, mainly nitrogen-doped TiO₂. This can be seen from Figures 4-1, 4-4, 4-5, 4-6, 4-9 and 4-10. As seen in Figure 4-7, this sample appeared dark blue rather than black for TiN-rich sample at 350 °C, yet different from the samples annealed at 500°C onwards which are mostly yellowish. Currently, there is no explanation for this anomaly as no further study has been done on this sample. One possible reason could be its poor crystallization, highly amorphous state as TiN is transformed into TiO₂, leading to poor interfacial charge transfer, therefore high recombination rate even though photosensitization can take place. Regardless, more study needs to be conducted to verify this.

Figure 4-14 shows the molecular structure of Rhodamine B. During the photodegradation of Rhodamine B, there are two competitive pathways identified, namely *N*-dealkylation and the destruction of its conjugated xanthene ring [195, 196]. The *N*-dealkylation of Rhodamine B, which has four terminal ethyl groups occurs as the progressive removal of these ethyl groups (de-ethylation process) [197-199]. This process is attributed to the photosensitization process and can be identified by progressive blue shift in the absorption maxima, $\lambda_{\max}$ of the dye since tetra-, tri-, di-, mono-, and un-ethylated Rhodamine B have $\lambda_{\max}$ of 554 nm, 539 nm, 522 nm, 510 nm and 498 nm, respectively [196]. The second degradation pathway occurs via photocatalytic process, in which the breaking of the middle conjugated xanthene ring takes place and the dye absorbance will decrease without any blue shift in absorption maxima [195, 197, 200].

Figure 4-14. Molecular structure of Rhodamine B dye.

Figure 4-15. Rhodamine B degradation by P25 and oxidized TiN powders under visible-light illumination, normalized to their concentrations after dark adsorption.

When the dye concentrations were normalized to their initial values after the dark adsorption-desorption equilibrium (at 2 hours) as shown in Figure 4-15, enhanced Rhodamine B removal rate was achieved by samples annealed at 500 °C and 550 °C compared to P25. This enhancement was therefore made possible by the nitrogen dopants

which enabled visible-light absorption by the powder that led to photocatalytic reactions on top of the photosensitization process.

Figure 4-16 shows how the absorbance of the Rhodamine B changed throughout the degradation test for the best-performing sample annealed at 500 °C. It can be seen that after 2 hours in the dark, the concentration reduction for the next 6 hours occurred without significant blue-shift. This indicates the cleavage of the middle xanthene ring due to visible-light photocatalytic process. For prolonged illumination, blue-shift due to *N*-dealkylation took place. Therefore, it is evidenced that both photosensitization and photocatalytic process took place for this sample to achieve an improved overall Rhodamine B removal rate. The process should occur first via the breaking of the middle xanthene ring to form smaller intermediates, followed by progressive removal of ethyl groups.

Figure 4-16. Change in absorbance spectrum of Rhodamine B in a suspension of TiN powder oxidized at 500 °C under dark and illuminated conditions.

4.4.2 Acid Orange 8 Removal Test

Since Rhodamine B is a cationic dye, the oxidized TiN powders were further tested using an anionic dye, Acid Orange 8 to investigate the removal efficiency. Acid Orange 8 has a similar pH of 5.5 at the concentration of 15 μ M. Figure 4-17 shows the molecular structure of Acid Orange 8, or AO8.

Figure 4-17. Molecular structure of Acid Orange 8 (AO8) dye.

AO8 is a part of the azo-dye family which has been studied extensively as target pollutant for TiO_2 photocatalytic removal. [201-203]. Similar to Rhodamine B, its photodegradation can occur due to both photosensitization and photocatalytic process. Extensive degradation pathway study by Stylidi et al. using AO7 shows that decoloration and complete mineralization occur via photosensitized cleavage of molecule at the azo bond ($-\text{N}=\text{N}-$) to form naphthalene- and benzene-type intermediates [193]. Successive oxidation on these intermediates then led to smaller products such as aromatic, then aliphatic acids in the form of acetic, formic and oxalic acids. Complete mineralization gives end products such as CO_2 , SO_4^{2-} , NH_4^+ and NO_3^- . In the case of AO8, similar intermediates and final products were detected, suggesting similar pathway [204]._Figure

4-18 shows the results of the Acid Orange Test. Clearly, apart from the physical absorption in the dark for the first 2 hours, there was no further removal of dye when the light was turned on.

Figure 4-18. Acid Orange 8 removal test by oxidized TiN powders under visible-light illumination.

The reason for this observation can be deduced from the Zeta-Potential measurement of the powders. Figure 4-19 compares the surface potential of the powders, averaged over five measurements when 1.0 g/L of powder was dispersed in DI water. The obtained values indicated that all powders have negative surface potential, which agreed well with their better performance in the degradation of cationic Rhodamine B compared to anionic Acid Orange 8. However, there is no direct relationship between the magnitude of the surface potential and the annealing temperature, as upon formation of TiO_2 at 400 °C, the obtained potentials are approximately -40 mV for all samples.

Figure 4-19. Zeta Potential of oxidized TiN powders at different annealing temperatures.

4.4.3 Anti-bacterial Performance on *E. Coli*

TiN powders and samples annealed at 450 °C, 500 °C and 550 °C were selected for *E. Coli* bactericidal test under visible-light with $\lambda \geq 435$ nm since they exhibited obvious visible-light absorption up to 525 nm due to nitrogen doping as shown in Figure 4-11. Control experiments, in which the bacteria were suspended in water under illumination but without any powder, were also conducted to ensure that the illumination did not reduce the bacteria viability significantly. Figure 4-20 shows the *E. Coli* survival ratio (population in CFU/ml normalized to time zero) over time under fluorescent light illumination. The powder annealed at 500 °C could reduce *E. Coli* population steadily upon illumination, killing 54% of *E. Coli* after 5 hours, which is more than twice the percentage killed by non-oxidized TiN. The bactericidal effects of powders annealed at 450 °C and 550 °C were similar, where up to 46% and 45% of *E. Coli* were killed, respectively.

Figure 4-20. Survival ratio of *E. Coli* in oxidized TiN powder suspensions over illumination time under 40W (1,700 Lux) fluorescent light.

Next, as seen from Figure 4-21, under much stronger Xenon light, the *E. Coli* population reduced quickly for all samples. This can be explained by the higher light intensity coupled with the heat generated from the Xenon lamp. Again, the powders annealed at 450 °C and 500 °C showed enhanced bacteria killing effect. With TiN, the percentage of *E. Coli* which survived after 2 hours was 23%, but with nanopowders annealed at 450 °C and 500 °C, only 10% and 4% of *E. Coli* survived, respectively. These results therefore demonstrate the visible-light photocatalytic activities of oxidized TiN nanopowders for *E. Coli* disinfection.

Figure 4-21. Survival ratio of *E. Coli* in oxidized TiN powder suspensions over illumination time under 250W (20,000 Lux) Xenon light.

4.4.4 CO₂ Emission from Photocatalytic Oxidation of Toluene

The TiN powders oxidized at 450 °C, 500 °C and 550 °C were further tested for the removal of gaseous toluene using an in-house, custom-built test system built by Ms. Zhang Li based on ISO standard for the testing of planar photocatalytic test piece. The powders were spray-coated onto polyester filter, and exposed to a continuous flow of toluene contaminated (200 ppm), humidified zero air flow while irradiated from the top to initiate photocatalytic reactions. The visible-light source used was made up of seven fluorescent tubes (Osram, 13 W each), and the effectiveness of the powders was evaluated based on the amount of CO₂ released from the toluene decomposition process. The CO₂ amount was determined using the methanizer with flame ionizer detector in a gas chromatography (GC) system (Perkin Elmer, Clarus 600) under different flow rates (50,

100 and 300 sccm) and relative humidities (0%, 40% and 70%). The obtained results are shown in Figure 4-22.

Figure 4-22. The evolution of CO₂ from the removal of gaseous toluene by oxidized TiN powder spray-coated on a polyester filter under visible-light illumination at different flow rates and humidity levels.

Firstly, by comparing the flow rates of the gas stream, it can be seen that at high flow rate of 300 sccm, there was no CO₂ evolution observed. When the flow rate was reduced to 100 sccm and 50 sccm, CO₂ was clearly detected with highest amount of 6 ppm obtained for the slowest flow rate. This signified that oxidation of toluene took place via photocatalytic reaction on the oxidized TiN powder surface. With slower flow rate, there would be more time for toluene transfer to the photocatalyst surface, enabling more photocatalytic oxidation and therefore CO₂ release. Meanwhile, it can be seen that for 0% relative humidity, the CO₂ evolution increased slowly with illumination time and became constant. When the humidity was further increased to 40%, significantly more CO₂ was detected. This observation highlighted the importance of water molecules in the photocatalytic removal of toluene and is consistent with the well-established knowledge regarding the role of hydroxyl radicals during the redox reactions that follow electron-hole pairs generation [17, 69, 70]. Nevertheless, with increased illumination time and relative humidity up to 70%, the CO₂ evolution did not increase further. In fact, it is obvious that compared to the concentration of toluene (200 ppm), the maximum CO₂ yield of 6 ppm is very low. This means that the oxidized powders had limited efficiency under visible-light illumination due to the low nitrogen content present. However, it can be seen that the sample oxidized at 500 °C produced the most CO₂, while the performance of 450 °C and 550 °C were comparable.

Based on the evaluation of the powders' performance with photodecomposition of Rhodamine B, *E. Coli* killing and oxidation of gaseous toluene, the best performance was achieved when the annealing temperature was set at 500 °C rather than 450 °C despite its highest total nitrogen content and light absorption. This means that not all light absorption

contribute to electron-hole pair generation, which was followed by separation and diffusion to the surface for redox reactions. Of the various nitrogen species detected by XPS, only interstitial nitrogen atoms with binding energy of 399.7 – 400.0 eV formed localized N 2p energy states within semiconductor TiO₂ band structure. Absorption by electrons from this N 2p to Ti 3d states produced electron-hole pairs that eventually contributed to photocatalytic reaction. For nitrogen atoms in residual TiN phase (397.1 – 397.5 eV), the light absorption was due to the vast density of states formed by the overlapping of Ti 3d and N 2p states and therefore, did not produce electron hole pairs [205]. Based on the atomic concentration of each nitrogen species listed in Table 4-3 and Table 4-4, sample annealed at 500 °C had the highest content of interstitially doped nitrogen, as shown by the highlighted row. This explained its highest observed photo-driven reaction rates compared to 450 °C and 550 °C.

4.5 Surface Photovoltage Study

Kelvin Probe based SPV is a non-contact method to measure the contact potential change as a result of illumination. Unlike diffuse reflectance spectra, the magnitude of the surface photovoltage does not solely depend on the number of electron hole pairs generated by photon absorption, but also the diffusion of these carriers to surface states which in turn, also depends on the charge separation efficiency. A larger surface photovoltage signal indicates that more charge carrier can diffuse to the particle surface to cause a larger contact potential difference. Figure 4-23 illustrates the light “On-Off” SPV evolution characteristics of the samples under the illumination of a 455 nm blue LED. All samples were kept in dark for more than 16 hours to stabilize their surface charges, followed by illumination for 700 seconds.

Figure 4-23. Surface potential change of oxidized TiN powder and P25 under blue LED illumination ($\lambda = 455$ nm).

The sample annealed at 450 °C showed the fastest SPV response to illumination and its SPV value stabilized at about 160 mV. Meanwhile, the 500 °C oxidized sample showed the highest SPV value of 180 mV. This is consistent with the XPS analysis whereby the 500°C oxidized sample had the highest amount of nitrogen dopants in interstitial sites, which can absorb visible-light photon to generate electron-hole pairs. By further increasing the oxidization temperature to 550 °C and 600 °C, the SPV magnitudes of the samples deteriorated due to lower nitrogen content remaining and hence less visible-light absorption. Particularly, the obtained SPV magnitudes agreed with the anti-bacterial performance exhibited by the samples annealed from 450 °C to 550 °C, showing the importance of the interstitially-doped nitrogen species.

For example, the performances of the powders in Figure 4-20 can be explained by the SPV response in Figure 4-23. When the LED illumination was turned on, the 550 °C showed the slowest response, on top of the smaller SPV value. While the SPV magnitude is believed to be related to the content of interstitial nitrogen, the ease of charge transfer to the surface (and therefore response time) is dependent on surface resistance. This slow response of the 550 °C due to its higher surface resistance could explain why its anti-bacterial performance was only obvious after prolonged illumination for 4-5 hours.

When the illumination was removed, it could be observed that the SPV of all samples decayed slowly. This charge decay is related to their surface electrical properties for charge diffusion and electron-hole pair recombination. By observing the slope of the spectra, the sample annealed at 450 °C had the fastest recombination rate, followed by 500 °C, 550 °C and 600 °C. From the XPS results, while the nitrogen content decreased with oxidization temperature, the surface oxygen stoichiometry became closer to the stoichiometric TiO₂ composition. As a result, the resistance at the surface of the powders increased with annealing temperature and charge diffusion from the surface was suppressed. This explained the slow decay of SPV response after the light was removed.

Based on the above results and discussions, the optimized photocatalytic performance of sample annealed at 500 °C can be attributed mainly to its highest interstitial nitrogen dopant content. At 450 °C, nitrogen remaining was mostly trapped as N₂ molecules, and a significant percentage still remained in TiN and oxynitride environments. The nitrogen at such binding positions would not be able to contribute to the formation of N 2p states above valence O 2p band that can absorb visible-light photons. Furthermore, the oxygen vacancies detected by XPS and diffuse reflectance could form trapping and recombination

sites that hinder charge transfer to particle surface for photocatalytic reactions [35, 99]. This explained its lower surface photovoltage magnitude and faster recombination rate, which resulted in relatively poorer performance compared to 500 °C. Sample annealed at 550 °C had less interstitial nitrogen compared to 500 °C and 450 °C, and accordingly, its anti-bacterial performance was the poorest. However its anatase-to-rutile ratio of almost 70:30 was similar to that of market leader P25, which helped to improve charge separation. Specific studies on nitrogen-doped mixed-phase TiO₂ had also found improved photocatalytic performance when rutile content increased [181, 206].

4.6 Conclusion

In this chapter, the oxidation of TiN powder and its characteristics at different annealing temperatures are presented. Based on the XRD results, the minimum temperature required to fully oxidize TiN to anatase TiO₂ was 450 °C. At higher annealing temperature, phase transition took place to form anatase-rutile mixed phase TiO₂. Nevertheless, the BET surface areas of these powders remained at approximately 30 m²/g up to 550 °C, which are consistent with their nano-sized particles observed under HR-TEM. Based on the HR-TEM observation of an amorphous overcoat and XRD analysis, the transformation of TiN to TiO₂ took place via an intermediate oxynitride phase, which was formed upon prolonged exposure of the TiN nanoparticles to air. Diffuse reflectance spectra showed that apart from the fundamental absorption edge of TiO₂ formed by the energy gap between Ti 3d and O 2p states, and extension of the absorption tail up to 525 nm was observed for powders annealed from 450 °C to 550 °C due to the nitrogen dopants. The powders were subjected to a series of photocatalytic tests for the removal of Rhodamine B, Acid Orange, *E. Coli* and gaseous toluene. Based on these results, 500 °C

appeared to be the optimum annealing temperature for best performance. Surface photovoltage study revealed that this sample produced the largest surface photovoltage upon illumination, which is related to its highest content of interstitially-doped nitrogen. Meanwhile, the charge recombination rate, as reflected by the photovoltage decay upon light removal; was observed to decrease with annealing temperature. This was due to the increase in surface resistance with improved oxygen stoichiometry and formation of mixed phase TiO_2 at higher annealing temperature. Although the nitrogen doped TiO_2 has managed to display visible-light photoactivities, their overall efficiency was quite low due to the low nitrogen content remaining at the higher temperatures required to form TiO_2 . Therefore, the oxidation process could be improved in the future to conserve more nitrogen at these temperatures.

CHAPTER 5 : SOL-GEL STUDY OF $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ THIN FILMS

Currently, the reported work on $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films and its coatings have been limited. The main reported methods in the literature are pulsed-laser deposition (PLD) [67], electrospinning and electrospraying [68, 133]. In these cases, the reported x values for the iron content have not exceeded 0.4. In addition, large area coating will be difficult in terms of uniformity and processing time. Therefore, this chapter reports the synthesis of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films for varying x values based on sol-gel. This method allows large area coating with good stoichiometry control. Furthermore, it does not require extensive equipment setup and high processing temperature.

Amongst the various challenges that need to be overcome in devising a sol-gel based preparation method for $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films, the choice of starting precursor is of utmost importance. This is due to the difference in reactivity between these starting precursors, and hence careful consideration must be given to control the behavior of these precursors in the sol by using stabilizer, or chelating agent. The sol prepared must not only be stable, but must have good reproducibility. The other major challenge is to obtain good quality thin film coatings. To achieve this, optimization of the parameters must be carried out during the thin film fabrication process. Problems faced include the adhesion to the chosen substrates and the formation of hillocks on the films surfaces. The former would result in the peeling of the film from the substrate while the latter produced non-uniform films. For ease of discussion, the $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films samples will be named as STF x , with x representing the iron content. For example, $\text{Sr}(\text{Ti}_{0.8}\text{Fe}_{0.2})\text{O}_{3-\delta}$ and $\text{Sr}(\text{Ti}_{0.3}\text{Fe}_{0.7})\text{O}_{3-\delta}$ thin films will be denoted as STF02 and STF07, respectively.

5.1 Conventional Sol-Gel Method Based on Hydrolysis of Metal Alkoxides

In the first part of this study on STF_x, conventional sol-gel method based on the hydrolysis of metal alkoxides was used. In the literature, there are many reports of successful preparation of other perovskite materials using this method, such as (Ba,Sr)TiO₃ [207-212] and SrTiO₃ [213, 214]. By extending the understanding from these works, iron (III) nitrate was introduced as precursor due to its common availability and good solubility in water. In addition, the use of acetic acid and acetylacetone as chelating agents was explored and compared.

5.1.1 Acetic Acid as Chelating Agent

Figure 5-1 shows the solution preparation route using acetic acid as a chelating agent for strontium acetate and iron (III) nitrate. Using this method, acetic acid act as both solvent and chelating agent for the Fe³⁺ and Sr²⁺ ions. Meanwhile, upon mixing with water, titanium (IV) butoxide will undergo reactive hydrolysis. Therefore, acetylacetone serves to replace one of its four butoxide groups to greatly control and reduce its hydrolysis rate.

For a start, STF02 thin films were prepared and annealed at different temperatures using the annealing parameters detailed in Chapter 3. Figure 5-2 shows the XRD spectra of 5 layers of STF02 thin films, about 170 nm thick, annealed at different temperatures on two different substrates. Since one of the possible applications of photocatalytic thin films is transparent coating on glass for self-cleaning windows, the study of this coating on glass can determine whether a low processing temperature which is sufficient for crystallization, yet below the softening temperature of glass can be achieved.

Figure 5-1. $Sr(Ti_{1-x}Fe_x)O_{3-\delta}$ solution preparation based on hydrolysis of metal alkoxides with acetic acid as chelating agent for Fe^{3+} .

In this case, it can be seen that crystallization begins from as low as 500 °C, forming a single cubic perovskite phase of STF02. At 525 °C, this crystallization is complete and all the major peaks can be detected sharply. Thereafter, to study its crystallization behavior at higher temperatures, the films were coated on silicon wafer, with a layer of 500 nm thermally grown SiO_2 in between for improved adhesion. There was continued grain growth with increasing annealing temperature, without the formation of secondary phase. This indicated that the solution preparation method in Figure 5-1 can be used to prepare STF02 thin films with crystallization temperature as low as 525 °C.

Figure 5-2. XRD spectra of $\text{Sr}(\text{Ti}_{0.8}\text{Fe}_{0.2})\text{O}_{3-\delta}$ thin films annealed at different temperatures on glass and silicon wafer (Si).

This has also highlighted the advantage of sol-gel method over the conventional solid-state reaction that requires high processing temperatures.

The thin film coating quality was then evaluated using Field-emission SEM (FE-SEM) and atomic force microscope (AFM). Figure 5-3 shows the surface and cross-sectional FE-SEM images of 5 layers of STF02 coated on 500 nm thermally grown SiO_2 and annealed at 525 °C, the minimum temperature for complete crystallization, according to Figure 5-2. It can be seen that the obtained film was not a continuous, smooth thin film as with the case of $(\text{Ba},\text{Sr})\text{TiO}_3$ thin films prepared using similar chemical routes [211, 215]. Serious blistering and peeling could be observed on the surface with size up to 2 μm . The cross-sectional image, however, revealed that the film was dense beneath with uniform thickness of approximately 170 nm for 5 layers of coating.

Figure 5-3. FE-SEM images of STF02 thin films, spin-coated 5 layers on silicon wafer with 500 nm of thermally grown SiO_2 .

Next, the effect of substrate on the surface morphology and roughness was observed using AFM scans. Similarly, 5 layers of STF02 were coated on the substrates and annealed at 525 °C. Scans were carried out over a surface area of 5 μm x 5 μm using the Nanoscope IIIA atomic force microscope in the tapping mode. Figure 5-4 compiles the AFM scans which show similar morphology to that of FE-SEM images where the films obtained were not smooth and dense regardless of substrate used. However, when the surface roughness was compared, STF02 coated on SiO_2 had the largest root-mean-squared (RMS) roughness of 31.7 nm, whereas for silicon and quartz, the RMS roughness were 24.9 nm and 28.0 nm, respectively. Regardless, this roughness difference is not

significant compared to the thickness of the film, which is about 170 nm, as shown in Fig. 5-3.

Figure 5-4. AFM scans of STF02 thin films, spin-coated 5 layers on different substrates and annealed at 525 °C.

Since a single, cubic perovskite phase for STF02 can be successfully formed using this simple conventional solution preparation route, it is therefore logical to extend to the higher iron content. $\text{Sr}(\text{Ti}_x\text{Fe}_{1-x})\text{O}_{3-\delta}$ thin films with $x = 0.5, 0.6, 0.9$ and 1.0 , henceforth denoted as STF05, STF06, STF09 and SF were prepared using the same solution preparation route and annealing temperature. A comparison of their crystallization behaviours is shown in Figure 5-5.

Figure 5-5. XRD spectra of $\text{Sr}(\text{Ti}_x\text{Fe}_{1-x})\text{O}_{3-\delta}$ and $\text{SrFeO}_{3-\delta}$ thin films annealed at 525 °C.

From Figure 5-5, it can be seen that the crystal phases obtained for the range of $x \geq 0.5$ to $x = 1.0$ are different from the simple cubic perovskite phase obtained for STF02. For STF05, STF06 and STF09, only a small trace of cubic perovskite phase was observed. Instead, Fe_2O_3 was the main phase, together with other secondary phases that could not be verified. Furthermore, based on the intensities of the peaks, the grain size obtained at higher x values was smaller for the same annealing temperature. This implied that with more iron, the required crystallization temperature increased. As a result, the $\text{SrFeO}_{3-\delta}$ thin film remained amorphous at the annealing temperature of 525 °C.

To understand why a single cubic perovskite phase could not be formed using the conventional sol-gel route for higher iron content, the dried solution was studied using DTA/TGA and the results are shown in Figure 5-6. For TiO_2 , the solution was prepared using the chemical route outlined in Figure 5-1 without strontium and iron precursors,

acetic acid and water. When dried at 80 °C on a hotplate, a clear and uniform gel was obtained. The DTA/TGA profile of the TiO_2 gel shown in Figure 5-6 (a) was used as a reference since amongst all the three metal precursors, only titanium (IV) butoxide was capable of undergoing reactive hydrolysis via its remaining three free butoxide groups. On the other hand, strontium acetates and iron (III) nitrates could be fully dissolved in water and acetic acid to form Sr^{2+} , CH_3COO^- , NO_3^- , and $[Fe(H_2O)_6]^{3+}$ complex which were well-mixed at molecular level. Some cations were also chelated by acetic acid to form metal chelates which helped to maintain their homogeneities. The hydrolysis reaction of TiO_2 was rather direct and simple; with an endothermic peak (T1) at 103 °C which was accompanied by a weight loss of 15.3% due to evaporation of solvent and any excess acetylacetone. At 393 °C, a final weight loss of 11.3% was observed. This corresponded to the decomposition of the alkoxide ligands and final formation of TiO_2 bonds which is an exothermic reaction (T2).

Comparing the DTA/TGA profiles across different iron content in Figure 5-6, it can be seen that evaporation of solvent and excess agents at approximately 100°C, marked as endothermic peak T1 was common for all samples. However, the process T2 which occurred as a result of the hydrolysis of TiO_2 was obvious only up to STF06. This trend shows that the reactive hydrolysis reaction in the solution slowed down with larger x value, which was expected since there were reduced titanium (IV) butoxide in the solution.

Figure 5-6. DTA/TGA profiles of dried gel and powders derived from TiO_2 , $\text{Sr}(\text{Ti}_x\text{Fe}_{1-x})\text{O}_{3-\delta}$ and $\text{SrFeO}_{3-\delta}$ solutions.

For STF02, STF05 and STF06, additional peaks and weight losses; marked as A, B, and C in Figure 5-6 were observed. Reaction A, which occurred at around 190 °C is endothermic, and therefore due to the energy absorbed to decompose the acetate and nitrates anions from the strontium and iron precursors. At higher temperature of 315 °C, an exothermic reaction B was detected. Since this peak was not observed in pure TiO_2 , this reaction must be due to the combustion of ligands surrounding strontium and iron cations to form intermediate phases. This was followed by reaction T2 where these intermediates underwent combustion together with the titanium intermediates to form $\text{Sr}(\text{Ti}_x\text{Fe}_{1-x})\text{O}_{3-\delta}$ as a result of reactive hydrolysis reaction. Based on Figure 5-2, the cubic perovskite phase of STF02 was only detected at 500 °C. Therefore, the $\text{Sr}(\text{Ti}_x\text{Fe}_{1-x})\text{O}_{3-\delta}$ formed after reaction T2 remained in the amorphous form.

Next, comparing Figure 5-6 (b) - (d) for STF02, STF05 and STF06; a prominent, large endothermic peak, C was observed for STF05 and STF06 only. This peak was accompanied by a large weight loss of approximately 25%. Since the onset of this reaction C was at 500 °C and the peak was centred at 550 °C, the XRD spectra of films annealed at 525 °C showed in Figure 5-5 would be able to reflect the phases formed by this reaction. Apart from the targeted $\text{Sr}(\text{Ti}_x\text{Fe}_{1-x})\text{O}_{3-\delta}$ cubic perovskite phase formed by reaction T2, Fe_2O_3 and other secondary phases were also formed in the films. Therefore reaction C was due to the formation of these phases.

Based on these observations, it can be seen that there were two competing processes in the solution; namely a reactive hydrolysis process due to titanium (IV) butoxide which formed a $\text{Sr}(\text{Ti}_x\text{Fe}_{1-x})\text{O}_{3-\delta}$ network, and the formation of Fe_2O_3 together with secondary phases which could be strontium-based. Due to significantly reduced titanium content at

higher x values, the latter process became dominant because the excess strontium and iron complexes could not participate in the hydrolysis process. Consequently for STF09 and SFO with extremely high iron content, peak T2 could not be detected anymore.

This DTA/TGA study revealed that using this conventional preparation method, the sol-gel mechanism could vary with the iron content. To successfully form a single cubic perovskite phase, the reactive hydrolysis reaction is critical and this depends solely on the titanium (IV) butoxide that decreases significantly at higher x values. Therefore this approach is only suitable for $x < 0.5$ in which the titanium (IV) butoxide content is higher than the iron (III) nitrate. In short, using conventional sol-gel, it is difficult to devise a single preparation protocol that is applicable for all x values from $SrTiO_3$ ($x = 0$) to $SrFeO_{3-\delta}$ ($x = 1$).

5.1.2 Acetylacetone as Chelating Agent

When inorganic metal salts like chlorides and nitrates dissolve in water, the metal cations usually form complexes with the anions Cl^- and NO_3^- . Upon heating and drying, the metal salts recrystallized. In sol-gel application, only the metal ions are desired in the final solution. It is then important to remove the anions from the complex solutions and at the same time ensure the stability of the metal cations. In the conventional preparation route with acetic acid chosen as the chelating agent for iron (III) nitrate and strontium acetate, formation of $SrCO_3$ and Fe_2O_3 could not be avoided but for $x \geq 0.5$. To improve the stability of the increased Fe^{3+} cations, the solution preparation route in Figure 5-1 was modified by using acetylacetone as the chelating agent for Fe^{3+} instead. Acetylacetone is a common diketone used to prepare transition metal complexes and is known to be a

stronger chelating agent due to the existence of two C=O groups. Since both Fe and Ti will occupy the same site in the perovskite structure, both precursors are allowed to mix together first before mixing them with the strontium complex solution. The improved solution preparation route is shown in Figure 5-7. To investigate the effectiveness of this improved route for both low and high iron content, $Sr(Ti_xFe_{1-x})O_{3-\delta}$ thin films with $x = 0.2, 0.4, 0.6$ and 0.8 were prepared and annealed at temperatures up to $800\text{ }^{\circ}\text{C}$ to ensure good crystallization.

Figure 5-7. $Sr(Ti_{1-x}Fe_x)O_{3-\delta}$ solution preparation based on hydrolysis of metal alkoxides with acetylacetonate as chelating agent for Fe^{3+} .

Figure 5-8 compares the $\text{Sr}(\text{Ti}_x\text{Fe}_{1-x})\text{O}_{3-\delta}$ thin films at different annealing temperatures. As with previous method, for the case of STF02 and STF04 where $x \leq 0.5$, good crystallization into a single cubic perovskite phase was observed; with STF04 requiring a higher crystallization temperature. For STF06 and STF08, the formation of SrCO_3 and Fe_2O_3 was prevented but the cubic perovskite phase had very weak diffraction signals; indicating poor crystallization. Therefore the preparation of $\text{Sr}(\text{Ti}_x\text{Fe}_{1-x})\text{O}_{3-\delta}$ thin films using conventional sol-gel method appeared to have its limitations and a different approach needed to be explored.

Figure 5-8. XRD spectra of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films with $0.2 \leq x \leq 0.8$ annealed at (a) 500 °C, (b) 650 °C and (c) 800 °C using acetylacetone as chelating agent for Fe^{3+} .

5.2 Modified Sol-Gel Based on Polymerizable Complex (Pechini's) Method

The Pechini's method is a 1967 patented [216] sol-gel technology utilizing the esterification between a multifunctional carboxylic acid and glycol to link metal ions in a three dimensional network, i.e. a polymerization reaction. The carboxylic acid also serves to chelate the metal ions to give good homogeneity at a molecular level, as illustrated in Figure 5-9. Usually, citric acid, a strong chelating agent is used. The Pechini's method is particularly popular for mixed metal oxides because not all metals have alkoxide precursors that are usually the starting materials for conventional sol-gel method readily available. Commonly used precursors for Pechini's method are metal salts such as nitrates, chlorides, acetates, sulfides and so on. Another major advantage of using metal salts over metal alkoxide is the ease of control of reaction rates. Especially in the preparation of multi-metal oxides, it is a great challenge to control the hydrolysis rates of their alkoxide precursors. In addition, metal salts have good solubility in water and many organic solvents.

Nanoparticles and thin films of multi-metal oxides have been successfully prepared using this method [217-220]. Majid et al. reported the coating of $SrFeO_{3-x}$ thin films on silicon and alumina but the films prepared by spin coating had poor adhesion and micro-cracks due to an inherent wettability issue of the solution [221]. To the best of our knowledge, there is no reported work in the literature for the preparation of $Sr(Ti_xFe_{1-x})O_{3-\delta}$ thin films using a modified Pechini's method. Therefore, the aim of this part of the project was to devise a preparation protocol for $Sr(Ti_xFe_{1-x})O_{3-\delta}$ thin films with $0 \leq x \leq 1.0$ based on the Pechini's method. Furthermore, the inherent wettability issue related to this method needs to be resolved to avoid restricting the thin films' applications.

Figure 5-9. Illustration of the solution chemistry and reactions for the preparation of multi-metal) oxide using Pechini's method [219, 222].

5.2.1 Fabrication of STF02 and STF08 Thin Films on Alumina Substrate

The previous work on conventional sol-gel method has highlighted the difficulty in preparing $Sr(Ti_xFe_{1-x})O_{3-\delta}$ thin films with higher iron content, as shown in Figures 5-5 and 5-8. Thus, for polymerizable complex method, the preparation of STF08 was first explored. Figure 5-10 shows the solution preparation route for STF08, using nitrate sources for both iron and strontium for their good solubilities.

Figure 5-10. $Sr(Ti_{1-x}Fe_x)O_{3-\delta}$ solution preparation route using Pechini's method.

The molar ratio used for this route is Sr : Ti + Fe : Citric Acid : Ethylene Glycol = 1 : 1 : 8 : 32, and the overall molarity of the solution is 0.10 M. Due to the solution's poor wettability and hence difficulty in coating on silicon wafer, alumina substrate was first used. To compare the effectiveness of the Pechini's method, STF08 thin films prepared using conventional sol-gel method were also coated on alumina substrate for comparison. Both films were annealed at 600 °C and 800 °C and their XRD spectra are compared in Figure 5-11. It can be seen from Figure 5-11 (a) that at 600 °C, the formation of the cubic perovskite phase can be clearly seen for the STF08 sample prepared using Pechini's method with the clear detection of four peaks; whereas no trace of crystallization can be

seen for the sample prepared by conventional sol-gel method. Even with further annealing up to 800 °C, only faint cubic perovskite peaks can be detected for this sample. Thus, it can be concluded that the Pechini's method can successfully produce single phase STF08 thin films at lower temperature than the conventional sol-gel method. At the same time, no trace of unwanted phases such as Fe_2O_3 was observed.

Figure 5-11. XRD spectra of STF08 thin films prepared using conventional sol-gel and Pechini's method; annealed at (a) 600 °C and (b) 800 °C.

Next, the thin films prepared using Pechini's method for $x \leq 0.5$ and $x \geq 0.5$ were compared using STF02 and STF08 as examples for low and high iron content film, respectively. Figure 5-12 compares the crystallization behavior of STF02 and STF08 for annealing temperatures between 500 °C to 700 °C.

Figure 5-12. XRD spectra of (a) STF02 and (b) STF08 thin films coated on alumina substrate annealed at various temperatures.

Figure 5-12 shows that the crystallization behaviours of both STF02 and STF08 prepared using Pechini's method are almost the same; in which a single cubic perovskite phase was detected from as low as 500 °C. With higher annealing temperature, the intensities of the main peaks increased, indicating grain growth without formation of other unwanted phases. This observation has shown that Pechini's method is a more suitable method for the fabrication of $\text{Sr}(\text{Ti}_x\text{Fe}_{1-x})\text{O}_{3-\delta}$ thin films with $0 \leq x \leq 1.0$ compared to the conventional sol-gel method.

5.2.2 Resolution of Inherent Wettability and Coating Limitation

Although the Pechini's method has shown great potential for the fabrication of $\text{Sr}(\text{Ti}_x\text{Fe}_{1-x})\text{O}_{3-\delta}$ thin films regardless of iron content, its inherent wettability issue seriously still limits the choice of substrate. This will hinder both the study and application of the films. It is therefore imperative to address this issue before further works can be carried out. Firstly, the silicon substrate with 500 nm of thermally grown SiO_2 was cleaned using acetone, iso-propanol and de-ionized water. It was then baked dry overnight and subjected to UV ozone treatment (Samco, Bench-top UV-1) for different durations. Water contact angle measurements were carried out immediately after the surface treatment. Since the sol-gel solution consists mainly of water and polar solvent, 2-methoxy-ethanol, the water contact angle is a useful indication of its surface wettability to enable good thin film coating. Figure 5-13 depicts how the water contact angle changes with UV treatment time. The contact angle was almost halved from 58.6° within 5 minutes of treatment and achieved a minimum of 21.7° after 20 minutes of treatment.

Figure 5-13. Water contact angle images of a thermally grown SiO_2 surface subjected to UV ozone treatment for different durations.

The effect of UV ozone treatment was studied using XPS, by comparing the surface chemistry of the substrate before and after treatment, as shown in Figure 5-14. For Si 2p, only one doublet pair corresponding to SiO_2 was detected, consistent with the lattice bonded O 1s peak observed. For both Si 2p and O 1s spectra, there is no observed difference before and after UV ozone treatment. However, the deconvolution of C 1s peak before UV ozone revealed C-H, C-O and C=O binding states. Therefore, besides the adventitious surface hydrocarbon species, there were some residual acetone and isopropanol from the substrate cleaning process. The C=O bond disappeared after the surface treatment, while C-O bond was greatly reduced. Therefore, the UV ozone treatment

effectively removed organic compound from the substrate surface to allow better surface wetting and improved the coating process.

Figure 5-14. Core level XPS spectra of thermally grown SiO_2 on silicon substrate before (top) and after (bottom) UV ozone treatment for 20 minutes.

Besides working on the substrate surface, the surface tension of the solution also needs to be reduced to minimize cracks during post-coating thermal processes. Polyvinylpyrrolidone (PVP), a stress-reducing organic polymer was added into the sol with a molar ratio of $Sr : PVP = 1 : 1$. The addition of PVP has been proven to be important in the preparation of sub-micron thick, crack-free and dense ceramic films [223-225], and more recently, sol-gel based thin film [226].

The optical microscope images in Figure 5-15 show the importance of both PVP addition and UV ozone treatment on the coating quality. As shown in Figure 5-15 (a), the as-prepared solution without PVP cannot wet the substrate entirely for spin coating. With either PVP addition or surface treatment only, the solution can be coated, but peeling and poor film coverage were observed after hard bake at 150 °C, revealing high stress and poor adhesion. However, with both PVP addition and surface treatment, repeated coating can be achieved. In Figure 5-15 (d), 5 layers of STF08 were successfully coated, and the film remained crack-free and uniform.

Figure 5-15. Optical microscope images of STF08 coatings on thermally grown SiO_2 surface; highlighting the importance of both PVP and UV ozone treatment.

5.2.3 Optimization of Thin Film Fabrication Process

Having resolved the wettability issue, STF_x thin films can now be coated on conventional silicon wafer for further study and applications. In the previous study, the molar ratio of the precursors and PVP used was Sr : Ti + Fe : Citric Acid (CA) : Ethylene Glycol (EG) : PVP = 1 : 1 : 8 : 32 : 1. Meanwhile, the final pH of the solution was adjusted to approximately 6.5. From the original patent of Pechini's method, the ratio of CA : EG used was 1 : 4. This ratio is commonly used for the preparation of oxide powders, pastes and thin films based on Pechini's method and involving the titanium alkoxide precursors [227-231]. As illustrated in Figure 5-9, the Pechini's method is based on the formation of the polymer network through continuous esterification reactions, which is a reversible process. In order to promote the formation of ester, the content of the precursors must be increased, and the byproduct, which is water must be removed to shift the equilibrium to the right hand side. This is the main reason for the use high citric acid content and excess ethylene glycol to remove water via the vaporization of ethylene glycol [222]. Meanwhile, higher pH promotes chelating process and improves the stability of metal citrates, especially for alkaline earth metals which have rather unstable citrate complexes [222, 231-233]. However, the use of large amount of precursor and high pH reduces the stability of the solution caused by the precipitation of citric acid and metal hydroxides. Therefore, it is important to optimize both parameters to achieve good thin film crystallization and at the same time, prolonged solution stability. This optimization was carried out using STF08 as a sample and the processing parameters are summarized in Table 5-1.

Table 5-1. Precursor content and sol pH for the preparation of STF08 thin films.

Sol	Molar Ratio of Sr : Ti + Fe : CA : EG	pH
A	1 : 1 : 8 : 32	As prepared (~0.4)
B	1 : 1 : 8 : 32	3.2
C	1 : 1 : 4 : 16	As prepared (~0.6)
D	1 : 1 : 4 : 16	3.1

pH adjustment was done by drop-wise addition of ammonium hydroxide solution (25%). PVP was added into the solution one hour before spin coating process. Prior to coating, the Si/SiO₂ substrates were cleaned and subjected to UV ozone treatment for 20 minutes. All samples were coated at 3000 rpm for 30 seconds, soft-baked at 150 °C and hard-baked at 300 °C for 5 minutes each. This was repeated until five layers of coating were achieved for each solution. Using a Lindberg quartz tube furnace, annealing was carried out under simulated air flow (N₂ : O₂ = 1 : 4) for 1 hour at 600 °C and 650 °C respectively.

Figure 5-16 compares the XRD spectra of STF08 thin films prepared with Sol A – D at 600 °C and 650 °C. At annealing temperature of 600 °C, Sol B with higher precursor content and pH value produced well-crystallized STF08 cubic perovskite film, while weaker peaks were detected for Sol D with lower precursor content. For Sol A and Sol C, the peaks were faint; indicating that the films were mostly in amorphous state. At 650 °C, thin film prepared with Sol D also became well-crystallized but the films prepared without any pH adjustments remained largely amorphous. These observations indicated that the effect of pH adjustment is more significant than the precursor content used. However,

with higher precursor content; the crystallization temperature would be lower. Since achieving a lower processing temperature is one of the aims of this project, the precursor content for further works was fixed according to Sol D with higher precursor content and pH adjustment to ~ 3.0 .

Figure 5-16. XRD spectra of STF08 thin films prepared with Sol A – D at annealing temperatures of (a) 600 °C and (b) 650 °C.

Although higher pH values are desirable for good crystallization, the solution stability study in Figure 5-17 shows that the pH value cannot be adjusted up infinitely. When the pH was adjusted up with ammonia, the colour of the aqueous solution changed according to the oxidation state of the iron complex formed, given by equations 5-1 to 5-3.

Figure 5-17. Effect of final pH on the oxidation state of iron complexes and solution stability.

At its natural pH of 0.6, the solution was mainly red due to $[Fe(H_2O)_6]^{3+}$ and this solution was very stable. When pH was adjusted to approximately 3.0, the solution turned green due to the formation of $[Fe(H_2O)_5OH]^{2+}$ and $[Fe(H_2O)_4OH_2]^{1+}$ complexes and slow precipitation was only obvious after two weeks of storage. Finally, at pH 7.0, white precipitation occurred instantly due to the formation of

5.3 Study of Sol-gel Mechanism

(a) Dissolution of metal salts

(b) Formation of metal complex

(c) Polymerization

(d) Pyrolysis

Processing

ABO_3

BO_2

AO_x

$A_aB_bO_q$

$—A$

Figure 5-18. Schematic representation of Pechini's method for the preparation of multi-metal oxide, ABO_3 [222].

The first step involves the dissolution of metal salts (nitrates, acetates, chlorides, sulfides, etc.) into excess ethylene glycol and citric acid. This results in fast formation of metal complexes which are mixed with good homogeneity at molecular level. When the solution is heated to 100 – 130 °C, free citric acid and ethylene glycol quickly undergo esterification to form polyester. At this point, the solution becomes a transparent gel. Next, a higher temperature is needed to remove any excess ethylene glycol, followed by heating at 450-600 °C to pyrolyse the organic compounds; forming a powder with homogeneously mixed metal oxides, carbonates or intermediate single phase compound. This powder precursor with the required stoichiometry can then be used for various processing methods to form the final ABO_3 . In this project, before the formation of the large polyester network, the solution was spun-coated on various substrates before hard-baking at 150 °C and 300 °C for 5 minutes each to achieve polyesterification and pyrolysis.

Based on this established understanding, the sol-gel mechanism involved in the preparation of STFx thin films was studied using differential thermogravimetry analyzer (DTA). Figure 5-19 compiles the DTA spectra of STFx thin films for selected x values ranging from 0 for SrTiO_3 to 1 for $\text{SrFeO}_{3-\delta}$. Comparing Figure 5-6 and Figure 5-19, the advantage of this method over conventional sol-gel method became obvious, whereby the DTA profile remained the same for all x values. This means that the same solution chemistry can be applied regardless of iron content, unlike the case of conventional sol-gel which was restricted to lower iron content ($x < 0.5$) due to the lack of reactive hydrolysis at higher iron content.

Figure 5-19. DTA/TGA profiles of dried gel derived from (a) SrTiO_3 , (b) – (e)

$\text{Sr}(\text{Ti}_x\text{Fe}_{1-x})\text{O}_{3-\delta}$ and (f) $\text{SrFeO}_{3-\delta}$ solutions prepared by Pechini's method.

A more detailed analysis of the DTA/TGA profiles showed that there were four stages of weight loss indicated by the dotted lines. The first gradual weight loss of approximately 10 % was accompanied by a broad, but small endothermic peak centred at 100 °C. This was due to the evaporation of excess solvent and water for enhanced esterification reaction between free citric acid and ethylene glycol. At this point, the metal chelates were trapped in the polymer network, thereby maintaining their molecular homogeneity throughout the solution.

Next, a drastic 40-50% weight loss was observed around 180 °C, and during this weight loss, the DTA showed a small endothermic peak at around 150-160 °C, followed by another soft exothermic peak at 180 °C when the weight loss was completed. This large weight loss was contributed by further removal of excess ethylene glycol, as well as endothermic thermal decomposition of the polymer network and nitrate ions from the strontium and iron precursors [234-237]. Therefore, the soft exothermic peak was due to the liberation of gaseous products such as nitrous oxides from the decomposition process.

Finally, two exothermic peaks were observed at approximately 275 °C and between 420-480 °C, with weight losses of 16-20% and 19-25%, respectively. The first peak corresponded to the decomposition of the metal citrates, to form intermediate phases, while the final weight loss indicated the pyrolysis process to form the targeted $SrTiO_3$, $STFx$ and $SrFeO_{3-\delta}$, followed by crystallization. Based on the extensive studies on $BaTiO_3$ and $SrTiO_3$ powders prepared by Pechini's method, two types of mechanisms were proposed. The first mechanism suggested one-step formation of perovskite $(Ba/Sr)TiO_3$ via an intermediate oxycarbonate phase, $(Ba/Sr)_2Ti_2O_5CO_3$ by a simple CO_2 release [238-240]. Another mechanism suggested formation of intermediate $SrCO_3$ and TiO_2 phases,

followed by solid state reaction at higher temperature to obtain single phase $SrTiO_3$ [241]. Using STF02 as an example, for the formation of a single STF02 phase, the reactions and theoretical weight losses for both mechanisms are as follow:

In Figure 5-19 (b), the final weight loss of almost 20% corresponded well with the second mechanism. Although the ideal mechanism would be the formation of intermediate $Sr_2Ti_{1.6}Fe_{0.4}O_5CO_3$ to prevent cation segregation, the rigid polymer network holding the metal citrates could still produce homogeneously distributed $SrCO_3$, TiO_2 and Fe_2O_3 . Furthermore, the formation of carbonate and oxide intermediates is common for preparation of multi-metal oxides using Pechini's method, since different metal citrate complexes have different stability [222]. Finally, with increasing iron content, a broad endothermic peak spanning from 600-900 °C was observed without any accompanying weight loss. This could be due to phase transformation, especially for $SrFeO_{3-\delta}$ which has been reported to have four different phases depending on the oxygen stoichiometry [116].

5.4 Conclusion

In this chapter, the solution preparation and thin film fabrication process for $Sr(Ti_xFe_{1-x})O_{3-\delta}$, in short STF_x were studied and optimized. Two sol-gel mechanisms were compared, namely conventional sol-gel method based on reactive hydrolysis of metal alkoxides versus a modified and improved Pechini's method based on polymerizable metal complexes. For conventional sol-gel, the reactive hydrolysis process was mainly

driven by titanium (IV) butoxide. With increasing iron content, the hydrolysis process reduced significantly and for $x \geq 0.5$, there was very little or no hydrolysis process at all, and the excess strontium and iron precursors formed SrCO_3 and Fe_2O_3 . Therefore, the usefulness of this method was restricted to lower iron content. In contrast, with the modified Pechini's method, both STF02 and STF08 films were successfully fabricated with good crystallization into a single cubic perovskite phase from as low as 600°C . The inherent wettability issue with this method has also been resolved using UV ozone treatment on the substrate and addition of a stress-reducing agent, PVP to enable coating on SiO_2 wafers for further characterizations. Finally, the processing parameters were optimized, and DTA and TGA study revealed the potential of using this method to prepare STF x thin films for $0 \leq x \leq 1$.

CHAPTER 6 : CHARACTERIZATIONS OF $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ THIN FILMS

In the previous chapter, a sol-gel route was devised based on the Pechini's method to prepare single phase, cubic perovskite STF02 and STF08 thin films successfully. The fabrication parameters were also optimized to ensure good crystallization at low temperature and adhesion during spin-coating. In this chapter, $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ or STF x thin films with varying iron contents were characterized with XRD, XPS and FE-SEM. Their bandgaps were estimated using Tauc Plot and finally, they were evaluated for their potential as photocatalyst using Rhodamine B and stearic acid. Their conductivities and surface potentials were further studied to explain their photocatalytic performance.

6.1 Crystallization Behaviour

Figure 6-1 compiles the XRD spectra of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films at various annealing temperatures. It can be seen that for x values up to 0.6, all the spectra have peaks which can be mapped to a single cubic perovskite phase throughout the whole temperature range. For STF08, the cubic perovskite phase was maintained up to 750 °C before a drastic phase change to the orthorhombic brownmillerite structure took place [65, 242, 243]. For $\text{SrFeO}_{3-\delta}$, a single cubic perovskite phase was obtained at 550 °C. Then, from 600 °C onwards, peaks which can be assigned to tetragonal perovskite [244-247] were observed although the cubic phase remained as the main phase up to 650 °C. Finally, brownmillerite phase was formed at 800 °C. The phase change associated with higher iron content has been widely reported for this system; especially $\text{SrFeO}_{3-\delta}$ which can exist in

four different phases depending on its oxygen stoichiometry and the ordering of the oxygen defect states [116, 123].

Figure 6-1. XRD spectra of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) as-deposited on SiO_2/Si substrate and after annealing at different temperatures.

Based on the XRD spectra, Figure 6-2 shows how the calculated lattice constant of the single cubic perovskite phase changed with iron content for $x = 0, 0.2, 0.4, 0.6$ and 0.8 . The lattice constant reduction due to the substitution of Ti with smaller Fe atoms was only obvious from $x = 0.4$ onwards. A similar observation on $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ powder was obtained by Steinsvik et al [124], and this is probably due to the stability of the initial SrTiO_3 perovskite structure at low iron content.

Figure 6-2. Change in $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ lattice constant with iron content.

From the above results, it can be verified that using Pechini's based sol-gel route, $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films with a single cubic perovskite structure can be obtained in the temperature range of $550 - 750\text{ }^\circ\text{C}$, even with large iron content up to STF08. In the case of $\text{SrFeO}_{3-\delta}$, the film crystallized into a single cubic perovskite phase at a low temperature of $550\text{ }^\circ\text{C}$. This observation, as opposed to the lack of or absent of crystallization using

the conventional sol-gel method (Figure 5-8) highlights the usefulness of the protocols developed in Chapter 5 in the preparation of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films.

6.2 Surface Morphology and Thickness

The surface morphology and coating quality were observed using field-emission scanning electron microscope (FE-SEM). All films consisted of five $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ layers, spun-coated on thermally grown SiO_2 (500 nm) on Si wafer and annealed at 600 °C to ensure sufficient crystallization into cubic perovskite phase. Figure 6-3 compares the surface morphologies of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films at the same magnification level. The images revealed that the coatings were uniform and crack-free. The films had increased porosity with iron content but the diameters of the pores remained well below 100 nm. Since the molar ratios of other precursors remained constant for all samples, the nanopores were therefore formed by the liberation of nitrous species from iron nitrate precursor during the forming process of the film. These nanopores will give the films larger surface-to-volume ratio compared to dense films for photocatalytic reactions and for other applications where surface area is important, such as gas sensing.

Next, the cross-sectional images of the films are presented in Figure 6-4 to compare the coating quality and thickness. The thicknesses of the films lied between 248 – 275 nm; indicating that the fabrication process can give good control and small variation of film thickness. The FE-SEM images presented have shown that the optimized $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin film fabrication process can produce both good crystallization at low temperature as well as beneficial surface nano-structure. The results have shown that by

overcoming the inherent wettability issue, uniform thin films with good adhesion to the substrate can be fabricated.

Figure 6-3. FE-SEM images of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films annealed at 600 °C.

Figure 6-4. Cross-sectional FE-SEM images of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films.

6.3 Surface Stoichiometry

As the films will be evaluated for their potential as photocatalyst, it is equally important to study the surface composition of the films using surface-sensitive X-ray Photoelectron Spectroscopy (XPS). The characterization parameters were outlined in Chapter 3 and the samples studied were SrTiO_3 , STF02, STF04, STF05, STF06, STF08 and $\text{SrFeO}_{3-\delta}$ annealed at 600 °C. A summary of the chemical states present and their atomic concentrations are shown in Table 6-1. The core level Ti 2p spectra are derived in Figure 6-5. Only one doublet pair could be detected which is evidence of the existence of a single titanium species; which in this case, is the Ti^{4+} in the lattice site of cubic perovskite phase. It can also be observed that with increasing iron content, the intensity of the Ti 2p peaks decreased as expected.

Next, Figure 6-6 shows the Fe 2p core level spectra of the samples. The occurrence of two iron species is evidenced from the presence of two doublet pairs. They

can be attributed to lattice irons with oxidation states of Fe^{3+} and Fe^{4+} [248-250]. In between the doublet pairs, a shake-up satellite peak contributed by Fe^{3+} can be detected with a binding energy centred at ~ 719 eV [251]. Therefore, in contrast to Ti^{4+} , the iron in the perovskite lattice consists of a mixture of Fe^{3+} and Fe^{4+} . Based on the atomic concentrations calculated in Table 6-1, the total Fe/Ti ratios obtained for STF02, STF04, STF05, STF06 and STF08 are very close to the ideal stoichiometries of 0.25, 0.67, 1, 1.5 and 4. This confirms that the sol-gel preparation route devised can provide a good control of precursor amount and achieve the required thin film stoichiometry.

Figure 6-5. Ti 2p XPS spectra of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films ($x = 0, 0.2, 0.4, 0.6, 0.8$).

Figure 6-6. Fe 2p XPS spectra of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films ($x = 0.2, 0.4, 0.6, 0.8, 1$).

Next, the Sr 3d core level spectra are presented in Figure 6-7. In all samples, the spectrum can be deconvoluted to two doublet pairs. The first pair with lower binding energy can be traced to Sr^{2+} located in the lattice site of the $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ perovskite phase; while the doublet with higher binding energy is due to Sr^{2+} in SrCO_3 [252-255]. It was further observed that for all samples, the lattice Sr was the dominant doublet. However, for $\text{SrFeO}_{3-\delta}$, it was obvious that more SrCO_3 bond was detected. From the atomic concentrations obtained in Table 6-1, the ratios of lattice Sr to the sum of Ti and Fe are well near the ideal value of 1. However, when the total amount of Sr is considered, the surface appeared to be strontium-rich; especially for the case of $\text{SrFeO}_{3-\delta}$. In particular, these extra Sr are bonded with surface carbonates to form SrCO_3 . This observation of strontium segregation on the surface of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ system is consistent with the

findings of Chen et al. [256], in which the cause of Sr diffusion to surface is due to its electrostatic and elastic interactions with the bulk crystal structure and the surface itself.

Similar trend can be seen in the O 1s core level spectra shown in Figure 6-8. The spectra were deconvoluted to three oxygen species. In the order of increasing binding energies, these species are lattice O^{2-} in perovskite phase [257-259], O^{2-} in carbonate compounds [260-264] and small trace of surface hydroxides [265]. Consistent with the trend observed for Sr 3d, there was significantly more carbonate O^{2-} detected compared to lattice species for $\text{SrFeO}_{3-\delta}$. As calculated in Table 6-1, the lattice oxygen stoichiometry, $\text{O}_{\text{lattice}}/\text{Fe}$ for the perovskite phase $\text{SrFeO}_{3-\delta}$ obtained was 2.83. Therefore, the mixed cubic and tetragonal perovskite phase obtained at 600 °C in Figure 6-1(f) was consistent with reported works on the phase relationship with oxygen non-stoichiometry for $\text{SrFeO}_{3-\delta}$ system [116, 266].

Figure 6-7. Sr 3d XPS spectra of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films ($x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1$).

Figure 6-8. O 1s XPS spectra of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films ($x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1$).

Finally, the C 1s spectra in Figure 6-9 showed consistent appearance of three carbon species. The main peak at 285 eV was due to surface adventitious hydrocarbon contamination, which was also the peak used for calibration. The second and third peak at 286 eV and 289 eV are due to carbon with single and double bond to oxygen, respectively in surface carbonate species [267-269]. An additional high energy peak at ~ 290 eV was detected for $\text{SrFeO}_{3-\delta}$. This peak was reported in the literature to be related to carbon double-bonded to oxygen in either carboxyl or ester [270-272]. In our case, it was most probably due to residual polyester which did not undergo complete pyrolysis to form $\text{SrFeO}_{3-\delta}$.

The lattice oxygen stoichiometry, $O_{\text{lattice}}/(Ti+Fe)$ in Table 6-1 showed consistent increase in oxygen vacancy from $SrTiO_3$ to STF08. From an ideal value of 3, the oxygen stoichiometry dropped to 2.40. As can be seen from Figure 6-6, the iron had a preferential oxidation state of Fe^{3+} which is more stable compared to Fe^{4+} . Therefore, with increasing substitution of Ti^{4+} with Fe^{3+}/Fe^{4+} , oxygen vacancies are needed to maintain overall charge balance. In the case of $SrFeO_{3-\delta}$, the oxygen vacancy was manifested as a phase change from a single cubic perovskite phase at 550 °C, to a mixture with tetragonal perovskite at 600 °C.

Figure 6-9. C 1s XPS spectra of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films ($x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1$).

Table 6-1. Summary of chemical states and atomic concentration of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films ($x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1$) annealed at 600 °C.

Elements	Binding Energy (eV)	Atomic Concentration (%)						
		SrTiO ₃	STF02	STF04	STF05	STF06	STF08	SrFeO _{3-δ}
O 1s								
Lattice	529.2	41.80	39.81	37.03	35.85	34.04	28.81	19.89
O-C=O	531.1	7.08	10.15	9.93	9.00	11.30	14.77	23.02
OH _{ads}	532.0	3.57	3.72	4.28	7.87	7.06	9.08	8.77
C 1s								
C-H	285.0	13.05	11.26	13.53	12.85	12.20	11.74	11.43
C-O	286.2	2.03	2.48	3.17	3.06	3.36	3.58	3.77
O-C=O	289.0	2.33	3.36	3.29	2.96	3.78	4.93	2.92
HO-C=O	289.9	0.00	0.00	0.00	0.00	0.00	0.00	8.03
Sr 3d								
Lattice(Sr ³⁺)	133.1	13.89	13.70	13.61	13.64	13.27	11.98	6.77
O-C=O	134.1	2.38	1.78	1.47	1.16	1.72	3.13	8.76
Ti 2p								
Lattice (Ti ⁴⁺)	458.0	13.87	11.07	8.21	6.82	5.38	2.43	0.00
Fe 2p								
Lattice (Fe ³⁺)	710.5	0.00	1.51	3.19	4.00	5.03	6.20	4.37
Lattice (Fe ⁴⁺)	712.7	0.00	0.84	1.73	2.13	2.15	2.54	1.91
Fe –satellite	719.0	0.00	0.33	0.58	0.67	0.71	0.81	0.65
Total		100.00	100.00	100.01	100.00	100.00	99.99	100.00
Fe/Ti		0.00	0.24	0.67	1.00	1.47	3.93	-
Sr _{lattice} /(Ti+Fe)		1.00	1.00	0.99	1.00	1.00	1.00	0.98
Sr/(Ti+Fe)		1.17	1.13	1.10	1.09	1.13	1.26	2.24
O _{lattice} /(Ti+Fe)		3.01	2.90	2.70	2.63	2.56	2.40	2.83

6.4 Bandgap Estimation

For optical study, the $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films were coated on quartz substrate and similarly annealed at 600 °C. The transmission (T) spectra of the films were obtained by a Shimadzu UV-2450 spectrometer to study their optical absorbance ($A = -\log T$). The obtained absorption spectra are shown in Figure 6-10. It can be seen that with increased iron content up to STF08, the visible-light absorption of the films increased. For $\text{SrFeO}_{3-\delta}$, the absorbance in visible-light range was between that of STF05 and STF06. This could be due to the phase difference between $\text{SrFeO}_{3-\delta}$ and the rest of the films at this annealing temperature. The optical bandgaps were further estimated using Tauc plot, $(\alpha h\nu)^{1/2}$ versus eV for indirect allowed transition as shown in Figure 6-11 [58, 146-148].

Figure 6-10. Optical absorbance of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ ($x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0$) thin films annealed at 600 °C.

Figure 6-11. (a) – (g) Tauc plots and (h) bandgap estimation of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ ($x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0$) thin films annealed at 600 °C.

From the Tauc plots, it was observed that the bandgap showed a significant reduction from 3.46 eV for SrTiO_3 to 1.1 eV when $x = 0.8$. This observed bandgap reduction with iron content is consistent with the observation by Rothschild et al. for cubic perovskite $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ [128]. However, for $\text{SrFeO}_{3-\delta}$, the extrapolation of its absorption edge in Figure 6-11 (g) gave a larger bandgap of 2.23 eV compared to STF08. The first possible reason for this is due to the oxygen non-stoichiometry of $\text{SrFeO}_{3-\delta}$. This inherent oxygen non-stoichiometry of $\text{SrFeO}_{3-\delta}$ has been reported to cause obvious phase, conductivity, and bandgap changes [65, 116, 273-276]. In his work on $\text{SrFeO}_{3-\delta}$, Kozhenikov observed that oxygen rich, perovskite SrFeO_3 has a smaller bandgap than oxygen-deficient, brownmillerite $\text{SrFeO}_{2.5}$ as the large amount of oxygen in SrFeO_3 formed impurity-like, acceptor states above the valence band [65]. A study of the film's transmission by Post et al. has also shown that the transmission of $\text{SrFeO}_{2.5}$ in visible-light region can be up to three orders of magnitude higher than SrFeO_3 [276].

Another reason for the larger bandgap obtained could be the effect of strontium segregation on its surface. Based on the XPS analysis, the $\text{SrFeO}_{3-\delta}$ film has a strontium-rich surface. Cation segregations on surface has been observed for SrTiO_3 [277], $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ [278] and SrFeO_3 [249, 256]. These extra strontium cations can exist in the form of SrO or SrCO_3 which, based on the Sr 3d and O 1s spectra in Figure 6-7 and 6-8, is more likely in this case. These compounds have larger bandgap than the bulk $\text{SrFeO}_{3-\delta}$ and therefore can affect the visible-light absorption, affecting the bandgap estimation. Nevertheless, as compared to SrTiO_3 , the $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films prepared have shown good visible-light absorption and significant bandgap reduction; which is one of the objectives set out for this project.

6.5 Evaluation of Photocatalytic Potential

In this part of the project, the $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films were subjected to a few photocatalytic tests to evaluate their potential as visible-light active photocatalyst. As outlined in Chapter 3, the Rhodamine B removal test was conducted by dipping the thin film samples coated on quartz into 20 ml of Rhodamine B solution with a concentration of 10 μM . Samples were kept in dark for 30 minutes to achieve physical absorption-desorption equilibrium. With our setup, the average power of the 350 mW LED white light which reached the sample surface was 27 mW/cm^2 over the range of 200 nm to 20 μm . Figure 6-12 shows the concentration, C of the dye; normalized to its initial concentration, C_0 at different illumination time for samples SrTiO_3 , STF01, STF02 and STF04. A blank quartz substrate was used as control experiment.

Figure 6-12. Rhodamine B removal test for SrTiO_3 and $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ ($x = 0.1, 0.2$ and 0.4) thin films under visible-light illumination.

After 6 hours of illumination, the Rhodamine B in the control experiment showed a further 9 % reduction in concentration due to slow physical adsorption. Of all samples, $SrTiO_3$ gave the best Rhodamine B removal of 35 %; followed by STF01 (28 %), STF02 (22 %) and STF04 (12 %). The trend is apparent here; i.e. reduced removal rate with increased iron doping. As discussed in Chapter 4, there are two pathways for Rhodamine B removal. The first pathway occurred via a photosensitization process and it involved progressive removal of the four ethyl groups in Rhodamine B [279-281]. This will translate into a blue-shift in the absorption spectrum. The second mechanism caused the conjugate xanthene ring to break due to photocatalytic process and the absorption spectrum displayed a continuous reduction without peak shift. Since the bandgap of $SrTiO_3$ is in the UV region, photocatalytic degradation of Rhodamine B is not possible and all degradation must take place via the photosensitization process. This is evidenced by the continuous blue-shift in the absorption maxima when $SrTiO_3$ was tested, as shown in Figure 6-13.

Figure 6-13. Absorbance of Rhodamine B under visible-light illumination in the presence of $SrTiO_3$ thin film.

To determine whether there is any presence of photocatalytic process for $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$, the contribution of photosensitization process must be eliminated. A bandpass-filter was used to cut-off wavelengths above 500 nm to ensure that Rhodamine B itself is unable to absorb any light. The Rhodamine B removal efficiency was then compared for SrTiO_3 and STF04 with and without the filter, as shown in Figure 6-14. The results showed that there was no photocatalytic process involved in the removal of Rhodamine B dye for STF04 despite its ability to absorb visible-light and estimated bandgap of 2.44 eV. Instead, only photosensitization process was involved and the effect of the iron-doping for $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films was the reduction of this photosensitization rate. In view of this, another pollutant, Bis-phenol A (BPA) was studied and STF08, which has the smallest estimated bandgap was evaluated. Using the same experimental setup and light source, the results obtained are shown in Figure 6-15.

Figure 6-14. Effect of light-filter ($300 \text{ nm} \leq \lambda \leq 500 \text{ nm}$) on Rhodamine B removal rates for SrTiO_3 and STF04.

Figure 6-15. Bis-phenol A (BPA) removal test for SrTiO_3 and $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ ($x = 0.4$ and 0.8) thin films under visible-light illumination.

Although the BPA molecule is simpler than Rhodamine B, the results show that no meaningful BPA removal can be achieved even though STF08 has good visible-light absorption. The films were then further tested for stearic acid degradation, which is a commonly used, quick test for thin film photocatalyst. As compared to Rhodamine B and Bis-phenol A tests, a layer of stearic acid was spun-coated directly on the film surface. This thin layer allowed good transfer of reactive oxidative species from the film to the stearic acid, yet ensured that almost all incident photons can reach the film. The amount of stearic acid on the film is proportional to the area beneath its FT-IR peaks. As can be seen from Figure 6-16, there was a better stearic acid adhesion on the SrTiO_3 surface compared to STF04 and STF08. When the sample was illuminated with the high intensity LED lamp, the stearic acid concentration did not show any appreciable change for all samples.

Figure 6-16. Stearic acid test for SrTiO_3 and $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ ($x = 0.4$ and 0.8) thin films under visible-light illumination.

Based on the above three tests, it is clear that despite their ability to absorb visible-light and advantageous nanoporous surface, the $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films evaluated did not display any photocatalytic characteristic. In a photocatalytic process, the generation of electron-hole pairs upon light absorption is the first essential step. Thereafter, good charge separation and transfer to the photocatalyst surface are equally critical to ensure successful redox reactions which lead to pollutant degradation. Similar to the nitrogen-doped TiO_2 discussed in Chapter 4, the charge separation efficiency of the films can be investigated using Kelvin Probe by observing the change in their contact potentials under visible-light illumination. This will provide a helpful insight into the absence of photocatalytic reaction for the films.

6.6 Study of Charge Separation Efficiency

For this study, all samples were coated on a layer of platinum which was sputtered onto standard silicon wafer. The platinum serves as the bottom contact for the surface potential measurement and all data were collected under normal air condition. The contact potential difference (CPD) in the dark was first established by storing the samples in dark for 16 hours. Thereafter, a high-intensity 200W Xenon lamp ($340 \text{ nm} \leq \lambda \leq 700 \text{ nm}$) was turned on for 15 minutes to observe the change in CPD. Then, the CPD was allowed to return slowly to its dark equilibrium and the rate of decay was observed.

In Figure 6-17, the surface photovoltage spectra of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films are compared against that of SrTiO_3 . For SrTiO_3 , the change in CPD upon illumination was fast and obvious. This indicated efficient electron-hole pair generation and transfer to the surface. After 15 minutes of illumination, the CPD reduction was more than 200 mV. This is consistent with the n-type conductivity behaviour of SrTiO_3 [53]. When the light was turned off, more than 4 hours were required for the CPD to return to its dark reading. In contrast, $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films exhibited p-type conductivity behaviour. There are two main observations relating the measured CPD to iron content. Firstly, with increasing iron content, the CPD change became less obvious. STF01 showed a CPD change of 100 mV, while both STF02 and STF04 recorded changes of approximately 50 mV only. This further decreased to about 25 mV for STF05. For STF06, STF08 and $\text{SrFeO}_{3-\delta}$, the changes were negligible. Therefore, optical study might have revealed increased visible-light absorbance with iron content (Figure 6-10), but not all of the electron-hole pairs generated can diffuse to the surface. Based on the CPD change, there would be very little or no reactive oxidative species produced to breakdown the target pollutants.

Figure 6-17. Xenon light "On-Off" surface photovoltage spectra of SrTiO_3 and

$\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$.

The second observation is related to the ability of the film surface to maintain the CPD change, as with the case of semiconductive SrTiO_3 . STF01 took approximately three hours to regain its dark CPD after illumination; but for STF02 to STF05, the CPD change could not be maintained although the samples were still illuminated. This means that the charged species did not stay very long at the surface and would be quickly swept away to the bulk of the film due to surface electric field [151]. Inevitably, charge recombination would then take place.

The reasons behind these two observations can be deduced from the electronic band structure and property changes of the $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ solid solution system. Rothschild et al. has proposed a comprehensive electronic band structure based on their results as shown in Figure 6-18 [66].

Figure 6-18. Schematic energy-band diagram of STF05 proposed by Rothschild et al. [66].

In this model, the valence band is mostly made up of Fe 3d and O 2p states in covalent admixtures. This is because of the close proximity of Fe^{4+}/Fe^{3+} states to the top of the intrinsic O 2p band. On the other hand, the conduction band is formed by Ti 3d states forming admixtures with Fe 3d states for Fe^{3+}/Fe^{2+} oxidation states. Comparing both bands, the overlapping at the conduction is more significant due to their energetics nature. At low iron concentrations, the Fe^{4+}/Fe^{3+} states appear as discrete acceptor states above the valence band, which explains the p-type conductivity behaviour observed in the surface photovoltage response [67, 138].

Meanwhile, the substitution of titanium by iron formed charge defects due to the difference in their preferred oxidation state. Based on the Ti 2p and Fe 2p XPS spectra in Figure 6-5 and Figure 6-6, only Ti^{4+} was detected, but iron existed as both Fe^{3+} and Fe^{4+} states. As a result, for every two Fe^{3+} states, one oxygen vacancy would be formed to maintain charge equality. Using the Kroger-Vink notation [282] for defect chemistry, a Fe^{3+} substituted Ti^{4+} is a defect point with one net negative charge (Fe'_{Ti}) while an oxygen vacancy will be defect point with two net positive charge ($V^{\bullet\bullet}_O$). The oxygen vacancy is located just below the conduction band with a small energy separation of 0.085 eV [128, 283]. These two species are dominant defects in acceptor doped- $SrTiO_3$; and due to their localized nature, Fe'_{Ti} will act as a sink for holes and $V^{\bullet\bullet}_O$ as electron traps [56, 111, 124, 284]. The immobilized electron-hole pairs will then recombine without transferring to the photocatalyst surface. At high iron content, the lattice parameter reduction and close proximity of iron caused the Fe states to form an energy band with increasing width; therefore increasing its overlapping with Ti 3d and O 2p [285]. This can be verified by the low energy XPS scans of the samples presented in Figure 6-19. The widening of Fe 3d

energy band effectively narrows down the bandgap to allow visible-light absorption. However, more oxygen vacancies will be formed and act as recombination sites, as shown in Table 6-1. This explains the first surface photovoltage observation of decreasing CPD change with iron content despite higher visible-light absorption.

Figure 6-19. Lower binding energy XPS scans for $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films showing increased Fe 3d width and overlapping with O 2p at higher iron content.

Next, the widening of the Fe states-derived band will also bring about increased conductivity. The increased overlapping allows higher mobility and delocalization for holes, thus the activation energy for electronic transport is reduced [122, 138]. Figure 6-20 shows the temperature dependent resistance of STF02 and STF08 thin films spin-coated onto inter-digitated gold electrode. It can be seen that at approximately 200 °C, the resistance of STF02 was six orders of magnitude higher than STF08. As a consequence, with increasing iron content, the charge retention on the film surface became poorer, causing the CPD to decrease quickly even under illumination. This means that electrons

and holes are unable to stay long enough on the surface to produce reactive oxidative species.

Figure 6-20. Resistance change of STF02 and STF08 sol-gel thin films as a function of temperature.

Although the oxygen vacancy and conductivity of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films are seen as the two major reasons for the lack of photocatalytic activity, more detailed and diverse characterizations need to be carried out in future to verify these observations and identify other possible reasons. For example, strontium segregation observed in XPS study will form insulating SrO or SrCO_3 islands on the films surface, which can also prevent efficient charge transport and the reduction kinetics of surface adsorbed oxygen by electrons [256]. With proper identification of these underlying problems, suitable modifications can be applied to fully harness the potential of these thin films as visible-light photocatalyst.

6.7 Conclusion

In this chapter, $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ thin films were prepared using the optimized sol-gel process and fabrication protocol devised in Chapter 5. The XRD spectra confirmed the formation of a single phase, cubic perovskite structure for $0 \leq x \leq 0.8$ from 500 °C to 750 °C. For $x = 1.0$ or $\text{SrFeO}_{3-\delta}$, this phase could be maintained up to 650 °C before phase transformation to tetragonal perovskite and brownmillerite phase at higher temperature. FE-SEM revealed uniform, nanoporous surfaces which gave the films large surface-to-volume ratio. The quantitative analysis of surface chemistry using XPS showed that there are more iron in the Fe^{3+} oxidation states than Fe^{4+} , causing the formation of oxygen vacancies to maintain charge balance in the $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ system. Furthermore, with higher iron content, the film surface became strontium-rich, due to strontium segregation in the form of SrCO_3 . Meanwhile, the films exhibited encouraging visible-light absorption, with significant bandgap reduction from 3.45 eV to 1.10 eV for SrTiO_3 and STF08, respectively. Despite this, evaluation of their photocatalytic potential using Rhodamine B, bis-phenol A and stearic acid gave disappointing results. There was no obvious photocatalytic reactions observed. From their surface photovoltage spectra, the amount of surface charge carrier was found to decrease with iron doping and the charge retention time also deteriorated. The reasons for these are believed to be the formation of oxygen vacancies and increased electronic conductivity at higher iron content. Therefore, there were insufficient electrons and holes on the surface for a prolonged period to allow meaningful redox reactions with adsorbed oxygen and water molecules.

CHAPTER 7 : CONCLUSION AND RECOMMENDATIONS

7.1 Conclusion

In the first part of this thesis, the study of nitrogen-doped TiO₂ for visible-light photocatalytic activities was carried out. In the literature, the commonly used approach was to introduce nitrogen dopant into TiO₂. In this project, a relatively low-cost approach via the oxidation of TiN was adopted. The ease of this process allows bulk production of nitrogen-doped TiO₂ without the need for extensive equipment setup and long processing hours. The nano-sized powders showed visible-light absorption up to 525 nm with enhanced Rhodamine B removal, gaseous toluene oxidation and effective *E. Coli* killing under visible-light illumination. In particular, at annealing temperature of 500 °C, the powder had the best photocatalytic performance. XPS study confirmed the existence of beneficial nitrogen-dopants in interstitial position which allowed visible-light absorption. Meanwhile, surface photovoltage spectra revealed its superior charge separation which is believed to be contributed by its optimum anatase to rutile ratio.

The second part of the thesis set out to explore a potential new candidate for visible-light photocatalyst in the form of Sr(Ti_{1-x}Fe_x)O_{3-δ} thin films. As a start, a sol-gel solution preparation route was devised based on conventional hydrolysis of metal alkoxides. With this method, the iron content was limited to $x \leq 0.5$ due to lack of hydrolysis at higher x values. Therefore, the Pechini's method based on polymerizable metal complexes was modified for thin film coating and optimized to produce repeatable, well-crystallised Sr(Ti_{1-x}Fe_x)O_{3-δ} thin films for all x values from as low as 550 °C. The inherent wettability issue with this method which prevented coating of uniform, sub-

micron thin films was successfully overcome by surface treatment and addition of stress-relieving agent into the sol.

Next, using the devised thin film fabrication protocol, the last part of the project involved systematic characterizations of the films and evaluation of their potential as new visible-light photocatalyst. The samples were found to crystallize into a single cubic perovskite phase for a wide range of annealing temperature. In terms of the main perovskite phase, XPS study showed that near ideal stoichiometry was achieved for most samples. However, the formation of oxygen vacancies and strontium segregation in the form of SrCO_3 was observed with increasing iron content. Nonetheless, the films showed good thickness and have uniform, nanoporous morphology when observed with FE-SEM with nanopores less than 100 nm in size for large surface-to-volume ratio. As expected, visible-light absorption and bandgap reduction with iron content was also confirmed by UV-Vis spectrometer. However, evaluation of their visible-light photo-activity with a few pollutants did not give positive results. Surface photovoltage study revealed the lack of charge transfer and short charge retention time on the surface. These are believed to be contributed by charge trapping in oxygen vacancies and discrete iron acceptor levels, causing recombination. On the other hand, the increased conductivity with iron content reduced the ability of the films to retain charge carriers on their surface, therefore preventing further oxidation and reduction processes from taking place.

7.2 Recommendations for Future Work

Based on the positive findings for nitrogen-doped TiO_2 prepared by oxidation of TiN, more works can be done to improve its overall photocatalytic performance and to widen its applications. These include :

a) Increasing nanoparticle surface area

The as-purchased TiN nanopowder had a BET of $80 \text{ m}^2/\text{g}$. As a result of the 2-hour oxidation, the surface area reduced to approximately $30 \text{ m}^2/\text{g}$ due to sintering. If the surface area can be increased to compensate this effect, a great improvement in its photocatalytic performance can be expected. One method to achieve larger surface area is by ball-milling. In one of our reported works, ball-milled $\text{SrFeO}_{3-\delta}$ nanopowder showed good performance in the degradation of methylene blue under visible-light, owing largely to its small crystallite size of less than 25 nm [63].

b) Thin film coating

The applications of the powder can be extended to self-cleaning surfaces by immobilizing them onto various supports using coating techniques such as spray-coating and spin-coating. One possible method is to suspend the powders in TiO_2 solution and spin-coat the mixture to obtain sub-micron thick films with good adhesion. An example of using this method for P25 coating is shown in Figure 7-1 below, where uniform coating can be obtained.

Figure 7-1. Sub-micron coating of P25 powder using TiO₂ as holding matrix, prepared by sol-gel spin-coating method.

c) Co-doping with other metals and non-metals.

There are many reported work in the literature on co-doped TiO₂. Generally, co-doping has been found to enhance electron-hole separation, pollutant absorption onto catalyst surface as well as improving physical properties such as crystallite size [286-290]. For this project, the as-purchased TiN can be suspended in precursor solutions containing the co-dopants before drying and oxidizing it, keeping the process relatively simple.

As for Sr(Ti_{1-x}Fe_x)O_{3-δ} thin films, the future approaches should be targeted at overcoming the issue of charge trapping and recombination, while at the same time enhance its overall physical properties. The results obtained in this project can serve as background knowledge for further development.

a) Using lower iron doping

From our findings, it is clear that bandgap reduction and visible-light reduction is not the only determining factor for good photocatalytic performance. The bandgap reduction due to increased iron doping has also introduced problems due to the formation of charged defects. In Figure 6-17 (b), a 10% doping (STF01) can produce a surface CPD change of 100 mV while still maintaining good charge retention. Therefore, iron doping level can be reduced to less than 10 %. Figure 7-2 shows the surface photovoltage spectrum of a 5 % iron-doped SrTiO₃. Upon illumination, the photovoltage response was equally positive and it could be sustained until the light was turned off. Therefore, it would be worthwhile to investigate the potential of these lightly-doped SrTiO₃.

Figure 7-2. Surface photovoltage spectrum of a 5 % iron-doped SrTiO₃ thin film.

b) Co-doping for charge compensation

Since the formation of oxygen vacancy in the Sr(Ti_{1-x}Fe_x)O_{3-δ} thin films was due to charge imbalance, co-doping is an effective way to overcome this problem. Oxygen vacancies in pure TiO₂ and SrTiO₃ are beneficial electron traps to prevent

its recombination with holes. However, for single dopant SrTiO_3 , holes usually have low mobility at the discrete acceptor level, placing them in close proximity with trapped electrons for fast recombination. In the literature, co-doping of antimony or tantalum with chromium has been found to be effective in suppressing oxygen vacancy formation for H_2 evolution from aqueous methanol was observed under visible-light illumination [55, 115].

c) Increasing surface area

Finally, an inherent problem with immobilized and coated photocatalyst is the much smaller surface area compared to nano-sized powders such as P25. If the photocatalytic rate is too low, no significant effect can be observed. Therefore, instead of using purely $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ sol-gel thin films, ball-milled nanopowders which have been reported to exhibit visible-light photocatalytic properties can be embedded into the nanoporous thin film [63].

7.3 Author's Publications

Journals

- 1) M. Ghaffari , **P. Y. Tan**, M. E. Oruc, O. K. Tan, M. S. Tse, M. Shannon , “Effect of ball milling on the characteristics of SrFeO_3 nano powder for visible light photocatalytic applications and its reaction kinetics”, *Catalysis Today*, 161 (1), 70-77, 17 March 2011.
- 2) M. Ghaffari, H. Huang, **P.Y. Tan**, O.K. Tan, “Synthesis and visible light photocatalytic properties of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ powder for indoor decontamination”, *Powder Technology*, 225, 221-226, July 2012.

Conferences

- 1) **P. Y. Tan**, Q. Luo, O. K. Tan, M. S. Tse, X. Q. Fang, M. Ghaffari, “Visible Light Photocatalytic Activity of Thermal Oxidized Titanium Nitride Powder”, 6th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications", Prague, Czech Republic, June 13-16, 2010. Book of abstracts (ISBN : 978-80-7080-750-7), page 94.
- 2) **P. Y. Tan**, O.K. Tan, A.M. Soutar, “Fabrication and Characterization of $\text{Sr}(\text{Ti}_{0.2}\text{Fe}_{0.8})\text{O}_{3-\delta}$ Thin Film by Sol-Gel Method”, Asia Pacific Interfinish 2010, Singapore, Oct 19-22, 2010.

- 3) **P. Y. Tan**, Q. Luo, O. K. Tan, M. S. Tse, X. Fang, L. Zhang, M. Ghaffari, “Nitrogen-doped TiO₂ for Visible-light Photocatalytic Applications Prepared by Oxidation of Titanium Nitride”, 16th International Conference on TiO₂ Photocatalysis: Fundamentals and Applications (TiO₂-16), San Diego, USA, Nov 7-10, 2011. Book of abstracts, page 156-157.
- 4) **P. Y. Tan**, Q. Luo, O.K. Tan, M.S. Tse, “Oxidized nano-sized titanium nitride for visible light anti-bacterial application: Co-effects of nitrogen and rutile phase content”. 15th International Congress on Catalysis, Munich, Germany, July 1-6, 2012. Poster program booklet, page 107.
- 5) M. Ghaffari, O. K. Tan, **P. Y. Tan**, “Preparation of Sr(Ti_{1-x}Fe_x)O_{3-δ} for enhancement of visible light photocatalytic properties: optimization of stoichiometry and reaction temperature”, 6th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications", Prague, Czech Republic, June 13-16, 2010. Book of abstracts (ISBN : 978-80-7080-750-7), page 98.
- 6) L. Zhang, M. S. Tse, **P. Y. Tan** and O. K. Tan, “Visible Light Photocatalytic Oxidation of Gas-Phase 2-propanol with Spray-Coated N-TiO₂ on Polyester Filters”, 5th MRS-S Conference on Advanced Materials, Singapore, March 20-22, 2012.
- 7) L. Zhang, **P.Y. Tan**, O.K. Tan, and M.S. Tse, "Visible light photocatalytic decontamination of gas-phase toluene with spray-coated TiO₂-xN_x", 15th

International Congress on Catalysis 2012, Munich, Germany, July 1-6, 2012.

Poster program booklet, page 107.

References

- [1] M. Fox, "Photocatalytic Oxidation of Organic Substances," *Photocatalysis and Environment: Trends and Applications*, pp. 445-467, 1988.
- [2] R. Konta, T. Ishii, H. Kato, and A. Kudo, "Photocatalytic Activities of Noble Metal Ion Doped SrTiO₃ under Visible Light Irradiation," *The Journal of Physical Chemistry B*, vol. 108, pp. 8992-8995, 2004.
- [3] A. Fujishima and K. Honda, "Electrochemical Photolysis of Water at a Semiconductor Electrode," *Nature*, vol. 238, pp. 37-38, 1972.
- [4] Y. Luo and D. F. Ollis, "Heterogeneous Photocatalytic Oxidation of Trichloroethylene and Toluene Mixtures in Air: Kinetic Promotion and Inhibition, Time-Dependent Catalyst Activity," *Journal of Catalysis*, vol. 163, pp. 1-11, 1996.
- [5] A. G. Agrios, K. A. Gray, and E. Weitz, "Photocatalytic Transformation of 2,4,5-Trichlorophenol on TiO₂ under Sub-Bandgap Illumination," *Langmuir*, pp. 1402-1409, 2003.
- [6] D. Gurny, A. G. Rincon, R. Hajdu, and C. Pulgarin, "Solar Photocatalysis for Detoxification and Disinfection of Water: Different Types of Suspended and Fixed TiO₂ Catalysts Study," *Solar Energy*, vol. 80, pp. 1376-1381, 2006.
- [7] C. R. Brundle, C. A. J. Evans, and S. Wilson, *Encyclopedia of Materials Characterization : Surfaces, Interfaces, Thin Films*, Stoneham, Massachusetts, United States: Manning Publications Co., 1992.
- [8] K. Sunada, T. Watanabe, and K. Hashimoto, "Studies on Photokilling of Bacteria on TiO₂ thin film," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 156, pp. 227-233, 2003.
- [9] K. Sunada, Y. Kikuchi, K. Hashimoto, and A. Fujishima, "Bactericidal and Detoxification Effects of TiO₂ Thin Film Photocatalysts," *Environmental Science and Technology*, vol. 32, pp. 726-728, 1998.
- [10] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, *et al.*, "Photogeneration of Highly Amphiphilic TiO₂ Surfaces," *Advanced Materials*, vol. 10, pp. 135-138, 1998.
- [11] A. Fujishima and X. Zhang, "Titanium Dioxide Photocatalysis : Present Situation and Future Approaches," *C.R. Chimie* vol. 9, pp. 750-760, 2006.
- [12] K. Hashimoto, H. Irie, and A. Fujishima, "TiO₂ Photocatalysis: A Historical Overview and Future Prospects," *Japanese Journal of Applied Physics*, vol. 44, pp. 8269-8285, 2005.
- [13] S. N. Frank and A. J. Bard, "Heterogeneous Photocatalytic Oxidation of Cyanide ion in aqueous solutions at Titanium Dioxide Powder," *Journal of the American Chemical Society*, vol. 99, pp. 303-304, 1977.
- [14] S. N. Frank and A. J. Bard, "Heterogeneous Photocatalytic Oxidation of Cyanide and Sulfide in Aqueous Solutions at Semiconductor Powders," *Journal of Physical Chemistry*, vol. 81, pp. 1484-1488, 1977.

- [15] R. R. Bacsa and J. Kiwi, "Effect of Rutile Phase on the Photocatalytic Properties of Nanocrystalline Titania during the degradation of p-coumaric acid," *Applied Catalysis B: Environmental*, vol. 16, pp. 19-29, 1998.
- [16] D. C. Hurum, A. G. Agrios, and K. A. Gray, "Explaining the Enhanced Photocatalytic Activity of Degussa P25 Mixed-Phase TiO₂ Using EPR," *Journal of Physical Chemistry B*, vol. 107, pp. 4545-4549, 2003.
- [17] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, "Environmental Applications of Semiconductor Photocatalysis," *Chemical Review*, vol. 95, pp. 69-96, 1995.
- [18] Z. Zou, J. Ye, K. Sayama, and H. Arakawa, "Direct Splitting of Water under Visible Light Irradiation with an Oxide Semiconductor Photocatalyst," *Nature*, vol. 414, pp. 625-627, 2001.
- [19] E. Borgarello, J. Kiwi, M. Gratzel, E. Pelizzetti, and M. Visca, "Visible Light Induced Water Cleavage in Colloidal Solutions of Chromium-doped Titanium Dioxide Particles," *Journal of the American Chemical Society*, vol. 104, pp. 2996-3002, 1982.
- [20] H. Yamashita, Y. Ichihashi, M. Takeuchi, S. Kishiguchi, and M. Anpo, "Characterization of Metal Ion-implanted Titanium Oxide Photocatalysts Operating Under Visible Light Irradiation," *Journal of Synchrotron Radiation*, vol. 6, pp. 451-452, 1999.
- [21] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, "Visible-light Photocatalysis in Nitrogen-doped Titanium Oxides," *Science*, vol. 293, pp. 269-271, 2001.
- [22] Y. Nosaka, M. Matsushita, J. Nishino, and A. Y. Nosaka, "Nitrogen-doped Titanium Dioxide Photocatalysts for Visible Response Prepared by Using Organic Compounds," *Science and Technology of Advanced Materials*, vol. 6, pp. 143-148, 2005.
- [23] A. A. Semenov, S. F. Karmanenko, B. A. Kalinikos, A. N. Slavin, G. Srinivasan, and J. V. Mantese, "Ferrite/ferroelectric Layered Structures for Magnetic and Electric Field Tunable Microwave Devices," *Integrated Ferroelectrics*, vol. 77, pp. 199-205, 2005.
- [24] T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto, and S. Sugihara, "Visible-light-active Titanium Oxide Photocatalyst Realized by an Oxygen-Deficient Structure and by Nitrogen Doping," *Applied Catalysis B: Environmental*, vol. 42, pp. 403-409, 2003.
- [25] Y. Kuroda, T. Mori, K. Yagi, N. Makihata, Y. Kawahara, M. Nagao, *et al.*, "Preparation of Visible-Light-Responsive TiO₂-xN_x Photocatalyst by a Sol-Gel Method: Analysis of the Active Center on TiO₂ that Reacts with NH₃," *Langmuir*, vol. 21, pp. 8026-8034, 2005.
- [26] T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto, and S. Sugihara, "Visible-light-active Titanium Oxide Photocatalyst Realized by an Oxygen-Deficient Structure and by Nitrogen Doping," *Applied Catalysis B: Environmental*, vol. 42, pp. 403-409, 2003.
- [27] E. A. Reyes-Garcia, Y. Sun, K. Reyes-Gil, and D. Raftery, "15N Solid State NMR and EPR Characterization of N-Doped TiO₂ Photocatalysts," *The Journal of Physical Chemistry C*, vol. 111, pp. 2738-2748, 2007.

- [28] G. R. Torres, T. Lindgren, J. Lu, C.-G. Granqvist, and S.-E. Lindquist, "Photoelectrochemical Study of Nitrogen-Doped Titanium Dioxide for Water Oxidation," *The Journal of Physical Chemistry B*, vol. 108, pp. 5995-6003, 2004.
- [29] M. Kitano, K. Funatsu, M. Matsuoka, M. Ueshima, and M. Anpo, "Preparation of Nitrogen-Substituted TiO₂ Thin Film Photocatalysts by the Radio Frequency Magnetron Sputtering Deposition Method and Their Photocatalytic Reactivity under Visible Light Irradiation," *The Journal of Physical Chemistry B*, vol. 110, pp. 25266-25272, 2006.
- [30] A. Nambu, J. Graciani, J. A. Rodriguez, Q. Wu, E. Fujita, and J. Fdez Sanz, "N doping of TiO₂ (110): Photoemission and Density-functional Studies," *Journal of Chemical Physics*, vol. 125, p. 094706, 2006.
- [31] H. M. Yates, M. G. Nolan, D. W. Sheel, and M. E. Pemble, "The Role of Nitrogen Doping on the Development of Visible Light-induced Photocatalytic Activity in Thin TiO₂ Films Grown on Glass by Chemical Vapour Deposition," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 179, pp. 213-223, 2006.
- [32] S. K. Pradhan, P. J. Reucroft, F. Yang, and A. Dozier, "Growth of TiO₂ Nanorods by Metalorganic Chemical Vapor Deposition," *Journal of Crystal Growth*, vol. 256, pp. 83-88, 2003.
- [33] M. Maeda and T. Watanabe, "Visible Light Photocatalysis of Nitrogen-Doped Titanium Oxide Films Prepared by Plasma-Enhanced Chemical Vapor Deposition," *Journal of the Electrochemical Society*, vol. 153, pp. C186-C189, 2006.
- [34] C. Burda, Y. Lou, X. Chen, A. C. S. Samia, J. Stout, and J. L. Gole, "Enhanced Nitrogen Doping in TiO₂ Nanoparticles," *Nano Letters*, vol. 3, pp. 1049-1051, 2003.
- [35] H. Irie, Y. Watanabe, and K. Hashimoto, "Nitrogen-Concentration Dependence on Photocatalytic Activity of TiO_{2-x}N_x Powders," *The Journal of Physical Chemistry B*, vol. 107, pp. 5483-5486, 2003.
- [36] Z. Zhang, J. B. M. Goodall, D. J. Morgan, S. Brown, R. J. H. Clark, J. C. Knowles, *et al.*, "Photocatalytic Activities of N-doped Nano-titanias and Titanium Nitride," *Journal of the European Ceramic Society*, vol. 29, pp. 2343-2353, 2009.
- [37] L. Wicikowski, B. Kusz, L. Murawski, K. Szaniawska, and B. Susla, "AFM and XPS Study of Nitrided TiO₂ and SiO₂-TiO₂ Sol-gel Derived Films," *Vacuum*, vol. 54, pp. 221-225, 1999.
- [38] A. Fujishima, X. Zhang, and D. A. Tryk, "TiO₂ Photocatalysis and Related Surface Phenomena," *Surface Science Reports*, vol. 63, pp. 515-582, 2008.
- [39] S. Niyomsoan, W. Grant, D. L. Olson, and B. Mishra, "Variation of Color in Titanium and Zirconium Nitride Decorative Thin Films," *Thin Solid Films*, vol. 415, pp. 187-194, 2002.
- [40] C. Ernsberger, J. Nickerson, T. Smith, A. E. Miller, and D. Banks, "Low Temperature Oxidation Behavior of Reactively Sputtered TiN by X-ray Photoelectron Spectroscopy and Contact Resistance Measurements," *Journal of Vacuum Science and Technology A*, vol. 4, pp. 2784-2788, 1986.
- [41] N. C. Saha and H. G. Tompkins, "Titanium Nitride Oxidation Chemistry - an X-Ray Photoelectron-Spectroscopy Study," *Journal of Applied Physics*, vol. 72, pp. 3072-3079, 1992.

- [42] J.-M. Chappé, N. Martin, J. Lintymer, F. Sthal, G. Terwagne, and J. Takadoum, "Titanium Oxynitride Thin Films Sputter Deposited by the Reactive Gas Pulsing Process," *Applied Surface Science*, vol. 253, pp. 5312-5316, 2007.
- [43] J.-M. Chappé, N. Martin, G. Terwagne, J. Lintymer, J. Gavaille, and J. Takadoum, "Water as Reactive Gas to Prepare Titanium Oxynitride Thin Films by Reactive Sputtering," *Thin Solid Films*, vol. 440, pp. 66-73, 2003.
- [44] A. Rizzo, M. A. Signore, L. Tapfer, E. Piscopiello, A. Cappello, E. Bemporad, *et al.*, "Graded Selective Coatings based on Zirconium and Titanium Oxynitride," *Journal of Physics D-Applied Physics*, vol. 42, 2009.
- [45] J. M. Chappe, J. Gavaille, N. Martin, J. Lintymer, and J. Takadoum, "Substrate Temperature and Water Vapour Effects on Structural and Mechanical Properties of TiO_xN_y coatings," *Journal of Materials Science*, vol. 41, pp. 5639-5645, 2006.
- [46] M. Braic, M. Balaceanu, A. Vladescu, A. Kiss, V. Braic, G. Epurescu, *et al.*, "Preparation and Characterization of Titanium Oxy-nitride Thin Films," *Applied Surface Science*, vol. 253, pp. 8210-8214, 2007.
- [47] M. H. Chan and F. H. Lu, "Preparation of Titanium Oxynitride Thin Films by Reactive Sputtering using Air/Ar Mixtures," *Surface & Coatings Technology*, vol. 203, pp. 614-618, 2008.
- [48] M. J. Jung, K. H. Nam, Y. M. Chung, J. H. Boo, and J. G. Han, "The Physiochemical Properties of TiO_xN_y Films with Controlled Oxygen Partial Pressure," *Surface and Coatings Technology*, vol. 171, pp. 71-74, 2003.
- [49] C. K. Jung, I. S. Bae, Y. H. Song, S. J. Cho, and J. H. Boo, "Characterization of TiO_xN_y Films Grown by PECVD Method: Structural and Optical Properties," in *Symposium on Science and Technology of Hybrid Materials held at the ICMAT 2005/IUMRS-ICAM 2005*, pp. 151-154, Singapore.
- [50] P. C. Joshi and S. B. Krupanidhi, "Strontium Titanate Thin Films by Rapid Thermal Processing," *Applied Physics Letter*, vol. 61, pp. 1525-1527, 1992.
- [51] F. M. Pontes, E. R. Leite, E. J. H. Lee, E. Longo, and J. A. Varela, "Dielectric Properties and Microstructure of $\text{SrTiO}_3/\text{BaTiO}_3$ Multilayer Thin Films Prepared by a Chemical Route," *Thin Solid Films*, vol. 385, pp. 260-265, 2001.
- [52] F. M. Pontes, E. R. Leite, E. J. H. Lee, E. Longo, and J. A. Varela, "Preparation, Microstructural and Electrical Characterization of SrTiO_3 Thin Films prepared by Chemical Route," *Journal of the European Ceramic Society*, vol. 21, pp. 419-426, 2001.
- [53] F. T. Wagner and G. A. Somorjai, "Photocatalytic and Photoelectrochemical Hydrogen-Production on Strontium-Titanate Single-Crystals," *Journal of the American Chemical Society*, vol. 102, pp. 5494-5502, 1980.
- [54] S. Ahuja and T. R. N. Kutty, "Nanoparticles of SrTiO_3 prepared by Gel to Crystallite Conversion and their Photocatalytic Activity in the mineralization of Phenol," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 97, pp. 99-107, 1996.
- [55] T. Ishii, H. Kato, and A. Kudo, " H_2 Evolution from an Aqueous Methanol Solution on SrTiO_3 Photocatalysts codoped with Chromium and Tantalum Ions under Visible Light Irradiation," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 16., pp. 181-186, 2004.

- [56] R. Konta, T. Ishii, H. Kato, and A. Kudo, "Photocatalytic Activities of Noble Metal Ion Doped SrTiO₃ under Visible Light Irradiation," *Journal of Physical Chemistry B*, vol. 108, pp. 8992-8995, 2004.
- [57] M. Miyauchi, M. Takashio, and H. Tobimatsu, "Photocatalytic Activity of SrTiO₃ Codoped with Nitrogen and Lanthanum under Visible Light Illumination," *Langmuir*, vol. 20, pp. 232-236, 2004.
- [58] T. Ohno, T. Tsubota, Y. Nakamura, and K. Sayama, "Preparation of S, C Cation-Co-doped SrTiO₃ and its Photocatalytic Activity under Visible Light," *Applied Catalysis A-General*, vol. 288, pp. 74-79, 2005.
- [59] E. Bakken, S. Stolen, T. Norby, R. Glenne, and M. Budd, "Redox energetics of SrFeO_{3-δ} - a Coulometric Titration Study," *Solid State Ionics*, vol. 167, pp. 367-377, 2004.
- [60] Y. Wang, J. Chen, and X. Wu, "Preparation and Gas-sensing Properties of Perovskite-type SrFeO₃ Oxide," *Materials Letters*, vol. 49, pp. 361-364, 2001.
- [61] C. Liang, D. Yang, Z. Yang, F. Hou, and M. Xu, "The Preparation and Oxygen Sensitivity of Strontium Ferrite Thin Films," *Surface and Coatings Technology*, vol. 200, pp. 2515-2517, 2005.
- [62] S. Shin, Y. Hatakeyama, K. Ogawa, and K. Shimomura, "Catalytic Decomposition of NO over Brownmillerite-like Compounds, Ca₂Fe₂O₅ and Sr₂Fe₂O₅," *Materials Research Bulletin*, vol. 14, pp. 133-136, 1979.
- [63] M. Ghaffari, P. Y. Tan, M. E. Oruc, O. K. Tan, M. S. Tse, and M. Shannon, "Effect of Ball Milling on the Characteristics of Nanostructure SrFeO₃ Powder for Photocatalytic Degradation of Methylene Blue under Visible Light Irradiation and its Reaction Kinetics," *Catalysis Today*, vol. 161, pp. 70-77, 2011.
- [64] R. Moos and K. H. Hardtl, "Defect Chemistry of Donor-Doped and Undoped Strontium Titanate Ceramics between 1000°C and 1400°C," *Journal of American Ceramic Society*, vol. 80, pp. 2549-2562, 1997.
- [65] V. L. Kozhevnikov, I. A. Leonidov, M. V. Patrakeev, E. B. Mitberg, and K. R. Poeppelmeier, "Electrical Properties of the Ferrite SrFeO_y at High Temperatures," *Journal of Solid State Chemistry*, vol. 158, pp. 320-326, 2001.
- [66] A. Rothschild, W. Menesklou, H. L. Tuller, and E. Ivers-Tiffée, "Electronic Structure, Defect Chemistry, and Transport Properties of SrTi_{1-x}Fe_xO_{3-y} solid solutions," *Chemistry of Materials*, vol. 18, pp. 3651-3659, 2006.
- [67] S. J. Litzelman, A. Rothschild, and H. L. Tuller, "The Electrical Properties and Stability of SrTi_{0.65}Fe_{0.35}O_{3-δ} Thin Films for Automotive Oxygen Sensor Applications," *Sensors and Actuators B-Chemical*, vol. 108, pp. 231-237, 2005.
- [68] K. Sahner, P. Gouma, and R. Moos, "Electrodeposited and Sol-gel Precipitated p-type SrTi_{1-x}Fe_xO_{3-δ} Semiconductors for Gas Sensing," *Sensors*, vol. 7, pp. 1871-1886, 2007.
- [69] H. I. De Lasa, B. Serrano, and M. Salaices, "Photocatalytic Reaction Engineering," *Springer Science + Business Media, New York*, 2005.
- [70] O. Legrini, E. Oliveros, and A. M. Braun, "Photochemical Processes for Water-Treatment," *Chemical Reviews*, vol. 93, pp. 671-698, 1993.
- [71] F. Benoit-Marquie, U. Wilkenhoner, V. Simon, A. M. Braun, E. Oliveros, and M.-T. Maurette, "VOC Photodegradation at the Gas-solid Interface of a TiO₂

- Photocatalyst: Part I: 1-butanol and 1-butylamine," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 132, pp. 225-232, 2000.
- [72] D. S. Muggli, J. T. McCue, and J. L. Falconer, "Mechanism of the Photocatalytic Oxidation of Ethanol on TiO₂," *Journal of Catalysis*, vol. 173, pp. 470-483, 1998.
- [73] U. Diebold, "The Surface Science of Titanium Dioxide," *Surface Science Reports*, vol. 48, pp. 53-229, 2003.
- [74] J. D. Brown and D. L. Williamson, "Mossbauer Study of the Kinetics of Fe³⁺ Photoreduction on TiO₂ Semiconductor Powders," *Journal of Physical Chemistry*, vol. 89, pp. 3076-3080, 1985.
- [75] L. Kavan, M. Gratzel, S. E. Gilbert, C. Klemen, and H. J. Scheel, "Electrochemical and Photoelectrochemical Investigation of Single-crystal Anatase," *Journal of the American Chemical Society*, vol. 118, pp. 6716-6723, 1996.
- [76] K. Kato, Y. Torii, and H. Taoda, "TiO₂ Coating Photocatalysts with Nanostructure and Preferred Orientation showing Excellent Activity for Decomposition of Aqueous Acetic Acid," *Journal of Materials Science Letters*, vol. 15, pp. 913-915, 1996.
- [77] G. Riegel and J. R. Bolton, "Photocatalytic Efficiency Variability in TiO₂ Particles," *Journal of Physical Chemistry*, vol. 99, pp. 4215-4224, 1995.
- [78] T. Watanabe, A. Nakajima, R. Wang, M. Minabe, S. Koizumi, A. Fujishima, *et al.*, "Photocatalytic Activity and Photoinduced Hydrophilicity of Titanium Dioxide Coated Glass," *Thin Solid Films*, vol. 351, pp. 260-263, 1999.
- [79] N. Sakai, R. Wang, A. Fujishima, T. Watanabe, and K. Hashimoto, "Effect of Ultrasonic Treatment on Highly Hydrophilic TiO₂ Surfaces," *Langmuir*, vol. 14, pp. 5918-5920, 1998.
- [80] G. Balasubramanian, D. D. Dionysiou, M. T. Suidan, I. Baudin, and J. M. Laine, "Evaluating the Activities of Immobilized TiO₂ Powder Films for the Photocatalytic Degradation of Organic Contaminants in Water," *Applied Catalysis B: Environmental*, vol. 47, pp. 73-84, 2004.
- [81] R. I. Bickley, T. Gonzalez-Carreno, J. S. Lees, L. Palmisano, and R. J. D. Tilley, "A Structural Investigation of Titanium Dioxide Photocatalysts," *Journal of Solid State Chemistry*, vol. 92, pp. 178-190, 1991.
- [82] C. F. Doodeve and J. A. Kitchener, "The Mechanism of Photosensitisation by Solids," *Transactions of the Faraday Society*, vol. 34, p. 902, 1938.
- [83] K. Kogo, H. Yoneyama, and H. Tamura, "Photocatalytic Oxidation of Cyanide on Platinized TiO₂," *Journal of Physical Chemistry*, vol. 84, pp. 1705-1710, 1980.
- [84] M. Kato and Y. Goto, "Fabrication of TiO₂ Coating on SiC Whisker by a Sol-Gel Method," *Journal of Materials Science Letters*, vol. 15, pp. 1291-1293, 1996.
- [85] R. D. Sun, A. Nakajima, A. Fujishima, T. Watanabe, and K. Hashimoto, "Photoinduced Surface Wettability Conversion of ZnO and TiO₂ Thin Films," *Journal of Physical Chemistry B*, vol. 105, pp. 1984-1990, 2001.
- [86] G. Balasubramanian, D. D. Dionysiou, and M. T. Suidan, "Titania Powder Modified Sol-Gel Process for Photocatalytic Applications," *Journal of Materials Science Letters*, vol. 38, pp. 823-831, 2003.

- [87] K. H. Yoon, J. S. Noh, C. H. Kwon, and M. Muhammed, "Photocatalytic Behaviour of TiO₂ Thin Films prepared by Sol-gel Process," *Materials Chemistry and Physics*, vol. 95, pp. 79-83, 2006.
- [88] T. Matsunaga, R. Tomoda, T. Nakajima, and H. Wake, "Photoelectrochemical Sterilization of Microbial Cells by Semiconductor Powders," *FEMS Microbiology Letters*, vol. 29, pp. 211-214, 1985.
- [89] D. M. Blake, P.-C. Maness, Z. Huang, E. J. Wolfrum, J. Huang, and W. A. Jacoby, "Application of the Photocatalytic Chemistry of Titanium Dioxide to Disinfection and the Killing of Cancer Cells " *Separation and Purification Methods*, vol. 28, pp. 1-50, 1999.
- [90] P.-C. Maness, S. Smolinski, D. M. Blake, Z. Huang, E. J. Wolfrum, and W. A. Jacoby, "Bactericidal Activity of Photocatalytic TiO₂ Reaction : Towards an Understanding of Its Killing Mechanism," *Applied and Environmental Microbiology*, vol. 65, pp. 4094-4098, 1999.
- [91] P. A. Christensen, T. P. Curtis, T. A. Egerton, S. A. M. Kosa, and J. R. Tinlin, "Photoelectrocatalytic and Photocatalytic Disinfection of *E. coli* Suspensions by Titanium Dioxide," *Applied Catalyst B : Environmental*, vol. 41, pp. 371-386, 2003.
- [92] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, *et al.*, "Light-induced Amphiphilic Surfaces," *Nature*, vol. 388, pp. 431-432, 1997.
- [93] C. C. Trapalis, P. Keivanidis, G. Kordas, M. Zaharescu, M. Crisan, A. Szatvanyi, *et al.*, "TiO₂(Fe³⁺) Nanostructured Thin Films with Antibacterial Properties," *Thin Solid Films*, vol. 433, pp. 186-190, 2003.
- [94] Z. Li, W. Shen, W. He, and X. Zu, "Effect of Fe-doped TiO₂ Nanoparticle Derived from Modified Hydrothermal Process on the Photocatalytic Degradation Performance on Methylene Blue," *Journal of Hazardous Materials*, vol. 155, pp. 590-594, 2008.
- [95] K. Sunada, T. Watanabe, and K. Hashimoto, "Bactericidal Activity of Copper-deposited TiO₂ Thin Film under Weak UV Light Illumination," *Environmental Science & Technology*, vol. 37, pp. 4785-4789, 2003.
- [96] J. C. Yu, W. K. Ho, J. G. Yu, H. Yip, P. K. Wong, and J. C. Zhao, "Efficient Visible-light-induced Photocatalytic Disinfection on Sulfur-doped Nanocrystalline Titania," *Environmental Science & Technology*, vol. 39, pp. 1175-1179, 2005.
- [97] R. Bacsá, J. Kiwi, T. Ohno, P. Albers, and V. Nadtochenko, "Preparation, Testing and Characterization of Doped TiO₂ Active in the Peroxidation of Biomolecules under Visible Light," *Journal of Physical Chemistry B*, vol. 109, pp. 5994-6003, 2005.
- [98] Z. Zhang, J. Goodall, D. Morgan, S. Brown, R. Clark, J. Knowles, *et al.*, "Photocatalytic Activities of N-doped Nano-titanias and Titanium Nitride," *Journal of the European Ceramic Society*, vol. 29, pp. 2343-2353, 2009.
- [99] I. Nakamura, N. Negishi, S. Kutsuna, T. Ihara, S. Sugihara, and K. Takeuchi, "Role of Oxygen Vacancy in Plasma Treated TiO₂ Photocatalyst with Visible Light Activity for NO Removal" *Journal of Molecular Catalysis A: Chemical*, vol. 161, pp. 205-212, 2000.
- [100] D. C. Cronmeyer, "Infrared Absorption of Reduced Rutile TiO₂ Single Crystals," *Physical Review*, vol. 113, pp. 1222-1226, 1959.

- [101] J. D. Liao, H. J. Chen, C. W. Chang, S. M. Chiu, and Z. S. Chen, "Thin-film Photo-catalytic TiO₂ Phase Prepared by Magnetron Sputtering Deposition, Plasma Ion Implantation and Metal Vapor Vacuum Arc Source," *Thin Solid Films*, vol. 515, pp. 176-185, 2006.
- [102] P. V. A. Padmanabhan, K. P. Sreekumar, T. K. Thiyagarajan, R. U. Satpute, K. Bhanumurthy, P. Sengupta, *et al.*, "Nano-crystalline Titanium Dioxide Formed by Reactive Plasma Synthesis," *Vacuum*, vol. 80, pp. 1252-1255, 2006.
- [103] K. Takeuchi, I. Nakamura, O. Matsumoto, S. Sugihara, M. Ando, and T. Ihara, "Preparation of Visible-light-responsive Titanium Oxide Photocatalysts by Plasma Treatment," *Chemistry Letters*, pp. 1354-1355, 2000.
- [104] D. W. Bahnemann, C. Kormann, and M. R. Hoffmann, "Preparation and Characterization of Quantum Size Zinc Oxide: A Detailed Spectroscopic Study," *Journal of Physical Chemistry*, vol. 91, pp. 3789-3798, 1987.
- [105] E. R. Carraway, A. J. Hoffman, and M. R. Hoffmann, "Photocatalytic Oxidation of Organic Acids on Quantum-Sized Semiconductor Colloids," *Environmental Science & Technology*, vol. 28, pp. 786-793, 1994.
- [106] T. Watanabe, A. Fujishima, and K. Honda, "Photoelectrochemical Reactions at SrTiO₃ Single Crystal Electrode," *Bulletin of the Chemical Society of Japan*, vol. 49, pp. 355-358, 1976.
- [107] J. G. Mavroides, J. A. Kafalas, and D. F. Kolesar, "Photoelectrolysis of Water in Cells with SrTiO₃ Anodes," *Applied Physics Letters*, vol. 28, pp. 241-243, 1976.
- [108] M. S. Wrighton, A. B. Ellis, P. T. Wolczanski, D. L. Morse, H. B. Abrahamson, and D. S. Ginley, "Strontium Titanate Photoelectrodes. Efficient Photoassisted Electrolysis of Water at Zero Applied Potential," *Journal of the American Chemical Society*, vol. 98, pp. 2774-2779, 1976.
- [109] M. S. Wrighton, P. T. Wolczanski, and A. B. Ellis, "Photoelectrolysis of Water by Irradiation of Platinized N-type Semiconducting Metal Oxides," *Journal of Solid State Chemistry*, vol. 22, pp. 17-29, 1977.
- [110] W. Zhang, Q. Xing, and Y. Huang, "Microstructures and Optical Properties of Strontium Titanate Nanocrystals Prepared by a Stearic-Acid Gel Process," *Modern Physics Letters B*, vol. 14, pp. 709-716, 2000.
- [111] T. Bieger, J. Maier, and R. Waser, "Optical Investigation of Oxygen Incorporation in SrTiO₃," *Solid State Ionics*, vol. 53-56, pp. 578-582, 1992.
- [112] C.-H. Chang and Y.-H. Shen, "Synthesis and Characterization of Chromium Doped SrTiO₃ photocatalyst," *Materials Letters*, vol. 60, pp. 129-132, 2006.
- [113] T. Xie, X. Sun, and J. Lin, "Enhanced Photocatalytic Degradation of RhB Driven by Visible Light-Induced MMCT of Ti(IV)-O-Fe(II) Formed in Fe-doped SrTiO₃," *Journal of Physical Chemistry C*, vol. 112, pp. 9753-9759, 2008.
- [114] J. Wang, S. Yin, M. Komatsu, Q. Zhang, F. Saito, and T. Sato, "Preparation and Characterization of Nitrogen Doped SrTiO₃ photocatalyst," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 165, pp. 149-156, 2004.
- [115] H. Kato and A. Kudo, "Visible-Light-Response and Photocatalytic Activities of TiO₂ and SrTiO₃ Photocatalysts Codoped with Antimony and Chromium," vol. 106, pp. 5029-5034, 2002.

- [116] Y. Takeda, K. Kanno, T. Takada, O. Yamamoto, M. Takano, N. Nakayama, *et al.*, "Phase Relation in the Oxygen Nonstoichiometric System, SrFeO_x ($2.5 \leq x \leq 3.0$)," *Journal of Solid State Chemistry*, vol. 63, pp. 237-249, 1986.
- [117] M. L. Post, J. J. Tunney, D. Yang, X. Du, and D. L. Singleton, "Material Chemistry of Perovskite Compounds as Chemical Sensors," *Sensors and Actuators B-Chemical*, vol. 59, pp. 190-194, 1999.
- [118] Y. D. Wang, J. B. Chen, and X. H. Wu, "Preparation and Gas-sensing Properties of Perovskite-type SrFeO_3 Oxide," *Materials Letters*, vol. 49, pp. 361-364, 2001.
- [119] C. Liang, D. A. Yang, J. J. Song, and M. X. Xu, "Oxygen Sensitivity of $\text{SrFeO}_{3-\delta}$ Thin Films Prepared by Sol-gel Method," in *High-Performance Ceramics III, Pts 1 and 2*, vol. 280-283, ed Zurich-Uetikon: Trans Tech Publications Ltd, 2005, pp. 315-318.
- [120] C. Liang, D. A. Yang, Z. Yang, F. Hou, and M. X. Xu, "The Preparation and Oxygen Sensitivity of Strontium Ferrite Thin Films," *Surface & Coatings Technology*, vol. 200, pp. 2515-2517, 2005.
- [121] H. X. Dai, C. F. Ng, and C. T. Au, "The Catalytic Performance and Characterization of a Durable Perovskite-type Chloro-oxide $\text{SrFeO}_{3-\delta}\text{Cl}_\delta$ Catalyst Selective for the Oxidative Dehydrogenation of Ethane " *Catalysis Letters*, vol. 57, pp. 115-120, 1999.
- [122] L. H. Brixner, "Preparation and Properties of the $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-x/2}\text{O}_{x/2}$ System," *Materials Research Bulletin*, vol. 3, pp. 299-308, 1968.
- [123] J. Mizusaki, M. Okayasu, S. Yamauchi, and K. Fueki, "Nonstoichiometry and Phase Relationship of the $\text{SrFeO}_{2.5}$ - SrFeO_3 System at High Temperature," *Journal of Solid State Chemistry*, vol. 99, pp. 166-172, 1992.
- [124] S. Steinsvik, R. Bugge, J. O. N. Gjønnes, J. Taftø, and T. Norby, "The Defect Structure of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-y}$ ($x = 0-0.8$) Investigated by Electrical Conductivity Measurements and Electron Energy Loss Spectroscopy (EELS)," *Journal of Physics and Chemistry of Solids*, vol. 58, pp. 969-976, 1997.
- [125] J. R. Jurado, F. M. Figueiredo, B. Gharbage, and J. R. Frade, "Electrochemical Permeability of $\text{Sr}_{0.7}(\text{Ti,Fe})\text{O}_{3-\delta}$ materials," *Solid State Ionics*, vol. 118, pp. 89-97, 1999.
- [126] C. Greaves and R. A. Buker, "The Defect Structure of $\text{Sr}_2\text{FeTiO}_{6-x}$," *Materials Research Bulletin*, vol. 21, pp. 823-833, 1986.
- [127] J. Rodriguez, J. A. Pereda, M. Vallet, J. G. Calbet, and J. Tejada, "Mossbauer Study of Vacancy Ordering in the System $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-y}$ ($0.50 \leq x \leq 0.70$)," *Materials Research Bulletin*, vol. 21, pp. 255-263, 1986.
- [128] A. Rothschild, S. J. Litzelman, H. L. Tuller, W. Menesklou, T. Schneider, and E. Ivers-Tiffée, "Temperature-independent Resistive Oxygen Sensors Based on $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ Solid Solutions," *Sensors and Actuators B-Chemical*, vol. 108, pp. 223-230, 2005.
- [129] W. Menesklou, H.-J. Schreiner, K. H. Hardtl, and E. Ivers-Tiffée, "High Temperature Oxygen Sensors Based on Doped SrTiO_3 ," *Sensors and Actuators B: Chemical*, vol. 59, pp. 184-189, 1999.
- [130] K. Sahner, R. Moos, M. Matam, J. J. Tunney, and M. Post, "Hydrocarbon Sensing with Thick and Thin Film p-type Conducting Perovskite Materials," *Sensors and Actuators B: Chemical*, vol. 108, p. 202, 2005.

- [131] S. J. Skinner and J. A. Kilner, "Oxygen Ion Conductors," *Materials Today*, vol. 6, pp. 30-36, 2003.
- [132] V. K. Varadan, D. K. Ghodgaonkar, V. V. Varadan, J. F. Kelly, and P. Glikerdas, "Ceramic Phase Shifters for Electronically Steerable Antenna Systems," *Microwave Journal*, vol. 35, pp. 116-&, 1992.
- [133] K. Sahner and R. Moos, "Modeling of Hydrocarbon Sensors based on P-type Semiconducting Perovskites," *Physical Chemistry Chemical Physics*, vol. 9, pp. 635-642, 2007.
- [134] K. Sahner, D. Schonauer, R. Moos, M. Matam, and M. L. Post, "Effect of Electrodes and Zeolite Cover Layer on Hydrocarbon Sensing with P-type Perovskite $\text{SrTi}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$," *Journal of Materials Science*, vol. 41, pp. 5828-5835, 2006.
- [135] R. Moos, F. Rettig, A. Hurland, and C. Plog, "Temperature-independent Resistive Oxygen Exhaust Gas Sensor for Lean-burn Engines in Thick-film Technology," *Sensors and Actuators B-Chemical*, vol. 93, pp. 43-50, 2003.
- [136] R. Moos, W. Menesklou, H.-J. Schreiner, and K. H. Hardtl, "Materials for Temperature Independent Resistive Oxygen Sensors for Combustion Exhaust Gas Control," *Sensors and Actuators B: Chemical*, vol. 67, pp. 178-183, 2000.
- [137] V. V. Kharton, A. V. Kovalevsky, A. P. Viskup, F. M. Figueiredo, J. R. Frade, A. A. Yaremchenko, *et al.*, "Faradaic Efficiency and Oxygen Permeability of $\text{Sr}_{0.97}\text{Ti}_{0.60}\text{Fe}_{0.40}\text{O}_{3-\delta}$ Perovskite," *Solid State Ionics*, vol. 128, pp. 117-130, 2000.
- [138] V. V. Kharton, A. P. Viskup, A. V. Kovalevsky, J. R. Jurado, E. N. Naumovich, A. A. Vecher, *et al.*, "Oxygen Ionic Conductivity of Ti-containing Strontium Ferrite," *Solid State Ionics*, vol. 133, pp. 57-65, 2000.
- [139] S. Steinsvik, Y. Larring, and T. Norby, "Hydrogen Ion Conduction in Iron-substituted Strontium Titanate $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-x/2}$ ($0 \leq x \leq 0.8$)," *Solid State Ionics*, vol. 143, pp. 103-116, 2001.
- [140] C. J. Brinker and G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*. Boston: Academic Press, 1990.
- [141] C. Technology. (1998, December). *Sol-Gel Technology*. Available: <http://www.chemat.com/html/solgel.html>
- [142] M. Wittmer, J. Noser, and H. Melchior, "Oxidation Kinetics of TiN Thin Films," *Journal of Applied Physics*, vol. 52, pp. 6659-6664, 1981.
- [143] H. G. Tompkins, "Oxidation of Titanium Nitride in Room Air and in Dry O_2 ," *Journal of Applied Physics*, vol. 70, pp. 3876-3880, 1991.
- [144] Z. Wu, F. Dong, W. Zhao, and S. Guo, "Visible Light Induced Electron Transfer Process over Nitrogen Doped TiO_2 Nanocrystals Prepared by Oxidation of Titanium Nitride," *Journal of Hazardous Materials*, vol. 157, pp. 57-63, 2008.
- [145] X. Zhou, F. Peng, H. Wang, H. Yu, and J. Yang, "Preparation of Nitrogen Doped TiO_2 Photocatalyst by Oxidation of Titanium Nitride with H_2O_2 ," *Materials Research Bulletin*, vol. 46, pp. 840-844, 2011.
- [146] J. Tauc, R. Grigorovici, and A. Vancu, "Optical Properties and Electronic Structures of Amorphous Germanium," *Phys. Stat. Sol.*, vol. 15, pp. 627-637, 1966.
- [147] E. Kim, Z. T. Jiang, and K. No, "Measurement and Calculation of Optical Bandgap of Chromium Aluminium Oxide Films," *Japanese Journal of Applied Physics*, vol. 39, pp. 4820-4825, 2000.

- [148] K. van Benthem, C. Elsaesser, and R. H. French, "Bulk Electronic Structure of SrTiO_3 : Experiment and Theory," *Journal of Applied Physics*, vol. 90, p. 6156, 2001.
- [149] P. Kubelka and F. Munk, *Z. Tech. Phys.*, vol. 12, p. 593, 1931.
- [150] I. Baikie. (2013). *The Kelvin Probe Principles*. Available: <http://www.kelvinprobe.info/technique-principles.htm>
- [151] L. Kronik and Y. Shapira, "Surface Photovoltage Phenomena: Theory, Experiment, and Applications," *Surface Science Reports*, vol. 37, pp. 1-206, 1999.
- [152] W. H. Brattain and W. Shockley, "Density of Surface States on Silicon Deduced from Contact Potential Measurements," *Physical Review*, vol. 72, p. 345, 1947.
- [153] C. G. B. Garrett and W. H. Brattain, "Physical Theory of Semiconductor Surfaces," *Physical Review*, vol. 99, pp. 376-387, 1955.
- [154] E. O. Johnson, "Measurement of Minority Carrier Lifetimes with the Surface Photovoltage," *Journal of Applied Physics*, vol. 28, pp. 1349-1353, 1957.
- [155] A. M. Goodman, "A Method for the Measurement of Short Minority Carrier Diffusion Lengths in Semiconductors," *Journal of Applied Physics*, vol. 32, pp. 2550-2552, 1961.
- [156] H. C. Gatos and J. Lagowski, "Surface Photovoltage Spectroscopy---A New Approach to the Study of High-Gap Semiconductor Surfaces," *Journal of Vacuum Science and Technology*, vol. 10, pp. 130-135, 1973.
- [157] J. Lagowski, P. Edelman, M. Dexter, and W. Henley, "Non-contact Mapping of Heavy Metal Contamination for Silicon IC Fabrication," *Semiconductor Science and Technology*, vol. 7, p. A185, 1992.
- [158] M. Leibovitch and L. Kronik, "Constructing Band Diagrams of Semiconductor Heterojunctions," *Applied Physics Letters*, vol. 66, p. 457, 1995.
- [159] M. Leibovitch, L. Kronik, B. Mishori, Y. Shapira, C. M. Hanson, A. R. Clawson, *et al.*, "Determining Band Offsets using Surface Photovoltage Spectroscopy: The $\text{InP}/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ Heterojunction," *Applied Physics Letters*, vol. 69, pp. 2587-2589, 1996.
- [160] L. Q. Jing, S. D. Li, S. Song, L. P. Xue, and H. G. Fu, "Investigation on the Electron Transfer Between Anatase and Rutile in Nano-sized TiO_2 by means of Surface Photovoltage Technique and its Effects on the Photocatalytic Activity," *Solar Energy Materials and Solar Cells*, vol. 92, pp. 1030-1036, 2008.
- [161] L. R. Sheppard, T. Dittrich, J. Nowotny, and T. Bak, "Surface Photovoltage Studies of Nonstoichiometric Rutile Titanium Dioxide," *Applied Physics Letters*, vol. 96, 2010.
- [162] D. S. Warren, Y. Shapira, H. Kisch, and A. J. McQuillan, "Apparent Semiconductor Type Reversal in Anatase TiO_2 Nanocrystalline Films," *The Journal of Physical Chemistry C*, vol. 111, pp. 14286-14289, 2007.
- [163] L. Han, Y. J. Xin, H. L. Liu, X. X. Ma, and G. Z. Tang, "Photoelectrocatalytic Properties of Nitrogen Doped TiO_2/Ti Photoelectrode Prepared by Plasma Based Ion Implantation under Visible Light," *Journal of Hazardous Materials*, vol. 175, pp. 524-531, 2010.
- [164] Y. Q. Wang, X. J. Yu, and D. Z. Sun, "Synthesis, Characterization, and Photocatalytic Activity of $\text{TiO}_{2-x}\text{N}_x$ Nanocatalyst," *Journal of Hazardous Materials*, vol. 144, pp. 328-333, 2007.

- [165] X. F. Chen, Q. Luo, M. D. Han, O. K. Tan, M. S. Tse, and H. Huang, "Mechanochemical Synthesis of Nano-structured $\text{Sr}(\text{Ti,Fe})\text{O}_3$ Solid-solution Powders and their Surface Photovoltage Responses," *Journal of Solid State Chemistry*, vol. 189, pp. 80-84, 2012.
- [166] C. L. Chow, H. Huang, W. C. Ang, H. Liu, Y. Huang, M. S. Tse, *et al.*, "Effect of Annealing Temperature on the Crystallization and Oxygen Sensing Property of Strontium Titanate Ferrite Sol-gel Thin Films," *Sensors and Actuators B: Chemical*, vol. 187, pp. 20-26, 2013.
- [167] H. Miao, S. Ratnasingam, C. S. Pu, M. M. Desai, and C. C. Sze, "Dual Fluorescence System for Flow Cytometric Analysis of Escherichia Coli Transcriptional Response in Multi-species Context," *Journal of Microbiological Methods*, vol. 76, pp. 109-119, 2009.
- [168] "Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics)-Test Method for Air-purification Performance of Semiconducting Photocatalytic Materials-Part 1: Removal of Nitric Oxide," ed. Switzerland: ISO, 2007.
- [169] "Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics)-Test Method for Air Purification Performance of Photocatalytic Materials-Part 2: Removal of Acetaldehyde," ed: Japanese Standards Association, 2008.
- [170] A. Trenczek-Zajac, K. Kowalski, K. Zakrzewska, and M. Radecka, "Nitrogen-doped Titanium Dioxide-Characterization of Structural and Optical Properties," *Materials Research Bulletin*, vol. 44, pp. 1547-1552, 2009.
- [171] R. A. Spurr and H. Myers, "Quantitative Analysis of Anatase-Rutile Mixtures with an X-Ray Diffractometer," *Analytical Chemistry*, vol. 29, pp. 760-762, 1957.
- [172] I. Milosev, H. H. Strehblow, B. Navinsek, and M. Metikoshukovic, "Electrochemical and Thermal-Oxidation of Tin Coatings Studied by XPS," *Surface and Interface Analysis*, vol. 23, pp. 529-539, 1995.
- [173] I. Bertóti, "Characterization of Nitride coatings by XPS," *Surface and Coatings Technology*, vol. 151-152, pp. 194-203, 2002.
- [174] A. Glaser, S. Surnev, F. P. Netzer, N. Fateh, G. A. Fontalvo, and C. Mitterer, "Oxidation of Vanadium Nitride and Titanium Nitride Coatings," *Surface Science*, vol. 601, pp. 1153-1159, 2007.
- [175] M. H. Chan and F. H. Lu, "X-ray Photoelectron Spectroscopy Analyses of Titanium Oxynitride Films Prepared by Magnetron Sputtering using Air/Argon mixtures," *Thin Solid Films*, vol. 517, pp. 5006-5009, 2009.
- [176] M. J. Vasile, A. B. Emerson, and F. A. Baiocchi, "The Characterization of Titanium Nitride by X-Ray Photoelectron Spectroscopy and Rutherford Backscattering," *Journal of Vacuum Science and Technology A*, vol. 8, p. 99, 1990.
- [177] I. Strydom and S. Hofmann, "The Contribution of Characteristic Energy Losses in the Core-level X-ray Photoelectron Spectroscopy Peaks of TiN and (Ti, Al)N Studied by Electron Energy Loss Spectroscopy and X-ray Photoelectron Spectroscopy," *Journal of Electron Spectroscopy and Related Phenomena*, vol. 56, pp. 85-103, 1991.
- [178] L. Porte, L. Roux, and J. Hanus, "Vacancy Effects in X-Ray Photoelectron Spectra of TiN_x ," *Physical Review B*, vol. 28, pp. 3214-3224, 1983.

- [179] M. J. Jung, K. H. Nam, Y. M. Chung, J. H. Boo, and J. G. Han, "The Physiochemical Properties of TiO_xN_y Films with Controlled Oxygen Partial Pressure," *Surface and Coatings Technology*, vol. 171, pp. 71-74, 2002.
- [180] O. Diwald, T. L. Thompson, T. Zubkov, S. D. Walck, and J. T. Yates, "Photochemical Activity of Nitrogen-Doped Rutile $\text{TiO}_2(110)$ in Visible Light," *The Journal of Physical Chemistry B*, vol. 108, pp. 6004-6008, 2004.
- [181] G. Liu, X. Wang, Z. Chen, H.-M. Cheng, and G. Q. Lu, "The Role of Crystal Phase in Determining Photocatalytic Activity of Nitrogen Doped TiO_2 ," *Journal of Colloid and Interface Science*, vol. 329, pp. 331-338, 2009.
- [182] V. A. Gubanov, *Electronic Structure of Refractory Carbides and Nitrides*. New York: Cambridge University Press, 1994.
- [183] S. Livraghi, M. C. Paganini, E. Giamello, A. Selloni, C. Di Valentin, and G. Pacchioni, "Origin of Photoactivity of Nitrogen-Doped Titanium Dioxide under Visible Light," *Journal of the American Chemical Society*, vol. 128, pp. 15666-15671, 2006.
- [184] Z. Lin, A. Orlov, R. M. Lambert, and M. C. Payne, "New Insights into the Origin of Visible Light Photocatalytic Activity of Nitrogen-Doped and Oxygen-Deficient Anatase TiO_2 ," *The Journal of Physical Chemistry B*, vol. 109, pp. 20948-20952, 2005.
- [185] Y. Nakano, T. Morikawa, T. Ohwaki, and Y. Taga, "Deep-level Optical Spectroscopy Investigation of N-doped TiO_2 films," *Applied Physics Letters*, vol. 86, p. 132104, 2005.
- [186] D. J. V. Pulsipher, I. T. Martin, and E. R. Fisher, "Controlled Nitrogen Doping and Film Colorimetrics in Porous TiO_2 Materials Using Plasma Processing," *ACS Applied Materials & Interfaces*, vol. 2, pp. 1743-1753, 2010.
- [187] V. N. Kuznetsov and N. Serpone, "Visible Light Absorption by Various Titanium Dioxide Specimens," *The Journal of Physical Chemistry B*, vol. 110, pp. 25203-25209, 2006.
- [188] C. Sousa, G. Pacchioni, and F. Illas, "Ab Initio Study of the Optical Transitions of F Centers at Low-coordinated Sites of the MgO surface," *Surface Science*, vol. 429, pp. 217-228, 1999.
- [189] N. Serpone, "Is the Band Gap of Pristine TiO_2 Narrowed by Anion- and Cation-Doping of Titanium Dioxide in Second-Generation Photocatalysts?," *The Journal of Physical Chemistry B*, vol. 110, pp. 24287-24293, 2006.
- [190] H. Meier, "Photosensitization of Inorganic Solids," *Photochemistry and Photobiology*, vol. 16, pp. 219-241, 1972.
- [191] H. Gerischer, "Electrochemical Techniques for the Study of Photosensitization," *Photochemistry and Photobiology*, vol. 16, pp. 243-260, 1972.
- [192] K. Vinodgopal, D. E. Wynkoop, and P. V. Kamat, "Environmental Photochemistry on Semiconductor Surfaces: Photosensitized Degradation of a Textile Azo Dye, Acid Orange 7, on TiO_2 Particles Using Visible Light," *Environmental Science & Technology*, vol. 30, pp. 1660-1666, 1996.
- [193] M. Styliadi, D. I. Kondarides, and X. E. Verykios, "Pathways of Solar Light-induced Photocatalytic Degradation of Azo Dyes in Aqueous TiO_2 Suspensions," *Applied Catalysis B: Environmental*, vol. 40, pp. 271-286, 2003.

- [194] C. Chen, X. Li, W. Ma, J. Zhao, H. Hidaka, and N. Serpone, "Effect of Transition Metal Ions on the TiO₂-Assisted Photodegradation of Dyes under Visible Irradiation: A Probe for the Interfacial Electron Transfer Process and Reaction Mechanism," *The Journal of Physical Chemistry B*, vol. 106, pp. 318-324, 2001.
- [195] P. Qu, J. Zhao, T. Shen, and H. Hidaka, "TiO₂-assisted Photodegradation of Dyes: A Study of Two Competitive Primary Processes in the Degradation of RB in an Aqueous TiO₂ Colloidal Solution," *Journal of Molecular Catalysis A: Chemical*, vol. 129, pp. 257-268, 1998.
- [196] T. Saison, N. Chemin, C. Chanéac, O. Durupthy, V. r. Ruaux, L. Mariey, *et al.*, "Bi₂O₃, BiVO₄, and Bi₂WO₆: Impact of Surface Properties on Photocatalytic Activity under Visible Light," *The Journal of Physical Chemistry C*, vol. 115, pp. 5657-5666, 2011.
- [197] T. Wu, G. Liu, J. Zhao, H. Hidaka, and N. Serpone, "Photoassisted Degradation of Dye Pollutants. V. Self-Photosensitized Oxidative Transformation of Rhodamine B under Visible Light Irradiation in Aqueous TiO₂ Dispersions," *The Journal of Physical Chemistry B*, vol. 102, pp. 5845-5851, 1998.
- [198] X. Li and J. Ye, "Photocatalytic Degradation of Rhodamine B over Pb₃Nb₄O₁₃/Fumed SiO₂ Composite under Visible Light Irradiation," *The Journal of Physical Chemistry C*, vol. 111, pp. 13109-13116, 2007.
- [199] T. Watanabe, T. Takizawa, and K. Honda, "Photocatalysis Through Excitation of Adsorbates. 1. Highly Efficient N-deethylation of Rhodamine B Adsorbed to Cadmium Sulfide," *The Journal of Physical Chemistry*, vol. 81, pp. 1845-1851, 1977.
- [200] X. Dai, Y. Luo, W. Zhang, and S. Fu, "Facile Hydrothermal Synthesis and Photocatalytic Activity of Bismuth Tungstate Hierarchical Hollow Spheres with an Ultrahigh Surface Area," *Dalton Transactions*, vol. 39, pp. 3426-3432, 2010.
- [201] C. Hu, J. C. Yu, Z. Hao, and P. K. Wong, "Effects of Acidity and Inorganic Ions on the Photocatalytic Degradation of Different Azo Dyes," *Applied Catalysis B: Environmental*, vol. 46, pp. 35-47, 2003.
- [202] C. Bauer, P. Jacques, and A. Kalt, "Photooxidation of an Azo Dye Induced by Visible Light Incident on the Surface of TiO₂," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 140, pp. 87-92, 2001.
- [203] K. Wang, J. Zhang, L. Lou, S. Yang, and Y. Chen, "UV or Visible Light Induced Photodegradation of AO7 on TiO₂ Particles: the Influence of Inorganic Anions," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 165, pp. 201-207, 2004.
- [204] M. Y. Leiw, G. H. Guai, X. Wang, M. S. Tse, C. M. Ng, and O. K. Tan, "Dark Ambient Degradation of Bisphenol A and Acid Orange 8 as Organic Pollutants by Perovskite SrFeO_{3-δ} Metal Oxide," *Journal of Hazardous Materials*, vol. 260, pp. 1-8, 2013.
- [205] L. Soriano, M. Abbate, H. Pen, P. Prieto, and J. M. Sanz, "The Electronic Structure of TiN and VN: X-ray and Electron Spectra Compared to Band Structure Calculations," *Solid State Communications*, vol. 102, pp. 291-296, 1997.
- [206] R. Beranek, B. Neumann, S. Sakthivel, M. Janczarek, T. Dittrich, H. Tributsch, *et al.*, "Exploring the Electronic Structure of Nitrogen-modified TiO₂ Photocatalysts

- through Photocurrent and Surface Photovoltage Studies," *Chemical Physics*, vol. 339, pp. 11-19, 2007.
- [207] X. Chen, W. Lu, W. Zhu, S. Yin Lim, and S. A. Akbar, "Structural and Thermal Analyses on Phase Evolution of Sol-gel (Ba,Sr)TiO₃ Thin Films," *Surface and Coatings Technology*, vol. 167, pp. 203-206, 2003.
- [208] L. L. Sun, L. I. Tan, O. K. Tan, Z. H. Wang, and W. G. Zhu, "Structure and Electrical Properties of Ba_{0.67}Sr_{0.33}TiO₃ Thin Film Fabricated by Sol-gel Based Composite Technique," *Journal of Electroceramics*, vol. 16, pp. 483-488, 2006.
- [209] Y. Chen, W. Chen, F. Guo, M. Y. Li, W. Liu, and X. Z. Zhao, "Synthesis and Characterization of Highly-ordered Barium-strontium Titanate Nanotube Arrays Fabricated by Sol-gel Method," *Chinese Physics B*, vol. 18, pp. 3922-3927, 2009.
- [210] H. Y. Wang, X. Yao, and L. Y. Zhang, "Preparation and Dielectric Properties of Barium Strontium Titanate Glass-ceramics Sintered from Sol-gel-derived Powders," *Ceramics International*, vol. 30, pp. 1749-1752, 2004.
- [211] X. Q. Fang, T. O. Kiang, and T. M. Siu, "Metal Oxide Barium Strontium Titanate Thin Films for Electrical Immunosensing Applications," *Science of Advanced Materials*, vol. 3, pp. 763-786, 2011.
- [212] X. Q. Fang, O. K. Tan, M. S. Tse, and E. E. Ooi, "A Label-free Immunosensor for Diagnosis of Dengue Infection with Simple Electrical Measurements," *Biosensors & Bioelectronics*, vol. 25, pp. 1137-1142, 2010.
- [213] G. Pfaff, "Sol-gel Synthesis of Strontium Titanate Powders of Various Compositions," *Journal of Materials Chemistry*, vol. 3, pp. 721-724, 1993.
- [214] R. Wurm, O. Dernovsek, and P. Greil, "Sol-gel Derived SrTiO₃ and SrZrO₃ Coatings on SiC and C-fibers," *Journal of Materials Science*, vol. 34, pp. 4031-4037, 1999.
- [215] X. Q. Fang, O. K. Tan, Y. Y. Gan, and M. S. Tse, "Novel Immunosensor Platform Based on Inorganic Barium Strontium Titanate Film for Human IgG Detection," *Sensors and Actuators B-Chemical*, vol. 149, pp. 381-388, 2010.
- [216] M. P. Pechini, "Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coating Methods using the Same to Form a Capacitor," 1967.
- [217] R. da Silva, M. Bernardi, and A. Hernandez, "Synthesis of Non-agglomerated Ba_{0.77}Ca_{0.23}TiO₃ Nanopowders by a Modified Polymeric Precursor Method," *Journal of Sol-Gel Science and Technology*, vol. 42, pp. 173-179, 2007.
- [218] A. Ianculescu, D. Berger, M. Viviani, C. E. Ciomaga, L. Mitoseriu, E. Vasile, *et al.*, "Investigation of Ba_{1-x}Sr_xTiO₃ Ceramics Prepared from Powders Synthesized by the Modified Pechini Route," in *International Conference on Electroceramics*, Toledo, Spain, pp. 3655-3658, 2006.
- [219] M. Liu and D. Wang, "Preparation of La_{1-z}Sr_zCo_{1-y}Fe_yO_{3-x} Thin Films, Membranes, and Coatings on Dense and Porous Substrates," *Journal of Materials Research*, vol. 10, pp. 3210-3221, 1995.
- [220] Y. L. Chai, D. T. Ray, G. J. Chen, and Y. H. Chang, "Synthesis of La_{0.8}Sr_{0.2}Co_{0.5}Ni_{0.5}O_{3-d} Thin Films for High Sensitivity CO Sensing Material using the Pechini process," *Journal of Alloys and Compounds*, vol. 333, pp. 147-153, 2002.

- [221] A. Majid, J. Tunney, M. Post, and J. Margeson, "Process Optimization and Characterization of Thin Films of SrFeO_{3-x} by the Pechini Method," *Journal of Sol-Gel Science and Technology*, vol. 38, pp. 271-275, 2006.
- [222] S. Sakka, *Handbook of Sol-gel Science and Technology : Processing, Characterization, and Applications* 1st ed. vol. 1: Kluwer Academic Publisher, 2005.
- [223] H. Kozuka, M. Kajimura, T. Hirano, and K. Katayama, "Crack-free, Thick Ceramic Coating Films via Non-repetitive Dip-Coating Using Polyvinylpyrrolidone as Stress-Relaxing Agent," *Journal of Sol-Gel Science and Technology*, vol. 19, pp. 205-209, 2000.
- [224] H. Kozuka, S. Takenaka, H. Tokita, and M. Okubayashi, "PVP-assisted Sol-gel Deposition of Single Layer Ferroelectric Thin Films over Submicron or Micron in Thickness," *Journal of the European Ceramic Society*, vol. 24, pp. 1585-1588, 2004.
- [225] J. Choi, G. Park, S. Lee, and H. Kim, "Sol-Gel Preparation of Thick PZN-PZT Film Using a Diol-Based Solution Containing Polyvinylpyrrolidone for Piezoelectric Applications," *Journal of American Ceramic Society*, vol. 88, pp. 3049-3054, 2005.
- [226] Z. H. Du, T. S. Zhang, M. M. Zhu, and J. Ma, "Direct Crystallization of Perovskite Phase in PMN-PT Thin Films Prepared by Polyvinylpyrrolidone Modified Sol-gel Processing and Their Properties," *Journal of Solid State Chemistry*, vol. 182, pp. 1780-1785, 2009.
- [227] U. O. Krasovec, M. Berginc, M. Hocevar, and M. Topic, "Unique TiO_2 Paste for High Efficiency Dye-sensitized Solar Cells," *Solar Energy Materials and Solar Cells*, vol. 93, pp. 379-381, 2009.
- [228] M. Hocevar, U. O. Krasovec, M. Berginc, G. Drazic, N. Hauptman, and M. Topic, "Development of TiO_2 Pastes Modified with Pechini Sol-gel Method for High Efficiency Dye-sensitized Solar Cell," in *14th International Sol-Gel Conference*, Montpellier, France, pp. 156-162, 2007.
- [229] V. Vinothini, P. Singh, and M. Balasubramanian, "Synthesis of Barium Titanate Nanopowder using Polymeric Precursor Method," *Ceramics International*, vol. 32, pp. 99-103, 2006.
- [230] M. Kakihana, T. Okubo, M. Arima, Y. Nakamura, M. Yashima, and M. Yoshimura, "Polymerized Complex Route to the Synthesis of Pure SrTiO_3 at Reduced Temperatures: Implication for Formation of Sr-Ti Heterometallic Citric Acid Complex," *Journal of Sol-Gel Science and Technology*, vol. 12, pp. 95-109, 1998.
- [231] M. Kakihana, M. Arima, Y. Nakamura, M. Yashima, and M. Yoshimura, "Spectroscopic Characterization of Precursors used in the Pechini-type Polymerizable Complex Processing of Barium Titanate," *Chemistry of Materials*, vol. 11, pp. 438-450, 1999.
- [232] T. T. Fang and J. D. Tsay, "Effect of pH on the Chemistry of the Barium Titanium Citrate Gel and its Thermal Decomposition Behavior," *Journal of the American Ceramic Society*, vol. 84, pp. 2475-2478, 2001.

- [233] T. T. Fang, M. S. Wu, and J. D. Tsai, "¹³C NMR Study of the Solution Chemistry of Barium Titanium Citrate Gels prepared using the Pechini process," *Journal of American Ceramics Society*, vol. 85, pp. 2984-2988, 2002.
- [234] S. Yuvaraj, L. Fan-Yuan, C. Tsong-Huei, and Y. Chuin-Tih, "Thermal Decomposition of Metal Nitrates in Air and Hydrogen Environments," *The Journal of Physical Chemistry B*, vol. 107, pp. 1044-1047, 2003.
- [235] A. Malecki, R. Gajerski, S. Labus, B. Prochowska-Klisch, and K. T. Wojciechowski, "Mechanism of Thermal Decomposition of d-metals Nitrates Hydrates," *Journal of Thermal Analysis and Calorimetry*, vol. 60, pp. 17-23, 2000.
- [236] T. Cseri, S. Bekassy, G. Kenessey, G. Liptay, and F. Figueras, "Characterization of Metal Nitrates and Clay Supported Metal Nitrates by Thermal Analysis," *Thermochimica Acta*, vol. 288, pp. 137-154, 1996.
- [237] H. Aono, J. Izumi, M. Tomida, and Y. Sadaoka, "Synthesis for Fine Perovskite-type Materials using Precursor Prepared by Metal Nitrates Solution Mixed with Organic Solvent," *Materials Chemistry and Physics*, vol. 130, pp. 973-979, 2011.
- [238] S. Kumar, G. L. Messing, and W. B. White, "Metal Organic Resin Derived Barium Titanate: I, Formation of Barium Titanium Oxycarbonate Intermediate," *Journal of the American Ceramic Society*, vol. 76, pp. 617-624, 1993.
- [239] M. Arima, M. Kakihana, Y. Nakamura, M. Yashima, and M. Yoshimura, "Polymerized Complex Route to Barium Titanate Powders using Barium-titanium mixed-metal Citric Acid Complex," *Journal of the American Ceramic Society*, vol. 79, pp. 2847-2856, 1996.
- [240] E. R. Leite, C. M. G. Sousa, E. Longo, and J. A. Varela, "Influence of Polymerization on the Synthesis of SrTiO₃: Part I. Characteristics of the Polymeric Precursors and Their Thermal Decomposition," *Ceramics International*, vol. 21, pp. 143-152, 1995.
- [241] D. Hennings and W. Mayr, "Thermal Decomposition of (BaTi) Citrates into Barium Titanate," *Journal of Solid State Chemistry*, vol. 26, pp. 329-338, 1978.
- [242] M. D. Carvalho, L. P. Ferreira, J. C. Waerenborgh, E. Tsipis, A. B. Lopes, and M. Godinho, "Structure and magnetic properties of Ca₂Fe_{1-x}Mn_xAlO_{5+δ}," *Journal of Solid State Chemistry*, vol. 181, pp. 2530-2541, 2008.
- [243] Y. Yang, Z. Cao, Y. Jiang, L. Liu, and Y. Sun, "Photoinduced Structural Transformation of SrFeO₃ and Ca₂Fe₂O₅ during Photodegradation of Methyl Orange," *Materials Science and Engineering B*, vol. 132, pp. 311-314, 2006.
- [244] S. Riaz, S. Shamaila, B. Khan, and S. Naseem, "Barium Titanate Films for Electronic Applications: Structural and Dielectric Properties," *Surface Review and Letters*, vol. 15, pp. 237-244, 2008.
- [245] B. J. Fang, C. L. Ding, Q. B. Du, and L. M. Zhou, "Effect of Oxide Doping on Electrical Properties of Tetragonal Perovskite Pb(Ni_{1/3}Nb_{2/3})O₃-PbTiO₃ Ferroelectric Ceramics," *Ferroelectrics*, vol. 393, pp. 94-105, 2009.
- [246] R. Genouel, C. Michel, N. Nguyen, M. Hervieu, and B. Raveau, "Ordered Substitution of Iron for Copper in the Tetragonal Perovskite La_{6.4}Sr_{1.6}Cu₈O₂₀," *Journal of Solid State Chemistry*, vol. 115, pp. 469-475, 1995.
- [247] D. Y. Lee, J.-Y. Park, K.-H. Lee, J.-H. Kang, Y.-J. Oh, and N.-I. Cho, "Synthesis and Characterization of Pb(Zr_{0.5}Ti_{0.5})O₃ Nanofibers," *Current Applied Physics*, vol. 11, pp. 1139-1143, 2011.

- [248] R. J. Lad and V. E. Henrich, "Structure of α -Fe₂O₃ Single Crystal Surfaces Following Ar⁺ Ion Bombardment and Annealing in O₂," *Surface Science*, vol. 193, pp. 81-93, 1988.
- [249] A. Bocquet, A. Fujimori, T. Mizokawa, T. Saitoh, H. Namatame, S. Suga, *et al.*, "Electronic structure of SrFe^{4+}O₃ and Related Fe Perovskite Oxides," *Physical Review B*, vol. 45, pp. 1561-1570, 1992.
- [250] T. Yamashita and P. Hayes, "Analysis of XPS spectra of Fe²⁺ and Fe³⁺ Ions in Oxide Materials," *Applied Surface Science*, vol. 254, pp. 2441-2449, 2008.
- [251] P. Mills and J. Sullivan, "A Study of the Core Level Electrons in Iron and its Three Oxides by Means of X-ray Photoelectron Spectroscopy," *Journal of Physics D: Applied Physics*, vol. 16, p. 723, 1983.
- [252] V. Young and T. Otagawa, "XPS Studies on Strontium Compounds," *Applications of Surface Science*, vol. 20, pp. 228-248, 1985.
- [253] R. Vasquez, "SrCO₃ by XPS," *Surface Science Spectra*, vol. 1, pp. 112-116, 1992.
- [254] M. Sosulnikov and Y. Teterin, "X-ray Photoelectron Studies of Ca, Sr and Ba and Their Oxides and Carbonates," *Journal of Electron Spectroscopy and Related Phenomena*, vol. 59, pp. 111-126, 1992.
- [255] B. Liu, Y. Zhang, and L. Tang, "X-ray Photoelectron Spectroscopic Studies of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} Cathode for Solid Oxide Fuel Cells," *International Journal of Hydrogen Energy*, vol. 34, pp. 435-439, 2009.
- [256] Y. Chen, W. Jung, Z. H. Cai, J. J. Kim, H. L. Tuller, and B. Yildiz, "Impact of Sr Segregation on the Electronic Structure and Oxygen Reduction Activity of SrTi_{1-x}Fe_xO₃ Surfaces," *Energy & Environmental Science*, vol. 5, pp. 7979-7988, 2012.
- [257] J. Jurado, F. Figueiredo, B. Gharbage, and J. Frade, "Electrochemical Permeability of Sr_{0.7}(Ti, Fe)O_{3- δ} Materials," *Solid State Ionics*, vol. 118, pp. 89-97, 1999.
- [258] V. Varadan, D. Ghodgaonkar, V. Varadan, J. Kelly, and P. Glikerdas, "Ceramic Phase Shifters for Electronically Steerable Antenna Systems," *Microwave Journal*, vol. 35, pp. 116-127, 1992.
- [259] A. Yan, V. Maragou, A. Arico, M. Cheng, and P. Tsiakaras, "Investigation of a Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} Based Cathode SOFC:: II. The effect of CO₂ on the Chemical Stability," *Applied Catalysis B: Environmental*, vol. 76, pp. 320-327, 2007.
- [260] R. Vasquez, "X-ray Photoelectron Spectroscopy Study of Sr and Ba Compounds," *Journal of Electron Spectroscopy and Related Phenomena*, vol. 56, pp. 217-240, 1991.
- [261] S. Petrovic, L. Karanovic, P. Stefanov, M. Zdujic, and A. Terlecki-Baricevic, "Catalytic Combustion of Methane over Pd Containing Perovskite Type Oxides," *Applied Catalysis B: Environmental*, vol. 58, pp. 133-141, 2005.
- [262] N. Batis, P. Delichere, and H. Batis, "Physicochemical and Catalytic Properties in Methane Combustion of La_{1-x}Ca_xMnO_{3-y} (0 ≤ x ≤ 1; -0.04 ≤ y ≤ 0.24) Perovskite-Type Oxide," *Applied Catalysis A: General*, vol. 282, pp. 173-180, 2005.
- [263] N. Merino, B. Barbero, P. Eloy, and L. Cadús, "La_{1-x}Ca_xCoO₃ Perovskite-type Oxides: Identification of the Surface Oxygen Species by XPS," *Applied Surface Science*, vol. 253, pp. 1489-1493, 2006.

- [264] D. Fino, N. Russo, E. Cauda, G. Saracco, and V. Specchia, "La-Li-Cr Perovskite Catalysts for Diesel Particulate Combustion," *Catalysis Today*, vol. 114, pp. 31-39, 2006.
- [265] S. J. Xiao, M. Textor, N. D. Spencer, M. Wieland, B. Keller, and H. Sigrist, "Immobilization of the Cell-adhesive Peptide Arg-Gly-Asp-Cys (RGDC) on Titanium Surfaces by Covalent Chemical Attachment," *Journal of Materials Science: Materials in Medicine*, vol. 8, pp. 867-872, 1997.
- [266] J. B. MacChesney, R. C. Sherwood, and J. F. Potter, "Electric and Magnetic Properties of the Strontium Ferrates," *The Journal of Chemical Physics*, vol. 43, pp. 1907 - 1913, 1965.
- [267] A. Mosset, I. Gautier-Luneau, and J. Galy, "Sol-gel Processed BaTiO₃: Structural Evolution from the Gel to the Crystalline Powder," *Journal of Non-Crystalline Solids*, vol. 100, pp. 339-344, 1988.
- [268] M. Viviani, M. T. Buscaglia, P. Nanni, R. Parodi, G. Gemme, and A. Dacca, "XPS Investigation of Surface Properties of Ba_(1-x)Sr_xTiO₃ Powders Prepared by Low Temperature Aqueous Synthesis," *Journal of the European Ceramic Society*, vol. 19, pp. 1047-1051, 1999.
- [269] R. Ayouchi, F. Martin, J. R. Ramos-Barrado, and D. Leinen, "Compositional, Structural and Electrical Characterization of Barium Titanate Thin Films Prepared on Fused Silica and Si(111) by Spray Pyrolysis," *Surface and Interface Analysis*, vol. 30, pp. 565-569, 2000.
- [270] S. Ferro, M. Dal Colle, and A. De Battisti, "Chemical Surface Characterization of Electrochemically and Thermally Oxidized Boron-doped Diamond Film Electrodes," *Carbon*, vol. 43, pp. 1191-1203, 2005.
- [271] S. Kundu, Y. Wang, W. Xia, and M. Muhler, "Thermal Stability and Reducibility of Oxygen-Containing Functional Groups on Multiwalled Carbon Nanotube Surfaces: A Quantitative High-Resolution XPS and TPD/TPR Study," *The Journal of Physical Chemistry C*, vol. 112, pp. 16869-16878, 2008.
- [272] C. Moreno-Castilla, M. V. López-Ramón, and F. Carrasco-Marín, "Changes in Surface Chemistry of Activated Carbons by Wet Oxidation," *Carbon*, vol. 38, pp. 1995-2001, 2000.
- [273] J. J. Tunney and M. L. Post, "The Electrical Conductance of SrFeO_{2.5+x} Thin Films," *Journal of Electroceramics*, vol. 5, pp. 63-69, 2000.
- [274] A. Fujimori, T. Mizokawa, T. Saitoh, and H. Namatame, "Electronic Structure of SrFe⁴⁺O₃ and Related Fe Perovskite Oxides," *Physical Review B*, vol. 45, pp. 1561-1570, 1992.
- [275] D. H. Kim, N. M. Aimon, L. Bi, G. F. Dionne, and C. A. Ross, "The Role of Deposition Conditions on the Structure and Magnetic Properties of SrTi_{1-x}Fe_xO₃ films," *Journal of Applied Physics*, vol. 111, 2012.
- [276] M. Post and J. Yao, "The Optical Transmission Properties of SrFeO_{2.5+x} Thin Films for Oxygen Sensing," presented at the The 8th International Conference on Solid-state Sensors and Actuators, Stockholm, Sweden, 1995.
- [277] K. Szot, M. Pawelczyk, J. Herion, C. Freiburg, J. Albers, R. Waser, *et al.*, "Nature of the Surface Layer in ABO₃-type Perovskites at Elevated Temperatures," *Applied Physics A: Materials Science & Processing*, vol. 62, p. 335, 1996.

- [278] W. Jung and H. L. Tuller, "Investigation of Surface Sr Segregation in Model Thin Film Solid Oxide Fuel Cell Perovskite Electrodes," *Energy & Environmental Science*, vol. 5, pp. 5370-5378, 2012.
- [279] T. Wu, G. Liu, J. Zhao, H. Hidaka, and N. Serpone, "Photoassisted Degradation of Dye Pollutants. V. Self-Photosensitized Oxidative Transformation of Rhodamine B under Visible Light Irradiation in Aqueous TiO₂ Dispersions," *J. Phys. Chem. B*, vol. 102, pp. 5845-5851, 1998.
- [280] X. Li and J. Ye, "Photocatalytic Degradation of Rhodamine B over Pb₃Nb₄O₁₃/Fumed SiO₂ Composite under Visible Light Irradiation," *J. Phys. Chem. C*, vol. 111, pp. 13109-13116, 2007.
- [281] T. Watanabe, T. Takizawa, and K. Honda, "Photocatalysis Through Excitation of Adsorbates. 1. Highly Efficient N-deethylation of Rhodamine B Adsorbed to Cadmium Sulfide," *J. Phys. Chem.*, vol. 81, pp. 1845-1851, 1977.
- [282] F. A. Kroger, *The Chemistry of Imperfect Crystals* vol. 3. Amsterdam: North-Holland, 1974.
- [283] F. J. Morin and J. R. Oliver, "Energy Levels of Iron and Aluminum in SrTiO₃," *Physical Review B*, vol. 8, pp. 5847-5854, 1973.
- [284] N. G. Eror and U. Balachandran, "High-Temperature Defect Structure of Acceptor-Doped Strontium Titanate," *Journal of the American Ceramic Society*, vol. 65, pp. 426-431, 1982.
- [285] R. A. Evarestov, S. Piskunov, E. A. Kotomin, and G. Borstel, "Single Impurities in Insulators: Ab-initio Study of Fe-doped SrTiO₃," *Physical Review B*, vol. 67, p. 064101, 2003.
- [286] A. Kudo, "Photocatalyst Materials for Water Splitting," *Catalysis Surveys from Asia*, vol. 7, pp. 31-38, 2003.
- [287] Y. Cong, J. L. Zhang, F. Chen, M. Anpo, and D. N. He, "Preparation, Photocatalytic Activity, and Mechanism of Nano-TiO₂ Co-doped with Nitrogen and Iron (III)," *Journal of Physical Chemistry C*, vol. 111, pp. 10618-10623, 2007.
- [288] H. M. Luo, T. Takata, Y. G. Lee, J. F. Zhao, K. Domen, and Y. S. Yan, "Photocatalytic Activity Enhancing for Titanium Dioxide by Co-doping with Bromine and Chlorine," *Chemistry of Materials*, vol. 16, pp. 846-849, 2004.
- [289] S. W. Kim, R. Khan, T. J. Kim, and W. J. Kim, "Synthesis, Characterization, and Application of Zr,S Co-doped TiO₂ as Visible-light Active Photocatalyst," *Bulletin of the Korean Chemical Society*, vol. 29, pp. 1217-1223, 2008.
- [290] Q. J. Xiang, J. G. Yu, and M. Jaroniec, "Nitrogen and Sulfur Co-doped TiO₂ Nanosheets with Exposed {001} Facets: Synthesis, Characterization and Visible-Light Photocatalytic Activity," *Physical Chemistry Chemical Physics*, vol. 13, pp. 4853-4861, 2011.