Photocatalytic properties of nanostructured $\text{SrTi}_{(1-x)}\text{Fe}_x\text{O}_{(3-\delta)}$

Mohammad Ghaffari

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**Photocatalytic Properties of
Nanostructured $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_{(3-\delta)}$**

MOHAMMAD GHAFARI

**School of Electrical and Electronic Engineering
2012**

Photocatalytic Properties of Nanostructured

Mohammad Ghaffari

School of Electrical and Electronic Engineering

Division of Microelectronic

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SUMMARY

Since 1972, titanium dioxide has been extensively investigated as a photocatalyst. Since the works of Fujishima and Honda on water-splitting using Titanium Dioxide (TiO_2) and platinum electrode, dubbed the Honda-Fujishima effect, TiO_2 has remained the major interest of researchers working in the field of photocatalyst. However, due to its large bandgap, pure TiO_2 absorption pattern is limited to the UV region. It means TiO_2 only absorbs UV light, which explains its inactivity under visible light. Thus, it is very crucial to create a visible light driven photocatalyst to increase the efficiency for solar energy or indoor light application. This study focuses on the various properties of $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_3$ nanoparticles. Different synthesis schemes were designed to produce new photocatalytic materials. Numerous techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electron microscopy both scanning (SEM) and transmission (TEM) were used for physical characterization. Photocatalytic properties were determined by the oxidation of methylene blue dye in water with results analyzed by high performance liquid chromatography (HPLC), and ultra violet – visible spectroscopy (UV-VIS).

The composition, morphology, structural, micro-structural, optical and photocatalytic properties of the novel materials were all studied. In this thesis, photocatalytic inactivation was investigated. For the purpose of materials design and improvement, the mechanism(s) of degradation during visible-light photocatalysis was also investigated.

The thesis research focuses on developing homogeneous $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_{3-\delta}$ photocatalysis with novel composition and structures to decrease and extend the

absorption band-edge of $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_{3-\delta}$ (STF_x ($x=0 \sim 1$)) into the visible-light region with improved stability, photocatalytic efficiency, and ease of the doping process.

The homogeneous $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_{3-\delta}$ (STF_x ($x=0 \sim 1$)) were successfully synthesized using three different methods, the high energy ball mill, wet chemical method and high temperature solid oxide reaction. They were being developed as new photocatalysts for desired features, including photo activity in a broad visible light range, enhanced photocatalytic performance.

The UPS (Ultra violet Photoelectron Spectroscopy (UPS) and X-ray Photoelectron Spectroscopy (XPS) studies were carried out and the analysis showed that the Sr ions were in 2+ oxidation state while the iron in STF_x perovskite structure participated in mixture of Fe^{3+} and Fe^{4+} ($\text{SrTi}_{(1-x)}[\text{Fe}^{3+}, \text{Fe}^{4+}]_{(x)}\text{O}_{(3-\delta)}$).

By using the X-ray absorption spectroscopy, the Fe(Ti) K-edge X-ray absorption fine structure spectra were recorded at room temperature to investigate the local structures of Fe replaced $\text{SrTi}_{(1-x)}\text{Fe}_x\text{O}_{(3-\delta)}$ ($0 \leq x \leq 1$). The local environment around Fe (Ti) centers and as well as the local distortion throughout the whole x series revealed by the X-ray absorption spectroscopy were explained in connection with the observed catalytic properties.

The band gap of STF_x material was successfully studied by UPS measurement, and the photo-voltage and photo-current study. The photo-voltage and photo-current results suggested that the conduction band position became more negative for STF_x by changing the x.

Finally, the photocatalyst performances were successfully carried out. The $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_{3-\delta}$ and STF_x materials showed convincing photocatalyst effects and high potential for use as visible light driven photocatalyst.

1 Introduction

1.1 Motivation

As reported by De Lasa [1], a photocatalytic reaction is a series of chemical events that follow the electron-hole pair (EHP) generation. The hole, h^+ is used for the oxidation process and the e^- is captured for the reduction process. A combination of redox processes lead to the formation of superoxide anions and hydrogen peroxide from oxygen. However, the EHP generation process is reversible, i.e. the recombination process. Recombination limits the efficiency of the photocatalytic process. Thus, electron and hole scavengers such as oxygen and water must be present to encourage EHP generation and prevent recombination [1].

Titanium dioxide, also named titania (TiO_2) has been extensively investigated as a photocatalyst. Since the works of Fujishima and Honda on water-splitting using Titanium Dioxide (TiO_2) and platinum electrode, dubbed the Honda-Fujishima effect in 1972 [2], TiO_2 has remained the major interest of researchers working in the field of photocatalyst. This is because TiO_2 is thermally stable, chemically and biologically inert, cheap and has the highest photocatalytic efficiency under UV light illumination. Also known as titanic anhydride, titanic acid anhydride, titanic oxide, or titania, its colour varies from white to gray, depending on the purity. In fact, the history of TiO_2 dates back to the ancient times where it was used as a source of white pigment in paints, paper, and cosmetics [2]. However, due to its large bandgap, pure TiO_2 absorption pattern is limited to the UV region which means TiO_2 only absorbs UV light. This explains its inactivity under visible light and has to be extended to the visible light region to increase the efficiency of this material for solar energy or indoor

light application. To address this requirement many studies were initially focused on doping titania with transition metals [3-5]. It was established that a metal dopant can be helpful depending on the type and concentrations of the metal. Generally, with increasing amount of a cation in TiO_2 , a shift of the absorption edge towards the visible light region is produced. However with the doping of the cation in TiO_2 , only segregation of M_2O_n occurred and due to agglomeration, the edge shifted to the visible range and no improvement in visible-light photoactivity was observed [5]. In some cases, the doping of certain transition metal ions into TiO_2 increased the potential of photo oxidation which was deleterious for photo oxidation [3]. More recently, research by doping with nitrogen [6-11], carbon [12, 13], sulphur [14, 15], phosphorus [16], or fluorine [17] in titania obtained visible-light activated photocatalysis. Among the nonmetallic dopants, most of the publications were devoted to the $\text{TiO}_{2-x}\text{N}_x$ materials. These anionic dopants showed good photocatalytic efficiency. With respect to the stability of the doped materials, $\text{TiO}_{2-x}\text{N}_x$ materials were found to be better than transition-metal dopants and moreover their preparation and doping process of were easier [18]. Nevertheless, a serious problem for the $\text{TiO}_{2-x}\text{N}_x$ materials and anion-doped TiO_2 is low quantum yield. The quantum yield of doped TiO_2 under visible-light irradiation is far lower than that of TiO_2 under UV irradiation. The quantum yield of undoped TiO_2 thin film reported by Miyauchi et al., was 18.5 under UV [19]. After annealing in NH_3 at 400 °C, the quantum yield of N-doped TiO_2 thin film was 15.4 under UV and 0.41 under the visible [18, 20, 21]. As early as 1980, the photocatalytic property of SrTiO_3 oxide was discovered [22-25]. Similar to TiO_2 , the doping of SrTiO_3 was investigated to move its absorption to the visible light range [25-27]. Another ferroelectric material, SrFeO_3 , was found to possess redox behavior

[28] and gas sensing properties [29-31]. In terms of bandgap energy, with increasing iron concentration, the bandgap reduced from 3.17 eV for SrTiO_3 to that of 1.80 eV for SrFeO_3 [32-34].

The aim of this study was to find solutions to this challenge. The general approach was to increase the photocatalytic efficiency by using $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_3$ (STF_x ($x=0 \sim 1$)) and SrFeO_3 as small band gap materials with good photocatalytic properties. Different synthesis schemes were designed to produce new photocatalytic materials. The composition, morphology, structural, micro-structural, optical and photocatalytic properties of the novel materials were all studied. In this study, photocatalytic inactivation was investigated. For the purpose of materials design and improvement, the mechanism(s) during visible-light photocatalysis was also investigated.

1.2 Objectives

This thesis research focuses on developing $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_{3-\delta}$ photocatalysis with novel composition and structures to decrease and extend the absorption band-edge of $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_{3-\delta}$ (STF_x ($x=0 \sim 1$)) into the visible-light region with improved stability, photocatalytic efficiency, and ease of the doping process. The Main objectives of this study are:

I. Synthesis and optimization of STF_x powder

Three different kinds of methods were adopted, namely ball milling, wet chemical and high temperature solid-state reaction. Initially, optimization of powder preparation was carried out to study the effects of different synthesis techniques and material compositions.

II. Study of physical, chemical, optical and photocatalytic properties

Different characterization techniques were applied to analyze the as prepared powders so as to develop an understanding of the relationship between synthesis, properties, and performance. The following characterization techniques were employed for the analysis of the samples:

- Physical : X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET) method
- Chemical : X-ray Photoelectron Spectroscopy (XPS)
- Band gap Study: Ultra violet Photoelectron Spectroscopy (UPS), X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS)
- Optical : UV-Vis Spectrometer
- Photocatalytic : Methylene Blue (MB)

III. Enhancement in photocatalytic properties

Based on the good attributes of a good photocatalyst, the performance of the powder was further enhanced by controlling the particle size. This provided the powder a large surface area for reaction.

IV. In-depth understanding of the mechanism for visible-light driven photocatalytic activities

Based on the characterization results, it was important to consolidate all observations to explain the photocatalytic performance of the STF_x ($x=0 \sim 1$). Reaction profiles were analyzed to understand the kinetics of reactions, and

thus, the underlying mechanism. This allowed a good understanding of the material and its photocatalytic performance.

1.3 Major contributions of the Thesis

The major contributions achieved in this research work are summarized as follows:

1. The $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_{3-\delta}$ (STF_x ($x=0\sim 1$)) were successfully synthesized with using three different methods; the high energy ball mill, wet chemical method and high temperature solid oxide reaction. The high temperature solid oxide method was chosen as the preparation method in this study because it provided materials with better thermal and chemical stability, the synthesis yielded high productivity and contained less amorphous content. The particle size, micro structure and band gap properties were characterized using XRD, SEM and TEM.
2. The STF_x ($x=0\sim 1$) were optimized and developed as new photocatalysts with desired features, including photo activity under the broad visible light range and enhanced photocatalytic performance.
3. The Ultra violet Photoelectron Spectroscopy (UPS) and X-ray Photoelectron Spectroscopy (XPS) studies have been performed to investigate the valance band and surface chemical of the STF_x material respectively. XPS results showed that Sr ions were in 2+ oxidation state and the existence of SrCO_3 on the surface of samples in addition to the $\text{SrO}_{(1-x)}$ for $\text{STF}_{x=1}$. Moreover, the analysis showed that iron in STF_x perovskite structure participated in mixture of Fe^{3+} and Fe^{4+} ($\text{SrTi}_{(1-x)}[\text{Fe}^{3+}, \text{Fe}^{4+}]_{(x)}\text{O}_{(3-\delta)}$). With increasing in iron dopant, the amount of Fe^{3+} and Fe^{4+} significantly increased. Oxygen vacancy was also

formed. Consequently, with increasing oxygen vacancy, the amount of oxygen lattice was reduced.

4. The local structure around Fe and Ti in the STF_x perovskite structure was investigated using the X-ray absorption spectroscopy. This analysis has provided useful local structural and electronic properties of the synthesized material. The coordination chemistry of iron (titanium) was of particular interest. Information about the valence state and charge transfer of iron (titanium) was obtained from the chemical shift of the absorption spectra. The pre-edge features of the X-ray absorption near edge structure (XANES) region were found related to the d-electron configuration and local symmetry of iron (titanium). The extended X-ray absorption fine structure (EXAFS) region was studied to probe the local geometric structures up to several coordination shells around iron (titanium) ions, where the Fe–O (Ti–O) distance was of interest in connection with the valence state of iron. In this work, the Fe(Ti) K-edge X-ray absorption fine structure spectra were recorded at room temperature to investigate the local structures of Fe replaced $\text{SrTi}_{(1-x)}\text{Fe}_x\text{O}_{(3-\delta)}$ ($0 \leq x \leq 1$). The local environment around Fe (Ti) centers as well as the local distortion throughout the whole x series revealed by the X-ray absorption spectroscopy were explained in connection with the observed catalytic properties.
5. A new photocatalyst reactor was successfully designed in collaboration with the department of Mechanical Engineering of University of Illinois at Urbana-Champaign. It was successfully used to compare the catalyst performances and measure the actual transport of light and species in photocatalytic systems. It served to address the difficulty in determining the quantum yield in

heterogeneous photocatalysis due to the scattering and reflection of light by dispersed catalyst in slurry reactors. It served also to find the efficiencies in different photocatalysts; the actual amount of absorbed light by the photocatalyst, and the created reactive excitation that reached the surface of the photocatalyst and caused the redox reaction in the degradation of pollutants.

6. The band gap of STF_x material was successfully studied by measuring the position of the valence band using the UPS measurement; together with the position of the conduction band carried out using the photo-voltage and photo-current study. The photo-voltage and photo-current results suggested that the conduction band position became more negative for STF_x .
7. One paper has been published in the high impact factor journal of Catalysis Today and one conference paper has been presented at the 6th European meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA6).

1.4 Organization of Thesis

This thesis is organized into the following 9 chapters:

In chapter 1, the motivations, objectives, main contributions, and organization of thesis are presented.

Chapter 2 is the literature review of topics related to this research project. The fundamental principles of redox reactions and photocatalytic reactions, and the history of TiO_2 as the forerunner material in this field are reviewed. Next, efforts done to improve its performance and its applications are discussed. The SrTiO_3 and $\text{SrFeO}_{3-\delta}$

are also reviewed. Related works and understanding of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ (STF_x) found in the literature are presented.

Chapter 3 explains the experimental setup used in this project, including the synthesis process of $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ (STF_x) powder, and characterizations using differential thermal and thermogravimetric analysis, X-ray diffraction, scanning electron microscopy, , UV-Vis spectrometer and XPS. For each characterization, fundamental knowledge governing its working principles is presented.

Chapter 4 presents the results and discussions on works done on $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$. In Chapter 5, the focus is on surface chemical study, X-Ray Photoelectron Spectroscopy (XPS) of the $\text{Sr}(\text{Ti}_{(1-x)}\text{Fe}_x)\text{O}_{3-\delta}$ powders.

Chapter 6 presents the Local structure study and investigation around Fe and Ti in $\text{SrTi}_{(1-x)}\text{Fe}_x\text{O}_{3-\delta}$ high temperature solid state reaction powders.

Chapter 7 and 8 detail the band gap study, conduction band measurement and photocatalysis properties and Methylene Blue degradation test of the $\text{Sr}(\text{Ti}_{(1-x)}\text{Fe}_x)\text{O}_{3-\delta}$ powders and present the relation between Fe doping and the changing the band gap of the material.

Lastly, Chapter 9 concludes the works done and recommendation for the future directions for this project.

2 Literature Review

2.1 Introduction

In the recent years, the process of destroying microorganisms, viruses and bacteria which is called Disinfection, was well studied. Disinfection process could be applied to various microorganisms such as bacteria, virus, protozoa, fungi, or cancerous cells found in air, water, surfaces and living organism. The main application of water disinfection is the protection of public health through the control of pathogens. The presence of microbiological contamination in the water caused waterborne diseases that lead to more than 12 million deaths per year worldwide. It was reported that 80% of all the diseases in the underdeveloped countries were because of water contaminations [35, 36].

Currently, there are three popular disinfection techniques: chlorination, ozonation, and Ultraviolet (UV) irradiation. These techniques are summarized in Table 2.1[37, 38].

Chlorine, as an oxidant, is effective in removing iron and manganese, and for destruction of taste and odor compounds. Gaseous chlorine is very dangerous for home applications. Although chlorine may prevent nitrates from being reduced to the toxic nitrite form, however, it will not remove the nitrates from water which is another disadvantage of the chlorination method. Ozonation and ultraviolet irradiation are good alternatives to chlorination.

Table 2.1 Comparison of common disinfection techniques [38].

Technique	Chlorination	Ozonation UV	UV irradiation
Primary user	Primary and secondary disinfectant; Residual effect	Odor control; Chemical oxidation; Primary disinfection but requires secondary disinfectant for residual effect	Primary physical disinfection; requires secondary chemical disinfectant for residual effect
Effectiveness	Effective against bacteria and viruses, but not effective against fungi or protozoa	Strongest disinfectant; effective against bacteria, viruses and protozoan cysts	Very effective against bacteria and viruses; Less effective against protozoa
By-product	Halogenated DBPs	Halogenated DBPs may be formed with bromide ion in raw water or chlorine in secondary disinfection; Other by products include organic acids and aldehydes	No known disinfection by-products formed
Advantages	Low cost; requires no energy to operate, easy to maintain	requires the most potent disinfectant, especially for resistant organisms such as viruses	Easy to install, operate and maintain; no chemical; no toxicity
Limitations	Requires periodic chemical addition; solid may jam and cause system to not work properly; Reduction of germicidal effect with elevated pH	High operation and maintenance cost. No residual effective. Ozone is toxic .	Requires low turbidity and low concentrations of iron, calcium, or phenols; Requires extremely high dosages for protozoa

Ozone is an unstable gas comprised of three oxygen atoms; it will readily degrade back to oxygen and, during this transition, a free oxygen atom, or free radical is formed. The free oxygen radical is highly reactive and short lived; under normal conditions it will only survive for milliseconds. Ozone is a colorless gas that has an odor similar to the smell of the air after a major thunderstorm. The ozonation process has the ability for destroying bacteria and other microorganisms. Moreover, ozonation is more effective against E.coli than chlorine. However, ozone is toxic and can be dangerous, and demands caution from users.

The ultraviolet irradiation method was found to be effective to inactivate waterborne pathogens. The main disadvantage associated with using UV disinfection is that there is no residual protection downstream as with the disinfection. Bacteria are only destroyed at one point in the water distribution system. Thus, to increase the outcome and efficiency of the UV process, the location of the light source is very important. Other variables that are important in UV disinfection are the water quality and the flow rate. If the water is too cloudy or dirty, the UV rays cannot properly penetrate through the water to kill the bacteria. Water turbidity decreases the disinfecting efficiency of the UV disinfection process. Thus, in the ultraviolet method proper pretreatment is necessary before the disinfection treatment. With respect to the flow rate, water will flow past the light source without enough time for UV exposure if the flow rate is too high. As a result, any disease-causing organisms that pass through the UV unit unharmed may cause dangers [39].

Photocatalyst is an environmental clean-up material that can remove organic compounds, such as odors and bacilli, under the influence of light. One of the earliest and most significant research works done in this field is the work of Fujishima, Honda

and coworkers. They demonstrated the photolysis of water molecules in a photo-electrochemical cell with a semiconductor electrode. This indicated that the water can be decomposed by near UV light without applying an external voltage [2, 40].

As suggested by the terms ‘photo’ and ‘catalyst’, a photocatalyst is defined as a substance that is activated by the absorption of a photon and acts as a catalyst to accelerate a reaction, itself remained unchanged and unconsumed [1, 41]. A good photocatalyst for cleaning and disinfection applications should have the following attributes:

1. Non-toxic
2. Good stability during the photocatalytic reaction
3. The ability to absorb as large as possible from the pattern of the irradiation source
4. High quantum yield and conversion efficiency
5. Low cost

2.2 Applications of Photocatalyst

One serious social problem that should not be neglected, and is growing around the world or in our daily lives, is environmental contamination. Some examples of such contamination can be listed as follows:

1. Processes in industrial and household wastes produce water pollution.
2. Air pollutants such as SO_x or NO_x can cause respiratory diseases.
3. Organic compounds appearing from newly developed building materials cause air contamination
4. Dioxin emerging from resin materials during incineration

One way to solve this problem is to use photocatalyst. Photocatalyst is a material that can gently harmonize the contaminated environment to restore original conditions by using natural energy which is a part of the environment and low-cost energy supply in our daily lives. The surface oxidation of the photocatalyst material eliminates harmful substances when it is exposed to the light of sun or fluorescent lamp.

By knowing this character and property of a photocatalyst, it can be used in various ways for purifying a contaminated environment. For examples, to eliminate organic compounds or bacteria, in water treatment and NO_x decomposition in the air, or room air purification [19].

The application of photocatalyst is generally divided into five major categories as follows (as shown in Figure 2.1):

1. Water treatment
2. Dirtiness prevention
3. Anti-bacteria
4. Deodorization
5. Purifying the air (NO_x decomposition)

The applications of photocatalyst are listed in Table 2.2 [42]. It shows that photocatalytic systems not only can convert unfailing light energy into chemical energy, but also can be used to restore safe environment that is mankind greatest wish and goal [43, 44].

Figure 2.1 Schematic of application of photocatalyst [45].

2.3 Photocatalytic Reaction

The photocatalytic activity is based on three stages as follows:

1) *Exposure to rays (UV or Visible light)*

With collision of the light (Ultraviolet or Visible rays) on the surface of the photocatalyst, the electron is excited to the conduction band. This will leave behind a positive hole at the valence band.

2) *OH radical appearance*

The positive hole has high tendency and power for oxidation and takes the electron from OH⁻(hydroxide ion) in water. With the loss of electron, the OH⁻ is transformed to OH radical, which is very unstable. At this time OH radical can reduce the pollutant by taking the electron from the pollutant.

3) *Decomposition of organic compounds*

The photo-excitation and de-excitation processes in the photocatalysis are illustrated in Figure 2.2. Moreover, the most relevant photochemical reactions during photocatalytic inactivation are listed in Equations (2.1) – (2.7) [44].

Figure 2.2 Reaction Schematic of photocatalysis at TiO_2 particle [19].

As shown, after the light irradiation, the TiO_2 particle can act as either an electron donor or acceptor for molecules in the surrounding media. It is important to prevent electron-hole recombination before a designated chemical reaction occurs on the TiO_2 surface. OH radical stabilizes its state by taking an electron (because the OH radical has strong oxidation power) from the adjacent organic compound. Thus the organic

compound loses its electron and decomposes and finally turns into carbon dioxide and water, and dissipate into the atmosphere.

Table 2.2 Selected applications of photocatalysis [46].

Property	Category	Application
Self-cleaning	Materials for residential and office buildings	Exterior tiles, kitchen and bathroom components, interior furnishings, plastic surfaces, aluminum sidings, building stone and curtains, paper window blinds
	Indoor and outdoor lamps and related systems	Translucent paper for indoor lamp covers, coatings on fluorescent lamps and highway tunnel lamp cover glass
	Material for roads	Tunnel wall, soundproofed wall, traffic signs and reflectors
	Others	Tent material, cloth for hospital garments and uniforms and spray coating for cars
Air cleaning	Indoor air cleaners	Room air cleaner, photocatalyst-equipped air conditioners and interior air cleaner for factories
	Outdoor air purifiers	Concrete for highways, roadways and footpaths, tunnel walls, soundproofed walls and building walls
Water purification	Drinking water	River water, ground water, lakes and water storage tanks
	Others	Fish feeding tanks, drainage water and industrial wastewater
Antitumor activity	Cancer therapy	Endoscopic-like instruments
Self-sterilizing	Hospital	Tiles to cover the floor and walls of operating rooms, silicone rubber for medical catheters and hospital garments and uniforms
	Others	Public restrooms, bathrooms and rat breeding rooms

The photocatalyst can be activated by light. There are various sources of light such as the sun, incandescent lamps, fluorescent lamps, light traps, disinfectant light, and so on. Those sources emit lights with different wavelengths necessary for their specific purposes. TiO_2 and SrTiO_3 , with the doping of some elements in the structure, are

semiconductors which turn to a high-energy state by receiving light energy, and release electrons from their illuminated surface. Semiconductors have two states. Initially, the location of the electrons are called 'valence band' and, if the energy received at this stage is high enough, electrons will jump up from the initial state 'valence band' to the final state so called 'conduction band'.

Thus, the energy that is needed for ejecting the electron from the conduction band to valence band is supplied by light, and also this light energy is coming from the energy of the light's wavelengths. For the calculation of the energy or wave length that is needed for the electrons, the following equation can be used.

$$E = h\nu \quad (2.8)$$

Where E , h , and ν are the energy, Plank's constant, and frequency respectively, and

$$\nu = c/\lambda \quad (2.9)$$

Where c is the light speed and λ is the wave length. Therefore

$$E = hc/\lambda \quad (2.10)$$

For example in the case of titanium dioxide, E is 3.2 eV ($3.2 \text{ eV} = 3.2 \times 1.6 \times 10^{-19} \text{ J}$), and also the other determinate values $c = 3.0 \times 10^8 \text{ m/s}$, $h = 6.63 \times 10^{-34} \text{ Js}$, hence the necessary excitation wavelength is approximately 380 nm. This value shows that the light needed to activate the photocatalyst, in this case (TiO_2), is ultraviolet light (Figure 2.3) [19].

Figure 2.3 Schematic of photocatalytic reaction [23].

The classification of photocatalytic reactions is generally based on two categories: “down-hill” and “up-hill” reactions. Breaking down the bonding in the material is known as degradation such as photo-oxidation of organic compounds using oxygen molecules and this reaction is a down-hill reaction. The reaction proceeds irreversibly. In the unalterable reaction, a photocatalyst acts as a trigger to produce $O_2^{\cdot-}$, $HO_2^{\cdot}$, $OH^{\cdot}$ and H^+ as active species for oxidation at the initial stage. This kind of reaction is shown in Figure 2.4 and is considered as a photoinduced reaction [47]. The application of this reaction is water splitting and in this application H_2 and O_2 are disassociated with a large positive change in the Gibbs free energy ($\Delta G^0 = 237 \text{ kJ/mol}$) and an up-hill reaction occurs. In this reaction, conversion of photon energy into chemical energy takes place (Figure 2.4), for example the photosynthesis of green plants. Therefore, this type of reaction is also called artificial photosynthesis.

Figure 2.4 Types of photocatalytic reactions [47].

The example of photocatalytic reaction in Figure 2.5 (in the case of water splitting) showed this principle. If the energy of the light incident on the catalyst is larger than the band gap, then electrons and holes are produced in the conduction and valence bands, respectively. The reduction reactions of photogenerated electrons and holes are very similar to electrolysis. Water molecules are oxidized by the holes to form O_2 and reduced by the electrons to form H_2 ; leading to overall water splitting. The value of the band gap and difference between the potentials of the conduction and valence bands are important factors for the semiconductor photocatalyst material. The reduction potential of the bottom level of the conduction band must be more negative than that of H^+/H_2 (0 V vs. NHE), while the oxidation potential of the top level of the valence band must be more positive than the oxidation potential O_2/H_2O (1.23 V) requirement. Other factors such as mobility, charge separation, and lifetime of photo generated electrons and holes also affect the photocatalytic process. These properties are shown in Figure 2.5. It shows the role of sacrificial reagents. By carrying out the photocatalytic reaction in aqueous solutions, which contain oxidizable reducing reagents such as alcohol

and SO_3^{-2} , photo generated holes irreversibly oxidize the reducing reagents instead of water.

Figure 2.5 Processes occurring in semiconductor photocatalyst under photo excitation [47].

Figure 2.6(a) shows the electron rich and H_2 evolution reaction and also in the presence of electron acceptors such as Ag^+ and Fe^{+3} ; the photo generated electrons in the conduction band are consumed by them and an O_2 evolution reaction is enhanced as shown in Figure 2.6(b) [47].

Figure 2.6 Photocatalytic H_2 or O_2 evolution in the presence of sacrificial reagents [47].

2.4 Photo-catalyst and their activities**2.4.1 Titanium Dioxide****2.4.1.1 Introduction**

Various semiconductor materials have been studied for their photocatalytic properties. TiO_2 has been always of great interest. This is mainly because of its unique properties of being inert, physically and chemically stable, non-toxic, inexpensive, and sensitive to UV light. Thus, TiO_2 has been the best candidate material. However, under visible light, TiO_2 displays almost no absorption, and hence, it is white. TiO_2 exists in the forms of anatase, rutile and brookite. Figure 2-7 and table 2-3 summarize the bulk properties of the three phases [48]. The two crystal phases of titanium dioxide that are commonly used in photocatalytic applications are rutile and anatase. Crystal system for the rutile and anatase structures of titanium dioxide are tetrahedral, differing in the number of atoms in the unit cell and the lattice constants a and c . Unit cell of rutile contains six atoms (Figure 2.7. a) and has lattice constants of $a = 4.593 \text{ \AA}$ and $c = 2.958 \text{ \AA}$ [49, 50], whereas the unit cell of anatase is surrounded by twelve atoms per unit cell (Figure 2.7. b) and has lattice constants of $a = 3.785 \text{ \AA}$ and $c = 9.511 \text{ \AA}$ [51]. Among these phases, anatase presents relatively greater photocatalytic activity and is used more frequently for photocatalytic oxidation reactions, while rutile is primarily used in pigments due to its light scattering properties [50]. Transformation temperatures of the amorphous-anatase-rutile phase depend on several variables such as: initial particle size [52-54], doping concentration [46, 55], original phase, [56, 57] and reaction atmosphere [58]. For room temperature bulk TiO_2 rutile is the most stable phase; however, the phase stability of nanoparticles depends on the particle size [50]. Zhang and Banfield [52] have shown that when particle size titania becomes less than

14 nm, anatase shows more stability than rutile. When the initial or raw material is amorphous, in bulk TiO_2 , first at a temperature between $400 - 450^\circ\text{C}$, the metastable anatase phase forms and then this anatase phase crystallizes into rutile at 700°C irreversibly. The generally recognized mechanism for the anatase-rutile transformation is the braking of the Ti-O bond in this transformation. This means that two Ti-O bonds in the anatase structure break and this process allows rearrangement of the Ti-O octahedral, which leads to a smaller volume and the formation of the rutile phase [59].

The dopant can affect the phase transformation process that this is related to the ionic radius of the dopant ion [60]. If the doping process leads to a stabilization of the rutile phase, then the activation energy of the transformation will be lowered. When a stabilization of the anatase phase occurs, the activation energy will be higher.

Figure 2.7 Crystal Structure of (a) rutile and (b) anatase phase of TiO_2 [50].

Table 2.3 Properties of bulk TiO_2 and its different phases.

Bulk TiO ₂						
<i>Atomic Radius</i> <i>(nm)</i>	O = 0.066 (Covalent)		Ti = 0.146 (Metallic)			
<i>Ionic Radius</i> <i>(nm)</i>	O (-2) = 0.14		Ti (+4) = 0.064			
Individual Phases						
<i>Crystal Structure</i>	<i>System</i>	<i>Density</i> <i>(kg/m³)</i>	<i>Lattice Constants (nm)</i>			
			<i>a</i>	<i>b</i>	<i>c</i>	<i>c/a</i>
Rutile	Tetragonal	4240	0.4584	-	0.2953	0.644
Anatase	Tetragonal	3830	0.3733	-	0.937	2.51
Brookite	Rhombohedral	4170	0.5436	0.9166	0.5135	0.944

2.4.1.2 History of TiO₂

In medical implants, public facilities and industrial pipelines the adhesion of bacteria onto the surfaces of numerous materials can lead to the formation of biofilms and the outbreak of infectious diseases [61]. Applying the antibacterial coatings to different types of surfaces can easily prevent harmful microorganisms from increasing and diminish such undesirable conditions [62]. Since the ancient times, TiO₂ has been employed as white pigment for cosmetic and industrial purposes. Earliest scientific works started in 1938, where TiO₂ was used to photo-bleach dyes under UV light, with and without oxygen [63]. Another group of researchers studied the autooxidation of TiO₂ under UV condition by dispersing the powder particles in alcohols and hydrocarbons [64]. However, active scientific research on TiO₂ was only triggered by the findings by Fujishima and Honda in 1972 [2].

Currently, the commercial photocatalyst used for such anti-bacterial application is the Titanium Dioxide (TiO_2). However TiO_2 works as photocatalyst only under ultraviolet light (UV) irradiation to form activated oxygen from water or oxygen in the air. The formed activated oxygen is strong enough to oxidize and decompose organic materials, smelly gas, and kill bacteria. The current research efforts aim at shifting the absorption edge and working wavelength of the photocatalyst to visible light to enhance their efficiency. The approach is to synthesize novel nano-structured high efficiency visible-light-driven photocatalyst for anti-bacterial application under visible light. The popular and well-developed TiO_2 will not be able to fulfill these dual purposes of high efficiency and bacteria killing effect under visible light. Its efficiency is poor as it requires the presence of UV light source that constitutes a maximum of 4 % of the total solar energy owing to its large band-gap of 3.2 eV. Also, its photocatalytic reaction rate under visible light is slower than the growth rate of the bacteria. In other words, the half-life cycle for TiO_2 is shorter than that for bacteria and hence will not be able to out-live the bacteria.

A study by the University of Arizona found [65] the typical worker's desk has hundreds times more bacteria per square inch than an office toilet seat. The message it carried is, "Bacteria affects our health and everyday life". This is especially so for people with weak immune systems, who often succumb to infections which sometimes can be fatal. Many research works were carried out with the objective of killing or reducing them to a harmless condition level. The use of photo-catalytic reaction to kill the bacteria has attracted worldwide attention since Fujishima & Honda had reported in Nature in 1972 [2]. Presently the most widely available anti-bacterial material is the popular and well-developed titanium oxide (TiO_2) photo-

catalyst [66]. A lot of research work carried out worldwide, so far, has been targeting the visible-light-driven photo-catalysts for deodorant, antifogging, and self-cleaning effects [67, 68]. However these available visible-light-driven photo-catalysts suffer poor photo-catalytic efficiency under visible light and hence are not suitable to be used for anti-bacterial applications. In order to qualify as anti-bacterial material under visible light, its photo-catalytic reaction rate under visible light must be faster than the growth rate of the bacteria in order to kill the bacteria.

2.4.1.3 Modified TiO₂ to shift Visible Light

TiO₂ has a wide bandgap as motioned earlier; only UV photons have enough energy to generate electron-hole-pairs for photocatalytic reactions. So many researchers attempted to change the bandgap and absorption edge towards the visible light using different kind of dopants (metallic and non-metallic base), to increase the quantum efficiency of the photocatalytic reactions.

The pattern of electromagnetic radiation striking the Earth's atmosphere is 100 to 10⁶ nanometer (nm). This can be divided into three main regions in increasing order of wavelengths; ultraviolet [24], visible and infrared [69] with energy distribution of approximately 3% UV, 47% visible light and 50% infrared light. UV light has the highest photon energy, and corresponds to the shorter wavelength (100-280 nm called UV_A, 280-315 nm called UV_B and 315-400 nm called UV_C). Although invisible to the human eye, UV light can cause changes in human skin colour, fading of fabric, and deterioration of plastic when exposed. Visible light has intermediate energy from 400 nm to 700 nm. Infrared, Infrared-A (700 nm to 1400 nm), Infrared-B (1400 nm to 3000 nm), Infrared-C (3000 nm to 1 mm), are responsible for the heat feeling from the sunlight. Figure 2.8 schematically shows the solar spectrums. This means that only

about 3~ 4 % of the solar spectrum can be utilized by pure TiO_2 . Hence, it is of great interest to develop photocatalysts that yield high reactivity under visible light that will allow the main part of the solar spectrum to be used to provide photocatalytic capability and therefore highly increase the efficiency of photocatalysts under sun light illumination.

Figure 2.8 Selected applications of photocatalysis [19].

A summary of the material or methods used for shifting the band edge of TiO_2 from the UV range toward visible light range is given as follows;

I. Doping with Non-Metals

As mentioned due to the large bandgap of TiO_2 , activity of titania is limited to the ultraviolet region. Thus, to overcome this limitation of TiO_2 and more effectively use the overall solar spectrum, non-metal elements are used to dope titania and modified the TiO_2 . In the literature, theoretical and experimental studies have shown that Boron(B), Carbon (C) , Nitrogen (N), Sulfur (S), Fluorine (F), Chlorine (Cl),

Bromine(Br), and Si doped in TiO_2 can result in a narrowing of the desired bandgap. Among these dopants, nitrogen is most widely-studied [14, 70-72]. Typically, there are three different methods for preparing the non-metal doped TiO_2 : wet chemistry, high temperature treatment, and ion implantation of TiO_2 nonmaterial. Among all observations, nitrogen-doped- TiO_2 has shown the best performance and result, whereas the substitutional doping produced an isolated, narrow band for a red shift of the absorption edge up to 540 nm. The doping of the non-metals also has some disadvantages; such as the narrowness of the energy band restricted hole mobility, that consequently affects the photocatalytic performance. The energy level should be broad enough for sufficient overlapping and integration with the O 2p energy band for efficient bandgap narrowing.

II. Small Bandgap Materials

Having small bandgap material is necessary for photocatalytic properties; however studies have shown that the small bandgap for such purpose is not enough. A few potential materials with small bandgaps have been studied. Table 2-4 compares the bandgap and corresponding radiation wavelength required for excitation [1]. The next most popular material after TiO_2 is ZnO. Other oxides do not show good photo activity although they have smaller bandgap. The chemical stability of the catalysts themselves during reactions is the main problem of the small bandgap materials. For example, in the photoelectrolysis of water using these materials as electrodes, the photogenerated holes will oxidize the catalysts themselves. Studies on ZnO have found that ZnO is unstable with respect to the incongruous dissolution. This forms Zn(OH)_2 on the ZnO particle surface, and prevents further photoactivity over time [73, 74].

Table 2.4 Bandgap energies of various materials studied as photocatalyst.

Semiconductor	Bandgap Energy (eV)	Wavelength (nm)
TiO₂ (rutile)	3.0	413
TiO₂ (anatase)	3.2	388
ZnO	3.2	388
ZnS	3.6	335
CdS	2.4	516
Fe₂O₃	2.3	539
WO₃	2.8	443

III. Doping with Transition Metals

One of the methods for shifting the optical absorption of TiO₂ from UV range to the visible spectral range is doping of TiO₂ with metal ions. Some researchers have used transition metals such as Chromium (Cr) [75], Iron (Fe) [76, 77], Copper, Cu [78] and Nickel (Ni) [79] to create local energy bands within the bandgap of the host semiconductor to shift the photocatalytic application from UV light to visible range. The energy gap from this local band to the conduction band edge lies in the visible light spectra. This idea is based on the theory 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 charge separation mechanism.

IV. Increasing Oxygen Vacancy and Surface Area

Some defects, such as oxygen vacancies in the lattice, act as electron scavengers [80, 81]. During preparation, such as using magnetron sputtering or ball mill or plasma treatment, oxygen vacancies are produced [82-84]. Since the photocatalytic reaction is kind of a surface reaction, the surface area of the photocatalyst is an important factor for increasing the efficiency and performance. Different preparation methods have been used to increase the surface area, particularly by using nano-sized TiO_2 powders [85, 86], or modified sol-gel method [87] or macroporous structured TiO_2 [88].

2.4.2 Strontium Titanate

Among the metal oxide photocatalyst, the perovskite-type has shown wide diversity of properties and consequently is very well-known. Figure 2.9 shows an ideal perovskite-type cubic structure of ABO_3 with the space group $Pm3m$. The coordination number of cation A is 12-fold and the B cation is 6-fold coordinated with the oxygen anions. The corner-sharing BO_6 octahedral form the skeleton of the structure in which the center position is occupied by the A cation. In perovskite structure compound, due to the susceptibility of partial substitution at both A and B sites, a wide range of cations and valences can be accommodated in this simple crystal structure, and so rendering perovskite to various and flexible chemical tailoring [89]. For example if the Cr cations are alternatively doped at the Sr^{2+} site rather than the Ti^{4+} site, different photophysical and photocatalytic properties might be obtained.

Strontium titanate (SrTiO_3) is a typical $\text{A}^{2+}\text{B}^{4+}\text{O}_3$ type perovskite and has been known as a photocatalyst capable of decomposing H_2O into H_2 and O_2 without applying an

external bias potential [90, 91]. To decrease the over voltage of H₂ evolution, surface modifications of SrTiO₃ with noble metals (e.g., Pt) or oxides (e.g., NiO_x) can be applied to prevent the recombination of photo induced electron/hole pairs produced during the reactions. The band gap of SrTiO₃ is 3.2 eV which is large and thus only reacts to UV light. To develop new visible-light driven photocatalyst the doping of foreign elements into such semiconductor with wide band gap can be made to introduce a new donor or acceptor level in the forbidden band to improve its absorption to visible light. For example chromium has been given much attention because the occupied Cr³⁺ level is usually about 2.2 eV lower than the conduction band bottom formed by Ti 3d (e.g.) or 1.0 eV higher than the valence band top formed by O_{2p} [24, 92].

One example proposed in this thesis for shifting the working wavelength from UV light to visible light is to use Sr(Ti_{1-x}Fe_x)O_{3-δ} (STF). This compound can be achieved with Fe substituting part of Ti in the B site of the ABO₃ perovskite structure of SrTiO₃ to form the solid solution of Sr(Ti, Fe)O₃ (STF) structure. This will change the optical band gap of the material accordingly and hence respond to light of wavelength closer to the visible light. By doing away with the UV light, the materials can be employed for many in-door applications where only the fluorescent light source is needed. The commercial potential can be significant and impactful.

Figure 2.9 Ideal ABO_3 perovskite structure. The BO_6 octahedron links through corners to form a three-dimensional cubic lattice, and the A cation is in the center of the cube [93].

To develop and produce new photocatalyst that works under visible light irradiation it is necessary to control the band structure as shown in Figure 2.10. For the photocatalyst to function in visible light, the band gap should be about 2.2-2.7 eV. In the case of TiO_2 the valence bands consist of O_{2p} orbitals and the potential of this valence band is significantly more positive than the oxidation potential of H_2O to O_2 ($E^\circ = 1.23$ eV). Hence, the potential for H_2 evolution inevitably needs to be wide in comparison to the band gap of oxide semiconductor photocatalyst. Therefore to make a narrow band gap, a valence band or an electron donor level has to be formed. The created levels should show two important characteristic. First, the created levels must dominate the thermo dynamical potential for oxidation of H_2O and second, possess the catalytic properties for the four-electron oxidation reaction. In summary, for the the evolution of visible light photocatalyst the following strategy can be observed:

(I) use doping method to introduce elements into the photocatalyst material with wide band gap, such as TiO_2 , to create a donor level over a valence band;

- (II) use elements to create a new valence band; and
- (III) create a solid solution of certain material to control the band structure.

Figure 2.10 Strategy of the development of photocatalyst with a visible light response [94].

SrTiO₃ was found to give sustained water conversion, while remaining indestructible itself. It was concluded that with external voltage applied, SrTiO₃ showed better current-voltage response and optical energy conversion efficiency than TiO₂ and SnO₂.

Figure 2.11 shows the energy band gap of some metal oxide. Except for TiO₂, SrTiO₃ and ZnO all other metal oxides do not satisfy the criteria as photocatalyst. With doping both the TiO₂ and SrTiO₃ can achieve lower band gap and higher efficiency for photocatalytic reaction.

In the metal oxide photocatalyst two big problems exist. One is that the edge of adsorption in the band gap is not in the visible light and another is that the time of charge carrier recombination is very short (about nanoseconds). To solve these issues two kinds of semiconductor materials with proper energy levels can be coupled together [95, 96]. By coupling two semiconductors together, the band gap can be

decreased and charge separation increased. Another method, which is similar to TiO_2 , is the doping of various transition and noble metals, and non-metals on SrTiO_3 to introduce the donor or acceptor level into the forbidden energy band. The doping of antimony or tantalum together with chromium into SrTiO_3 via solid-state reaction shifted the absorption to visible light region and H_2 evolution from aqueous methanol was observed [24, 92]. Table 2-5 summarizes the works and the maximum absorption wavelengths observed from diffuse reflectance measurement. Another candidate for the doping in SrTiO_3 structure is Fe_2O_3 . Fe_2O_3 and Fe have suitable adsorption edge for visible light due to a narrow energy band gap (2.2 eV). Furthermore, Fe_2O_3 is in abundance in the earth and its cost is relatively low, hence Fe_2O_3 is potentially good candidate for doping into SrTiO_3 .

Figure 2.11 Diagram depicting the redox potentials of valence and conduction bands and band-gap energies for various metal oxides estimated at pH 7. The redox potential positions of H^+/H_2 and $\text{OH}^-/\text{OH}^\cdot$ at pH 7 is also illustrated [97].

Table 2.5 Summary of SrTiO₃ doping's and optical/photocatalytic Properties

Dopants (* = Co-doped)	Maximum Absorption Wavelength	Photoactivity	Reference
*Antimony, Sb *Chromium, Cr	520 nm $\approx$ 2.4 eV	H ₂ evolution from aqueous methanol Incident light > 420 nm	[92]
*Tantalum, Ta *Chromium, Cr	700 nm $\approx$ 1.8 eV	H ₂ evolution from aqueous methanol Incident light > 440 nm	[24]
Rhodium, Rh	730 nm $\approx$ 1.7 eV	H ₂ evolution from aqueous methanol Incident light > 440 nm	[25]
*Nitrogen, N *Lanthanum, La	Broad shoulder above 500 nm	Acetone evolution from gaseous 2- propanol Incident light : (410-500 nm)	[26]
*Sulphur, S *Carbon, C	606 nm $\approx$ 2.05 eV	Acetone evolution from aqueous 2-propanol Incident light > 500 nm	[27]

2.4.3 Strontium Titanate Ferrite

In the search for new materials based on p-type semiconducting perovskites for gas sensing applications, sensors based on perovskite SrTi_{1-x}Fe_xO_{3-d} (STF_x, where x denotes the Fe content), were found to present higher catalytic activity than the n-type sensors [98]. Strontium Titanate Ferrite, Sr(Ti_{1-x}Fe_x)O_{3-δ}, is a continuous solid state solution between strontium ferrite, SrFeO₃ and strontium titanate, SrTiO₃. Figure 2.12 shows the cubic perovskite unit cell for SrTiO₃. In this structure, iron atoms can substitute titanium atom and due to the difference in their preferential oxidation states (+4 for Ti and +3 for Fe) therefore, the presence of oxygen vacancies in Sr(Ti_{1-x}Fe_x)O_{3-δ}, is obligatory to maintain charge balance in the system [99].

Figure 2.12 Unit cell of SrTiO_3 , exhibiting the cubic perovskite structure [45] .

Rothschild, et al. have simulated the effect of iron doped on the energy band structure of STF_x system [80] (Figure 2-13). SrTiO_3 has the maximum bandgap and with increasing of value of Fe dopant, the band gap decreases and SrFeO_3 has the minimum bandgap. The bandgap relation with x was proposed to follow the second order polynomial $E_g(x) = 3.26 - 1.93x + 0.54x^2$ eV, as shown in Figure 2-13 [33].

Figure 2.13 Bandgap of STF_x as a function of x . (■ = measured data, --- = fitted) [33].

The system exists as a single phase cubic structure at low iron concentration, whereby the lattice parameter, a_0 and bandgap, E_g decreases with increasing Fe. However, at higher iron concentrations, $x = 0.6$ and $x = 0.8$, a superstructure with lattice parameters $a' = 2a_0$, $b' = 2b_0$ and $c' = c_0$, where $a_0 = b_0 = c_0$, are the lattice parameters of ordinary perovskite; was observed by TEM [100]. The changes in these values are shown in Table 2-6 [100, 101].

As mentioned, STF_x exhibits good gas sensor properties, the semi-conducting compound in the $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ system is sensitive to traces of hydrocarbon gases in the surrounding atmosphere. These non-stoichiometric oxides which exhibit p-type conducting behavior at elevated temperatures and under oxidizing conditions are novel materials for application as resistive hydrocarbon gas sensors. Figure 2.14 shows the temperature coefficient of resistance for the system as a function of composition, oxygen partial pressure and temperature. The conductivity curve of STF_x at different value of partial pressure shows that STF_x functions as different type of semiconductor. At low oxygen partial pressure, the material is an n-type semiconductor. Dominant carrier at high oxygen partial pressure is hole and finally, at the intermediate oxygen partial pressure, it is an ionic conductor. Figure 2.14.(a) explains that with increasing the iron concentration the conductivity increases. This is due to the acceptor role of the iron, decreased bandgap and the decreased activation energy for defects mobility, allowing more carriers to be generated and ease of ionic flow. It is most remarkable to observe the conductivity at $x = 0.35$, whereby the conductivity of STF_x at high oxygen partial pressure coalesce to the same value. This mean the sensor is independent to temperature fluctuation at this composition and

oxygen concentration. This observation has promoted STF_x as a potential candidate to replace zirconia for lean engine sensor [33, 102].

Figure 2.14 Conductivity isotherms of STF_x at different (a) x values and (b) operating temperatures [102].

In STF_x the inherent non-stoichiometry leads to this system having a strong sensitivity to partial oxygen pressure and for this reason is used as an oxygen sensor. There are also reports about the substitution of Fe with Ti site to stabilizing the perovskite structure with short-range ordering of oxygen vacancy about the random Fe substituted site [100, 103-105] as compared to the long-range ordering observed in SrFeO_3 [100, 101].

Rothschild et al simulated bandgap of STF_x and proposed energy band equation of this compound, and the energy diagram were illustrated in Figure 2-15 as opposed to oxygen partial pressure in the x-axis.

Table 2.6 Changes of lattice parameter (a_0), Occupancy vacancy (y), bandgap (E_g) and enthalpy of annihilation of oxygen vacancy, ΔH_a as a function of x in $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-y}$.

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 Fermi energy level, E_F decreases with increase oxygen pressure. The Fermi energy level, E_F decreases with increase oxygen pressure. With increasing iron concentration, the acceptor level ($\text{Fe}^{+3}/\text{Fe}^{+4}$) broadens, effectively narrowing the bandgap and moving the Fermi level closer to the valence band [102].

Figure 2.15 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 [106].

2.4.4 Strontium Ferrite ($\text{SrFeO}_{3-\delta}$ or $\text{SrFeO}_{2.5+x}$)

One of ferromagnetic material is strontium ferrite which is inherently non-stoichiometric. It is hard to achieve stoichiometric SrFeO_3 because iron participates in the compound and reaction with oxidation state of +2 or +3 iron. In order to maintain charge balance, oxygen deficiency is formed and the structure becomes non-stoichiometric. $\text{SrFeO}_{3-\delta}$ shows suitable properties for practical use in ion transport membranes.

Many studies have been done to understand the structural characteristics of SrFeO_3 because of its interesting order-disorder transition and extremely high oxygen deficiency [107-110] in addition. The non-stoichiometry (δ) and phase behavior of bulk SrFeO_3 at $10^{-5} \leq p\text{O}_2 \leq 1$ atm were reported at elevated temperature [111]. $\text{SrFeO}_{3-\delta}$ at higher temperature has a disordered cubic perovskite structure, irrespective of the oxygen deficiency (δ). Nevertheless, undergoes phase transitions on lowering the temperature SrFeO_3 , disordered cubic perovskite due to the high vacancy concentration transform to vacancy-ordered phases. Depending on the oxygen partial pressure during fabrication and temperatures, four different ordered phases were formed [112-114]; $\text{SrFeO}_{2.5}$ with the orthorhombic brownmillerite (BR, $x = 0$) structure, $\text{SrFeO}_{2.75}$ and $\text{SrFeO}_{2.875}$ with orthorhombic-perovskite (OP, $x = 0.23$) and tetragonal-perovskite (TP, $x = 0.36$), respectively and cubic distorted perovskite (CP, $x = 0.4-0.5$) structures. The stability of each of these three phases were in a very narrow composition region with two-phase regions between them. A phase diagram of temperature vs δ was reported by Takeda et al. [113], and is shown in Figure 2-16. Cubic perovskite structure can be obtained by processing at high oxygen partial pressure and lower temperature. Also, depending on the composition, the vacancy

disordered BR, OP and TP can transform to the vacancy disordered CP structure at different temperatures.

The Fe^{3+} ions in brownmillerite $\text{SrFeO}_{2.5}$ occupy both distorted octahedral (O_h) and tetrahedral (T_d) sites equally, and the ordered $\text{SrFeO}_{2.75}$ and $\text{SrFeO}_{2.875}$ consist of 6-coordinated O_h and 5-coordinated square pyramidal iron atoms [101, 109, 115].

$\text{SrFeO}_{3-\delta}$ also has shown oxygen sensors properties; its conductivity has been studied as a function of oxygen vacancy. At high temperature (700-950 °C) and high oxygen partial pressure ($p_{\text{O}_2} > 10^{-4}$ atm), it is a mixed conductor with both oxygen vacancy and electron-hole as the carrier. The electron-hole conduction in the brownmillerite structure is governed by the band gap of approximately 2.0 eV (Figure 2-17) [32].

The brownmillerite-like compound $\text{Sr}_2\text{Fe}_2\text{O}_5$, which has a perovskite structure with the oxygen vacancies randomly distributed, showed remarkable nitrogen oxide (NO) decomposition to N_2 and O_2 at 700-900 °C. This results highlighted the importance of oxygen vacancies and their random ordering for efficient decomposition [116].

Figure 2.16 Phase diagram of $\text{SrFeO}_{2.5+x}$, $0 \leq x \leq 0.5$ [113]

Figure 2.17 Density of states, $N(E)$ for $\text{SrFeO}_{2.5+\delta}$ as δ changes from 0 to 0.5 and oxygen vacancy increases [32].

2.4.5 Applications and Recent Works on $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$

Recently, some applications for STF_x have been reported in electrical resistance of porous thick films [117], polycrystalline thin films [117, 118], oxygen sensors [101, 119], hydrocarbon sensors [117], fuel cells [101, 120], oxygen separation membranes [115] and phase shifters in communication system [121]. However, most recent works mainly focus on oxygen and ionic conductions applications. Table 2.7 summarizes a few recent works on $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$.

Table 2.7 Recent works on STF_x and their significance.

<i>Year</i>	<i>Preparation Method</i>	<i>Findings/Significance</i>	<i>Reference</i>
2007	High temperature solid state reactions <ul style="list-style-type: none">• Micro-scaled powder, screen-printed thick films Wet chemical <ul style="list-style-type: none">• Sol-precipitated nano-powder, screen printed thick films	<ul style="list-style-type: none">○ Novel modeling approach for p-type sensors towards reducing gas○ Bulk reactions, instead of redox reactions on surface are used to explain the sensitivity of the sensor at intermediate temperature○ Study of the effects of film thickness	[122]

2007	<p>Wet chemical</p> <ul style="list-style-type: none"> • Sol-precipitated nano-powder, screen-printed thick films • Electrospun thin films • Electrospray thin films 	<ul style="list-style-type: none"> ○ Enhanced surface-to-volume ratio ○ Increased selectivity for hydrocarbon sensing, e.g. propane ○ Modeling of functionality of p-type STF_x sensor 	[123]
2006	<p>High temperature solid state reactions</p> <ul style="list-style-type: none"> • Oxide powder 	<ul style="list-style-type: none"> ○ Proposed electronic structure, defect chemistry and transport properties 	[33]
2006	<p>High temperature solid state reactions</p> <ul style="list-style-type: none"> • Micro-scaled powder, screen-printed thick films • Pellet, pulsed-laser deposited thin films 	<ul style="list-style-type: none"> ○ Effects of Pt, Au, and zeolite cover layer for gas sensor electrodes on the selectivity and sensitivity to hydrocarbons 	[98]
2006	<p>High temperature solid state reactions</p> <ul style="list-style-type: none"> • Oxide powder 	<ul style="list-style-type: none"> ○ Mixed ionic conductivity at high temperatures ○ Type of conductor (electron, hole, or oxygen vacancy, interstitial) dependent on partial oxygen pressure ○ Study the effects of concentration on crystal, electronics and defect structures, as well as transport properties 	[33]
2005	<p>High temperature solid state reactions</p>	<ul style="list-style-type: none"> ○ Systematic analysis of TCR with composition 	[114]

	<ul style="list-style-type: none"> • Oxide powder 	<ul style="list-style-type: none"> ○ Correlate with decreasing bandgap ○ Zero TCR at $x = 0.35$ ○ Proposed band diagram 	
2005	Pulsed laser deposition <ul style="list-style-type: none"> • Thin films 	<ul style="list-style-type: none"> ○ MgO is suitable as substrate for thin film, as compared to sapphire, where interfacial reaction can occur at high temperature ○ Depletion of Fe and Sr ions at interface for both substrates ○ Conductivity one order of magnitude lower than that of bulk powder 	[124]
2003	High temperature solid state reactions <ul style="list-style-type: none"> • Screen-printed thick films on electrodes 	<ul style="list-style-type: none"> ○ Tackled the sensor device fabrication from powder to thick film for applications in real exhaust engine ○ Introduced a sulphur absorber film to enhance sensor stability towards sulphur compounds commonly found in actual exhaust engine 	[125]
2000	High temperature solid state reactions <ul style="list-style-type: none"> • Pressed and sintered compact 	<ul style="list-style-type: none"> ○ Doping of acceptor and donor to manipulate the oxygen partial pressure range for temperature-independent sensing ○ Acceptor (Ga) lowers the range ○ Donor (La) increases the range ○ Co-doping extends the whole range 	[126]

3 Experimental

3.1 Synthesis of STF_x powder

In this section three approaches were used for the synthesis of STF_x.

a) Approach 1: Mechanical alloying Ball Milling

Mechanical alloying (MA) is a kind of solid-state powder processing technique concluding repeated welding, fracturing, and re-welding of powder particles by high energy collision from the balls in a high-energy ball mill. This process is the innovation of Benjamin thirty years ago [127, 128]. In the beginning, mechanical alloying was developed to produce oxide-dispersion strengthened (ODS) nickel- and iron-base super alloys for applications in the aerospace industry, MA has now attracted much attention and inspired research interest because of its promising results, wide possible application and potential scientific values. MA has an ability of synthesizing a diversity of equilibrium and non-equilibrium alloy phases starting from blended elemental or pre-alloyed powders. The non-equilibrium phases synthesized include supersaturated solid solutions, metastable crystalline and quasi-crystalline phases, nanostructures, and amorphous alloys [129]. Mechanical alloying has been applied to many different material systems and utilized in different fields of material processing.

A ball milling machine, a type of grinder, is a cylindrical device used to grind (or mix) materials like ores, chemicals, ceramic raw materials and paints. Ball mills system includes a turn disc and some bowls that the turn disc rotates in one certain direction around a horizontal axis, and bowls rotate in the opposite direction. The rotation of bowls around its axes produces a centrifugal force that is applied to the raw material

and milling balls in the bowls. Different materials are used for media, including ceramic balls, flint pebbles and stainless steel balls. The raw material welded, fractured, and re-welded under high-energy collision. Figure 3.1 presents working principle of the ball milling technique.

Figure 3.1 Schematic of working principle of ball milling technique [128].

The mechanical alloying can be done by using different apparatus, namely, attritor, planetary mill and horizontal mill. The principal mechanism for all techniques are the same as planetary mill which could be done with a small amount of raw materials. Hence the system is suitable for research in laboratory and most people reported the use of this method.

There are many types of grinding media suitable for use in a ball mill, each material having its own specific properties and advantages. Common in some applications are

stainless steel balls. While usually very effective, due to their high density and low contamination of the material being processed, stainless steel balls are unsuitable for some applications.

Ball milling has its advantages in terms of composition requirements, particle size and more importantly, although the process results in fracturing and deformation of the particles, there is no change in proportion of the materials along the way.

The equipment includes 2 to 4 milling vials and balls with ranging size and density. The vials are placed on a disc, where the disc and vials rotate in opposite directions. The balls are placed inside the vials to 'mix' the particles. There are 4 stages of the milling process. In the initial stage, collision between the balls and the particles change the shape of the particles. In the intermediate stage, fracturing of the particles occur. In the final stage, a refined and homogeneous alloy is formed and in the completion stage, a deformed metastable structure is formed [129].

99.9% pure SrCO_3 , TiO_2 and Fe_2O_3 powders produced by Aldrich were used as raw materials for the synthesis of ball mill STF using the high energy ball-milling process. The tungsten carbide vials (volume of 250 ml) and balls (inner diameters of 10 mm and 20 mm) with relatively high density of 14.75 g/cm^3 were used for the high energy ball-milling process to increase the impact energy. The milling speed was set at 200 rpm and the balls-to-powder weight ratio was kept as 20:1. The milling was carried out using the planetary ball mill (Fritsch Pulverisette 5) in 30-minute cycles with 25 minutes of milling followed by 5 minutes of pause to prevent overheating of the milling machine from prolonged milling.

In this research to decrease the particle size of high temperature solid state reaction STF_x , the Spex milling/mixer was used. The Spex shaker mill is a vibratory mill; its

vial is agitated at high frequency in a complex cycle that involves motion in three orthogonal directions. The reciprocating velocity of the vial in the Spex 8000 series shaker mill is directly proportional to the motor's rotational speed. Under various loading conditions, the rotational speed of the actuator input shaft was measured with a stroboscope. The nominal rotational speed was 1054 rpm, which translated to an oscillation frequency of 17.6 Hz. The vial speed was not varied in the present examples, but it offers additional means of control over the milling process as the vial speed directly influences the impact velocity and frequency of collisions, and hence the energy transferred to the powder from the plastic deformation. Steel milling vials and balls were used in this and the remaining examples [129].

b) Approach 2: Wet Chemical method

A sol-gel combustion technique was used for the preparation of SrFeO_3 powder. This is a novel way with a unique combination of the chemical sol-gel process and the combustion process based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and some organic fuel, giving a voluminous and fluffy product with large surface area. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and citric acid were used as starting materials. Appropriate amounts of ferric nitrate (Aldrich, $\geq 98\%$), strontium nitrate (Aldrich, $\geq 99\%$) and citric acid (Aldrich, $\geq 99.5\%$) powders were dissolved into distilled water. Then the sol was heated on a hot plate with continuous stirring to evaporate the water. The sol was heated on a plate at 90°C and converted to a gel and the heating was continued until the combustion took place automatically. The combustion product was then calcined at 900°C for 4 hrs [93, 130-134].

c) Approach 3: High Temperature Solid State reaction method,

The conventional method of producing STF is a solid-state reaction. This process is based on the diffusion of atoms at elevated temperatures in a high temperature furnace.

High temperature STF powder was produced in four steps:

- 1- 99.9% pure SrCO_3 , TiO_2 and Fe_2O_3 powders (produced by Aldrich) were mixed in an agate mortar.
- 2- The mixture was calcinated at 1200 °C for 24 hours.
- 3- The calcinated powder was furnace cooled to room temperature and ground again in agate mortar.
- 4- Grinded powder was backed again at 1200 °C for 24 hours and furnace cooled to room temperature.

Table 3.1 presents the yield of the products by different methods listed in Table 1.

Table 3.1 The yield of the products by different methods.

Preparation Method	Initial powders (gr)	Final products (gr)	Yield of the products (%)
Wet chemical	25	10	40
High energy ball mill	40	15	33
High temperature solid oxide reaction	55	50	90

3.2 Characterization**3.2.1 Phase detection**

For the crystal structure determination, estimation of crystallite size and calculating the proportion of each phase present, X-ray diffraction techniques are widely used. The X-ray diffraction (XRD) pattern of a pure substance is, therefore, like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. To determine the interplanar spacing of the unknown materials, typically monochromatic x-rays are used. The samples are analyzed as powders with grains in random orientations to insure that all crystallographic directions are "sampled" by the beam. When the Bragg conditions for constructive interference are obtained, a "reflection" is produced, and the relative peak height is generally proportional to the number of grains in a preferred orientation [135].

To determine the crystal size and structure of nanoparticles, XRD is amongst the most commonly used techniques. Bragg's Law (Equation 3.1) states that when a monochromatic X-ray beam with wavelength λ is projected onto a crystalline material with atomic spacing d at an angle θ , diffraction occurs when the distance traveled by the rays reflected from successive planes differs by a complete number n , of wavelengths.

$$n\lambda = 2d\sin\theta \quad (3.1)$$

Hence, by using x-ray, with a known wavelength, and measuring θ , the Bragg's law can determine the d-spacing of any crystal, crystallographic orientations in the material and the size of the crystals as shown in Figure 3.2. Plotting the positions and intensities of the diffracted peaks produces a pattern, which is characteristic of the

sample. Where a mixture of different phases is present, the resultant diffractogram is formed by addition of the individual patterns.

Referring to the Figure 3.2, consider an X-ray source incident onto two atoms of a crystal plane with crystals d -spacing apart. The incident angle = θ and rays are diffracted at two different planes with the plane spacing, d ; a phase difference is created between the two diffracted beams (1' and 2'). The rays are scattered in all directions unless two particular directions are completely in phase.

The path difference for ray diffracted by the second crystal plane with reference to the first diffracted ray, is $AB + BC = 2d\sin \theta$ which equates to the number of wavelength in the path difference. In equation 3.1 for certain value of d and λ , there are several angle θ at which diffraction may occur and n indicates the order of reflection [135].

Figure 3.2 Bragg diffraction in a crystal with spacing " d " [136].

For crystallites less than 100 nm in size, appreciable broadening in the diffraction peaks occurs. This broadening can be used to estimate the average particle size by use of the Scherer's equation (Equation 3.2).

$$D \approx (0.9\lambda)/(\beta \cos\theta) \quad (3.2)$$

Where D is the mean particle size, β is the full width at half maximum of the peak (peak broadening), λ is the wavelength of the X-ray and θ is the diffraction angle.

In this study, the Shimadzu diffractometer that uses $\text{CuK}\alpha$ ($\lambda=1.5405\text{\AA}$) radiation equipped with a pyrolytic graphite monochromator was used. For all measurements performed, the step size and scan rate have been kept constant at 0.05° and 1°min^{-1} , respectively. Data were collected in the range $10^\circ \leq 2\theta \leq 110^\circ$. Peak profile for the XRD data were fitted with the program TOPAS. Samples were prepared by pressing the as-prepared powders into the window of a standard glass powder sample holder which were then placed vertically in the path of the X-ray beam.

3.2.1.1 Rietveld refinements

The Rietveld refinements of the XRD data for STF_x powders, were carried out using perovskite structure (symmetry space group: $\text{Pm}\bar{3}\text{-m}$) and 91062-ICSD standard card number to compute the crystallite size, lattice parameter, strain and oxygen vacancy. Rietveld Analysis is a qualitative/quantitative method of analyzing the whole diffraction patterns for X-ray or neutron powder diffraction. In Rietveld method a single-number integrated intensity I_{obs} is replaced (i.e. spread out) by a peak with heights y_i along the points of a step scan in 2-theta . The R-bragg values for the different phases by Rietveld refinement are below 10; which

are considered as quite authentic values for the existence of the respective mentioned phases. The R values are useful indicators for the evaluation of a refinement, especially in the case of small improvements to the model, but they should not be overly interpreted [137].

3.2.2 Microstructure study

Electron microscopy, both Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM), is an excellent fundamental technique to obtain a clear picture of the properties of nanomaterial. XRD provides useful information about the crystallinity, particle size and different phases in a sample; however for information on the shape, separation, agglomeration and elemental composition of the particles, electron microscopes are very useful. The difference between optical microscopes and electron microscopes is the image source. Electron microscopes work using the same principles as optical microscopes except that they apply focused electron beam to image the specimen instead of visible light. There are three steps involved for producing TEM images:

1. The production and acceleration of an electron beam.
2. Focusing of the electron beam using metal apertures and magnetic lenses into a thin focused monochromatic beam.
3. Transforming the interactions of the e-beam with the specimen into an image.

The interaction of an electron beam with the specimen results in elastic and inelastic scattering of electrons leading to generation of [138]:

1. Back scattered electrons that are used for elemental analyses.
2. Secondary electrons that are exploited for topographical imaging.
3. Auger electrons and X-rays that are used for surface compositional analysis.

For both SEM and TEM there are two methods for generating the electron beam. The first method is to pump enough thermal energy into them so that they are driven off (thermionic emission); the second method is to put them in a strong enough electric field so that any of them that stray too far will be pulled off (field emission). Figure 3.3 shows the principle features of both light and electron microscopes.

3.2.2.1 Scanning Electron Microscopy

In a typical SEM the energy ranging of electron beam is 100-100,000 eV. Electron beam is focused by one or two condenser lenses and passes through scanning coils or deflector plates which deflect the beam horizontally and vertically so that it scans in a faster fashion over a rectangular area of the sample. The interaction between the electron beam and the sample results in the emission of electrons (backscattered and secondary) and X-rays, which are detected and used to produce an image. The most common imaging is secondary electrons, this mode monitors low energy (<50 eV). The electrons are detected by a scintillator-photomultiplier and the resulting signal is rendered into a two-dimensional intensity distribution that can be viewed and saved as a digital image. With increasing the incidence angle of the electron beam, the escape distance of one side of the beam will emit less secondary electrons. Thus, steep surfaces and edges will be brighter than flat surfaces resulting in images with a well-defined, three dimensional appearance. A Jeol JSM-6340 Microscope was used to study the surface morphology of the powders samples in this thesis.

Figure 3.3 Principle features of light and electron microscopes [69].

3.2.2.2 Transmission Electron Microscopy

In Transmission Electron Microscopy (TEM) the sample interacts with the electron beam generally by diffraction rather than absorption, moreover the intensity of the transmitted beam is still affected by the volume and density of the material through which it passes. The orientation of the planes of atoms in a crystal, relative to the electron beam, can also affect the intensity of the diffraction. At certain angles the electron beam is diffracted strongly from the axis of the incoming beam, while at other angles the beam is largely transmitted. A high contrast image can therefore be formed by blocking electrons reflected away from the optical axis of the microscope and by placing the aperture to allow only un-scattered electrons through. This produces a variation in the electron intensity that reveals information on the crystal structure and can be viewed on a fluorescent screen, or recorded on photographic film or captured electronically [138, 139].

It is also possible to produce an image from electrons deflected by a particular crystal plane. Since the wavelength of electron beam is only a fraction of a nanometer and the

spacing between atoms in a solid is only slightly larger, the atoms act as a diffraction grating to the electrons resulting in some fraction of the electrons being scattered at particular angles, which are determined by the crystal structure of the sample, while others continue to pass through the sample without deflection. The ensuing image on the TEM screen will be a series of spots with each spot corresponding to a satisfied diffraction condition of the sample crystal structure, the selected area diffraction (SAD) pattern. As a diffraction technique, SAD can be used to identify crystal structures and examine crystal defects [138, 139]. In this project the particle size and shape were evaluated by transmission electron microscopy (Jeol JEM-2000EX).

3.2.3 Optical Study

Ultraviolet–visible spectroscopy refers to absorption spectroscopy in the range of ultraviolet-visible spectrum. The principle of this equipment is based on adsorption or transmission of light by sample; it means the intensity of light measured after passing through a sample (I), and by comparing I with the intensity of light before it passes through the sample (I_0) the absorption of the sample can be observed. The ratio I / I_0 is called the transmittance, and is usually expressed as a percentage (%T) (equation 3.4). The wavelengths can be varied from the UV light to visible range. Typically, a reference sample is used which has little or no absorption in this wavelength range. Once the energy of the light beam goes beyond the bandgap of the material, a large absorption will occur. This provides a rough indication of the bandgap of a material.

3.2.4 Surface Chemical Study and X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a non-destructive technique that measures the surface chemistry of material. This qualitative surface analysis technique is used to determine the chemical and electronic state of the surface of a material. When exposing a material under X-ray irradiation in high vacuum ($\leq 10^{-8}$ torr), emission of core level electrons from the surface occurs as shown in Figure 3.4 XPS only can detect those electrons that have truly emitted from surface of the sample into the vacuum of the instrument. The penetrate depth of X-rays in XPS is around 1–5 μm of the material, however all of the photo-emitted electrons come from the top 10-12 nm of the material and all of the other photo-emitted electrons that come from deeper than 10-12 nm are recaptured or trapped in various excited conditions. Generally, mono-energetic soft X-rays such as Mg K_{α} (1253.6 eV) or Al K_{α} (1486.6 eV) are employed as the excitation source. The number of electrons emitted is counted and the kinetic energy of the electrons for generating the XPS spectra is measured. With the value of the kinetic energy, the binding energy of the electrons to the surface atoms can then be calculated by Equation 3.3 [140].

$$BE = h\nu - KE - \phi_s \quad (3.3)$$

Where h is Plank constant, ν is the energy of the X-ray photon, BE is the binding energy of the orbital where the electron originates and ϕ_s is the spectrometer work function. By using binding energy of the electrons, more information about the oxidation state and chemical bonding of the material surface can be deduced.

Figure 3.4 Electron emission from Carbon caused by an X-ray photon [141] .

Characteristic pattern of XPS peaks for each element is located at particular binding energy values. This property provides the identification of each element on the surface of the material. Each peak in the XPS spectrum relates to the electron configuration of the element analyzed (e.g. 1s, 2s, 2p, 3s, etc), and the number of electrons identified for each of the peaks is directly correlated to the quantity of element in the material. To measure the atomic percentage values of each element, the XPS collected raw data is modified by using a relative sensitivity factor and finally normalized over all of the elements detected [50]. Surface element atomic concentration (%) is calculated using Equation 3-4 [140].

$$\% n_i = 100 \left[\frac{\frac{I_{ij}}{\sigma_{ij} E^{0.7}}}{\sum \frac{I_{ij}}{\sigma_{ij} E^{0.7}}} \right]$$

$$I_{ij} = K \cdot T(E) \cdot L_{ij}(\gamma) \cdot \sigma_{ij} \cdot n_i \cdot \lambda(E) \cdot \cos(\theta) \quad (3-4)$$

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} : photo ionization 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.

XPS analysis was done using a Kratos spectrometer with monochromatic Al $K\alpha$ (1486.71 eV) X-ray source. The survey spectra were collected in the range of 0-1200 eV in 1 eV step for each sample. High-resolution spectra were also performed on each specific peak. A Shirley background subtraction using a Lorentzian-Gaussian method was made before all the spectra were deconvoluted and curve fitting was performed [140].

3.2.4.1 Ultraviolet photoelectron spectroscopy (UPS)

Ultraviolet photoelectron spectroscopy (UPS) refers to the measurement of the kinetic energy of photoelectrons produced by ultraviolet photons. The UPS is applicable to measure molecular energy levels in the valence band. Photon source in the UPS is a helium discharge lamp which emits a wavelength of 58.4 nm (corresponding to energy of 21.2 eV). The main aim in both XPS and UPS is to obtain information

about the binding energy, chemical state, electronic state and composition from the surface of materials.

An energy spectrum of photoelectrons is produced using magnetic or electrostatic fields and directed through a slit into a vacuum region. Since the energy source in UPS is in the UV region, the sensitivity and depth profile is limited to very near of the surface, up to around 10 nm. Moreover conventional UPS has relatively poor resolution. Figure 3.5 presents a schematic of a basic UPS instrument. Table 3.2 shows a brief comparison and summary between XPS and UPS.

Figure 3.5 Schematic of a UPS instrument [94].

Table 3.2 Brief comparison and summery between XPS and UPS [94] .

Application	XPS	UPS
Materials on surfaces	✓	✓
Depth profiling	✓	-
Angle dependent studies	✓	✓
Binding energy	✓	✓
Valence band fine structure	-	✓
Elemental composition	✓	-
Empirical formulas	✓	-
Electron energy levels	✓	✓

3.2.5 Local structure study

X-ray Absorption Fine-Structure (XAFS) is the modulation of the x-ray absorption coefficient at energies near and above an x-ray absorption edge. The XAFS spectroscopy provides a wide range of data on the chemical oxidation state, local atomic and electronic structures, valence state, local symmetry, bond length, coordination number, coordination chemistry, and disordering factor of the atoms immediately surrounding the selected element. XAFS is applicable for different kind of samples such as thin film, powder and bulk. Moreover XAFS is generally used in a wide area and different scientific fields such as environmental science, catalysts research, material science and biology [142, 143].

The simplest XAFS experiments are done in transmission mode. By using synchrotron radiation source to provide polychromatic x-rays and then by diffraction of X-ray from a silicon double crystal monochromator, a desired energy band is selected. Figure 3.6 shows a schematic of a XAFS setup [143].

Figure 3.6 Schematic of XAFS setup [143].

XAFS is also referred to as X-ray Absorption Spectroscopy (XAS) and can be divided 2 regimes:

1. XANES: X-ray Absorption Near-Edge Spectroscopy

2. EXAFS: Extended X-ray Absorption Fine-Structure which contains related, but slightly different information about an element local coordination and chemical state.

Each regime carries very important and unique information. The XANES is more sensitive to the oxidation state and coordination chemistry (e.g., octahedral, tetrahedral coordination) of the absorbing atom and XANES itself includes three parts; Pre-edge, Edge and XANES. The EXAFS is used to determine the distances, coordination number, and species of the neighbors of the absorbing atom. Figure 3.7 (a) and (b) present the XANES and EXAFS regions [142, 143].

Figure 3.7 XANES and EXAFS regions [144].

When an x-ray is absorbed by an atom, a core-level electron (K, L, or M shell) is promoted out of the atom and into the continuum. The atom is left in an excited state with an empty electronic level (a core hole). The electron ejected from the atom is called the photo-electron. The XAS measurement is also based on the adsorption

coefficient of the material. The transmitted intensity I of an incident x-ray beam (I_0) as it passes through a material of thickness t is given by the absorption coefficient μ :

$$I = I_0 e^{-\mu t} \quad (3.5)$$

Where I_0 is the x-ray intensity hitting the material, and I is the intensity transmitted through the material. In EXAFS study, in order to measure the oscillations above the absorption edge, the EXAFS fine-structure function $\chi(E)$, is defined as

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E)} \quad (3.6)$$

Where $\mu_0(E)$ is a smooth background function representing the absorption of an isolated atom, $\mu(E)$ is the measured absorption coefficient and $\mu_0(E)$ is the measured jump in the absorption $\mu(E)$ at the threshold energy E_0 .

In the present work, the XAFS characterization was performed at the X-ray demonstration and development (XDD) beam line of Singapore Synchrotron Light Source (SSLS). The X-ray absorption spectroscopy in SSLS facility allows for the measurement in the intermediate energy range of 2.5–10 keV.

3.2.6 Liquid Chromatography (LC) and High Performance Liquid Chromatography (HPLC)

LC or Liquid chromatography refers to a separation procedure in liquid phase and it was the first type of chromatography that was discovered [145]. Liquid chromatography can be applied in a plane or a column. Currently liquid chromatography that commonly operates very small packing particles and a relatively high pressure is known as high performance liquid chromatography (HPLC). In the HPLC technique, a pump provides the higher pressure required to inject the analyte

mixture through the densely packed column; in order to detect, quantify and purify the individual components of the mixture. Based on the polarity of the mobile and stationary phases, the HPLC method has two different modes: normal phase liquid chromatography (NPLC) and reversed phase liquid chromatography (RPLC). In the first mode (NPLC) the stationary phase is more polar than the mobile phase (e.g. toluene as the mobile phase, silica as the stationary phase) whereas in RPLC it is reverse (e.g. water-methanol mixture as the mobile phase and C18 = octadecylsilyl as the stationary phase).

3.2.7 Methylene Blue degradation study

In order to test the photocatalytic behavior of the STF_x samples, photodegradation of methylene blue in water has been chosen as a test reaction. As explained, when a photocatalyst material is exposed to light such as visible or UV light, electrons and holes are generated. These created holes are very powerful for oxidizing many organic structures and pollutants. The molecule of methylene blue structure break down and degraded to more simple products. In this study, photocatalytic reaction was conducted using two different setups.

1- Slurry Reactor:

A 50 mL cell culture vessel with continuous magnetic stirring was used. The as-prepared STF_x was used as photocatalyst and a mixture of DI water with methylene blue (MB, 0.0313 M for 10.8 μmol/L) was also used as control sample. P25 TiO₂ powders, a standard photocatalyst, were also used in the photo catalytic experiments as a comparison. Four (12-inch), 8-W fluorescent tubes (UVP Inc.) were used as the illumination light sources. The spectrum of the fluorescent light and long-pass filter are shown as the red and black curves respectively in Figure 3.8. To study their visible

light performance, a long pass filter with cut-off frequency of 435 nm was used to block out major UV peaks. Aqueous solutions of methylene blue (MB, 0.0313M for 10.8 $\mu\text{mol/L}$) and photocatalyst particles (pure TiO_2 , STF_x particles and Degussa P25) were placed in a cell culture vessel. The concentration of methylene blue over time was measured using a Shimadzu UV-Vis spectrometer in the absorption mode.

Figure 3.8 Pattern of fluorescent light source (in red) and long-pass filter (in black) used for methylene blue degradation experiment.

2- Fixed bed reactor :

Comparing catalyst performance and measuring the actual transport of light and species remain a challenge in photocatalytic characterization systems. The absolute measure of the efficiency of photochemical process can be described as the quantum yield (ϕ). It defines the number of amount of light used for generating electron-hole pair (Q_{used}) over the actual amount of absorbed light (Q_{abs}):

$$\phi = \frac{Q_{used}}{Q_{abs}} \quad (3.7)$$

It is difficult to determine the quantum yield in heterogeneous photocatalysis due to scattering and reflection of light by the dispersed catalyst in slurry reactors. Therefore,

it is important to address the following questions in order to determine the efficiencies for different photocatalysts: What is the actual amount of absorbed light by the photocatalyst? How much of the absorbed light is used to create the reactive excitons that reach the surface of the photocatalyst to cause a redox reaction? How does the degradation of pollutant change when the amount of catalyst changes?

In existing literature, most of the photodegradation studies were performed in slurry reactors. The freely dispersed catalyst particles in the liquid were exposed to the light and the degradation of organic compound was measured. Such high surface area slurry reactors normally showed high photocatalytic activity as compared to the other reactor types such as the fixed bed or immobilized catalyst on a support. However, it has limitations in quantifying the transport of light through the reactor, with reactants and products to and from the surface of the photocatalyst. For example, light scattering occurs in the slurry reactor and it is difficult to measure the actual amount of light reaching each individual catalyst particle. The particle size distribution of the catalyst will also change the absorption and scattering spectrum. Besides, the light is also absorbed by water and the pollutants and their intermediates, hence will affect the measurement.

One approach is to use a fixed bed reactor instead of slurry reactor to compare catalysts correctly. In this experimental system, the same light whose intensity is known was used and a fixed catalyst amount was used in each experiment. By the help of this system, we will measure actual amount of absorbed light and products to and from the catalyst surface with changing the amount of catalyst.

While measuring transport phenomena in a fixed bed reactor, it is critical to determine the key parameters. For example, the light intensity, thickness of catalyst bed and

particle concentration play important role while comparing different catalysts. Figure 3.9 depicts the schematic of a fixed bed of photocatalyst. The catalyst is illuminated by known UV/Vis light intensity. The catalyst bed is totally illuminated with this constant and known light. In the bulk solution, refraction occurs and light exponentially decays within the catalyst bed as shown by curve I in the figure. The concentration of the model pollutant does not change in bulk solution and when it reacts with catalyst it decays within the catalyst bed as light as shown by curve C in the figure. It is expected that when the thickness of catalyst bed increases, total degradation rate will increase until a point where the light intensity becomes too weak to be effective.

Figure 3.9 Schematic of an illuminated fixed bed reactor

3.2.8.1 Photo reactor

Figure 3.9 shows the schematic of the photo reactor experimental system used. The catalyst bed was illuminated by light source. A UV-Vis filter set was used to choose specific wavelengths. The catalyst was put in the reactor with filter in milligrams and target pollutant was circulated by the pump. The outlet stream flowed through the

flow cell that was connected to spectrometer. The concentration of the target pollutant was measured by spectrometer and the degradation of pollutant can be determined continuously in the circulating system. 12 mg of catalysts with 30 ml of pollutant were used each time. The flow rate in the reactor was 2 ml/ min. The main benefits of this reactor are:

- With the Spectro Suit software, the no. of photons can be measured and with the amount of catalyst and bed reactor known, the efficiency of catalyst can be measured and compared.
- There was no powder wasted during measurement.
- There was good repeatability of the experiment.
- Online monitoring was also made possible.

The details of this setup can be found in the appendix A.

4 SrTi_(1-x)Fe_(x)O_{3-δ} solid solution; Synthesize, Characteristics properties and their variation

The effects of the preparation methods of the powder were investigated among the ball-mill processes, wet chemical and high temperatures solid state reaction. Subsequently the high temperature solid state reaction process was chosen for the STF_x perovskite-type compound synthesis. The morphology, crystalline structure, particle size and size distribution of the obtained samples were characterized by energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), UV–vis spectrometer, scanning electron microscope (SEM), and transmission electron microscopy (TEM).

4.1 Crystallographic Study and Phase Analysis

4.1.1 Crystallographic Study

The objective of the study was to determine the crystal structure and phase of the STF_x powder. Using the Rietveld refinements, the grain size, strain and oxygen vacancy were calculated. XRD was used to investigate the phase of STF_x powder samples prepared using the different methods. Figure 4.1.(a) shows XRD patterns of SrFeO_{3-δ} (STF_{x=1}) powder samples synthesized by high energy ball milling for 120 h, high temperature solid state reaction and wet chemical routes. The STF_{x=1} powders prepared by wet chemical and high temperature techniques were single phase. It was found that the ball milled STF_{x=1} powders consisted of three phases: SrTiFeO₃, SrCO₃ and Sr₃Fe₂OH₁₂. Figure 4.1.(b) shows the XRD patterns of STF_x powders synthesized by 120 hr ball milling. The XRD pattern confirmed that STF_x powders (0.6 < x < 0.9) produced by ball mill were not single phase and the amount of impurity phases increased with increased amount (x) of Fe dopant.

Table 4.1 summaries the values of the crystallite size, lattice parameter, oxygen vacancy, lattice strain and R-Bragg of STF_x (x=1) ball mill powder, wet chemical and high temperature solid state powders measured with Rietveld refinement.

Table 4.1 The Crystallite size, Lattice parameter, Oxygen vacancy, Lattice strain and R-Bragg values of STF₁ Ball mill powder, Wet chemical and High temperature solid state reaction powders measured with Rietveld refinement.

Method	Crystallite Size (nm)	Lattice Parameter(nm)	Oxygen Vacancy	Lattice Strain (%)	R- Bragg
Ball Mill powder	17	0.3904	0.9351	0.9846 (L)*	1.698
Wet Chemical	160	0.3860	0.3156	0.4046 (G)	2.875
Solid state reaction	446	0.3862	0.2166	0.3349 (G)	7.978

* Strain L and G means Lorentzian and Gaussians respectively (This described the symmetrical part of an X-ray diffraction peak) [137].

Figure 4.2 shows the comparison of crystallite size and lattice parameter for STF₁ powders with different synthesis methods. The crystallite size of high temperature solid state powder was the largest as was expected due to its higher production temperature and longer time. The lattice parameter of the ball mill powder was larger than the other powders due to high defect concentration produced by ball milling as will be discussed below (in this section).

The XRD spectra showed the peak shifting in the high temperature solid state reaction powder with increasing Fe concentration (Figure 4.3.(a) and 4.3.(b)) This peak shift is an evidence for an increased substitutional doping of Fe in STF_x. The ionic radius of Fe³⁺ (0.585 Å) is smaller than that of Ti⁴⁺ (0.605 Å). Hence by increasing the Fe concentration the lattice parameters and inter planar spacing in STF_x will decrease and based on the Bragg equation, the peaks will shift to larger θ .

Figure 4.2. (a) Crystallite size of the STF₁ powders synthesized by ball milling for 120 hr, wet chemical, solid state reaction, (b) Comparison of Lattice parameter for ball mill 120 hr milling, wet chemical, high temperature solid state reactions and reference [91062-ICSD] SFO powders.

Figures 4.4.(a) and 4.4.(b) show the variation of lattice parameter and oxygen vacancy and corresponding occupancy of oxygen in the series of high temperature solid state reaction STF powders. The data were consistent with reported work [146].

Table 4.2 shows values of the crystallite size, lattice parameter, oxygen vacancy, lattice strain and R-Bragg of high temperature solid state reaction STF_x powders obtained with Rietveld refinement. The doping of Fe can induce a high tendency of oxidization. Thus, the crystallite size increased as well. Moreover, the lattice parameters in the samples due to difference of the ionic radius of the Fe and Ti decreased from 3.9083 nm to 3.8601 nm. The increase in the oxygen vacancy was a result of charge neutrality. The δ must decrease with increasing doping of Fe to maintain the charge neutrality of the material.

Figure 4.3. (a) XRD Patterns of STF_x High Temperature solid state reaction powders (b) Peak shift in main peak SFO high temperature powders.

Table 4.2 The Crystallite size, Lattice parameter, Oxygen vacancy, Lattice strain and R-Bragg values of STF_x high temperature solid state reaction powders measured with Rietveld refinement.

Value of x @ Sr(Ti _{1-x} Fe _x)O _{3-δ}	Crystallite Size (nm)	Lattice Parameter(nm)	Oxygen Vacancy (δ)	Lattice Strain (%)	R-Bragg
0	243.6	0.3908	0.018	0.0116 (L)	2.021
0.2	280.4	0.3901	0.051	0.3519 (L)	2.132
0.4	320.2	0.3893	0.144	0.6372 (L)	1.544
0.6	350.5	0.3884	0.158	0.4981 (L)	2.554
0.8	378.3	0.3875	0.221	0.2377 (L)	1.860
1	445	0.3860	0.269	0.3348 (L)	7.98

In addition the ball mill powders with multiple phases were sintered in furnace. It was found that the minimum temperature for transition from multi-phase to single phase was at 1200 °C for 5 hrs. Figure 4.5.(a) and (b) show the STF_{0.7} ball mill powder XRD spectra before and after sintering.

Figure 4.4. (a) Lattice parameter of STF_x high temperature solid state reaction powders (b) Occupancy and Vacancy of Oxygen for high temperature STF_x powders.

The peak shifting of main peak in STF_{0.7} powder sample after sintering in 1200 °C is shown in Figure 4.5.(c). The impurity phase has been removed after sintering in 1200 °C. Most of these impurities came from SrCO₃ that dissociated at 1200 °C.

Figure 4.5. (a) Comparison of XRD Pattern for STF_{0.7} Ball mill powder before and after sintering with STF_{0.7} high temperature solid state powder (b) XRD Patterns of STF_x Ball mill powders with different value of x after sintering at 1200 °C (c) peak shift in main peak of Sr(Ti_{1-x}Fe_x)O_{3-δ}.

4.1.2 Amorphous Content Measurement

It was reported by L. Gao and Q. Zhang that TiO₂ nanoparticles contained in the anatase phase and mixed-phases, and their photocatalytic activities increased significantly with decreased content of amorphous [147]. This effect resulted from the insulation of the amorphous parts, which formed the recombination centers for the photo-generated electrons and photo-generated holes. For complete crystalline TiO₂

(rutile) nanoparticles, their photocatalytic activity was much higher than that of samples with larger crystalline size. The results indicated that the existence of amorphous has detrimental effects on photocatalytic properties.

The amount of the amorphous content using the different sample preparation methods was investigated and then one with the lowest amorphous content was chosen as the main synthesis method.

Rietveld methodology [148] has had a very important impact on a broad scientific community as it is possible to address many problems concerning crystalline materials [149]. A set of guidelines for the use of Rietveld refinement has been presented by the International Union of Crystallography Commission on Powder Diffraction [137]. The Rietveld method is better suited for Quantitative analysis (RQA) than other methods, such as reference intensity ratio (RIR) analysis, because it uses a wide diffraction range. The analysis of a wide pattern minimize the inaccuracies arising from systematic errors within the raw data, caused by e.g. peak overlap, preferred orientation, sample broadening and lack of a pure standard. However, the crystal structures of all crystalline phases must be known in order to calculate the powder patterns [150-153].

In principle, the determination of the amorphous phases of a given sample using Rietveld quantitative analyses (RQA) should be straightforward. Initially, a mixture of a weighed amount of a suitable standard sample, with negligible or known amorphous content, and the investigated material was prepared. Next, the Mixture was analyzed by powder diffraction and Rietveld phase analysis [150-153]. If the sample contained amorphous phases, the crystalline phase present in that sample would have a smaller Rietveld refined weight ratio than that calculated from the weight mixture.

Concurrently, the standard phase fraction would be overestimated. The amorphous phase content corresponded to the small overestimate of the crystalline standard in the Rietveld refinement. Such analyses can be applied to a single crystalline phase or multi-phase sample. However, to obtain a good analysis of the amorphous content, all systematic errors in the powder diffraction data must be minimized. It is important to obtain precise and accurate multiphase refinements. In fact, such analyses were not usually carried out because the required accuracy in the Rietveld analysis was not commonly fulfilled. Hence, a proper amorphous phase analysis, reproducible Rietveld refinements, with phase fraction deviations lower than 0.4%, must be required.

In this work, the Rietveld quantitative amorphous content analysis (RQACA) which is a precise and accurate tool that allows the measurement of the amorphous phase content with accuracy close to 1% was used. A protocol for such accurate analyses was presented. The influence of systematic errors, such as strong preferred orientation and micro absorption effects, were also addressed [150-153]. RQACA relates the overall amorphous content, A (%), to the small overestimation of an internal crystalline standard in the Rietveld refinement. A can be obtained from the following equation, which can be easily derived by considering a standard sample free of amorphous phases:

$$\%A = [(1 - (W_s/R_s)) / (100 - W_s)] * 10^4 \quad (4.1)$$

Where W_s (%) is the weighed concentration of the internal standard and R_s (%) is the Rietveld analyzed concentration of the internal standard.

In this study, Cr_2O_3 was used as the internal standard [50%W-50%W] (weight percent), and mixed for 5 min using the spex milling machine. The composition of mixture used for measurement is summarized in Table 4.3.

Rietveld analysis with the Cr_2O_3 (symmetry space group: R-3cH), 202619 - ICSD standard card number, TiO_2 (symmetry space group: P 42/m n m) and 24294 - ICSD standard card number were used as internal standard powders for overestimation and under estimation measurements, respectively. Figure 4.6 shows the Rietveld analysis for measurement of amorphous contents in ball mill and high temperature solid state reaction powder. The powders prepared using different methods and the amorphous contents were measured and shown in table 4.3.

Figure 4.6. Rietveld analysis for (a) SFO Ball mill powder after 120 hr milling (b) SFO Ball mill powder after 120 hr milling with Cr_2O_3 as internal standard (c) SFO high temperature solid state reaction powder (d) SFO high temperature solid state reaction powder with Cr_2O_3 as internal standard .

Table 4.3. Phase percentage of SrFeO_3 and Cr_2O_3 used for the measurement of amorphous content

Type of Powder	Phase percentage		Amorphous Content (%) Obtained
	% SrFeO_3	% Cr_2O_3	
Ball mill	27.79	66.83	50.36
Wet Chemical	36.19	58.33	28.55
High Temperature	49.04	50.96	< 2

4.1.3 Effect of milling time on the microstructure of high temperature solid state SrFeO_3 powder

The presence of amorphous content can decrease the PCO properties, however the particle size and hence the surface area of the powders needed to be considered. As observed, the samples prepared by high temperature solid state reaction mechanism had big particle size that reduced the PCO effect. Hence the ball milling process was used to further decrease the particle size. The effect of different milling time using spex machine on the defect and amorphous content of the high temperature solid state SFO powders was investigated. Table 4.4 summarizes the values of crystallite size, lattice parameter, oxygen vacancy, lattice strain and R-Bragg of STFx ($x=1$) powders at different time of milling measured with Rietveld refinement.

Figure 4.7 depicts the lattice strain, crystallite size and lattice parameter of samples measured with Rietveld analysis. With increasing milling time, the crystallite size decreased and reached a saturation value of 25 nm. The change in lattice parameter value was due to the heavy cold-work plastically and lattice expansion of phases. Plastic deformation which is carried out in a temperature region and over a time

interval such that the strain hardening is not relieved is called cold work. Simultaneously, the lattice strain increased due to the generation of dislocations and other crystal defects. However, beyond certain milling time when the crystallite size reached a saturation value, continued milling did not produce any more dislocations (due to the difficulty of generating dislocations at very small grain sizes), but the existing dislocations were rearranged and annihilated. Therefore, the lattice strain showed a decrease in value [129, 154, 155].

In every plastic deformation during milling, the average atomic level of dislocation was controlled thermodynamically based on the theory that defines the LES (Low-Energy Structures) hypothesis. Accordingly, among all potentially accessible structures, plastic deformation generated the structure with the lowest free energy. For the particular case of dislocation-mediated plastic deformation, limited only by dislocation mobility, availability of slip systems and insignificant entropy; the dislocation structure always approached the lowest possible mechanical energy of the present dislocation population. In some cases would lead to the softening after one level and hardening in other hand that resulted in the decreasing strain [129, 154, 155]. Figure 4.7.(a) shows the average atomic level strain that initially increased due to the increasing dislocation density. At a certain dislocation density within heavily strained regions, the crystal disintegrated into the sub grains that were initially separated by low-angle grain boundaries. It has been found that the density of vacancies increased asymptotically with the number of collisions, namely, the density of the vacancies increased rapidly at the initial stage of ball milling but the rate of increase became slower with further ball milling. After some specific duration, the concentration of vacancies saturated as it reached its maximum value [156].

Figure 4.7. Rietveld analysis calculation for STF _{1.0} high temperature solid state reaction powder (a) crystal size and Strain (b) Lattice parameter.

Table 4.4 The Crystallite size, lattice parameter, oxygen vacancy, lattice strain and R-Bragg values of STF_x (x=1) powders at different time of milling that measured with Rietveld refinement.

Time of milling (min)	Crystallite Size (nm)	Lattice Parameter(nm)	Oxygen Vacancy (δ)	Lattice Strain (%)	R-Bragg
0	260.9	3.8604	0.4167	0.4241 (G)	5.702
7	93.9	3.8612	0.3237	0.4647 (G)	2.733
15	58.0	3.8621	0.3213	0.7336 (G)	2.282
30	31.9	3.8649	0.3855	0.8714 (G)	1.894
45	28.8	3.8650	0.3834	0.6997 (G)	2.145
60	25.0	3.8658	0.3957	0.7317 (G)	2.631

4.2 Microstructure analysis

4.2.1 Scanning Electron Microscopy

The morphology of the powders was investigated using the scanning electron microscopy. From SEM image in Figure 4.8, it was apparent that each powder has different morphology. For quantitative analysis Energy Dispersive X-ray analysis was used to check the composition and distribution of elements in the powder. Figure 4.8

shows the result for Ball mill, wet chemical and high temperature solid state reaction powders. Agglomeration of particles in large aggregates can be observed after 120 hr of ball milling. Figure 4.8.(b) indicated the topography and morphology of wet chemical powders. The images showed high porosity of this powder and BET result further confirmed. Fig 4.8.(c) shows the SEM picture of High Temperature solid state $\text{STF}_{(x=1)}$ powder.

Figure 4.8. SEM picture from surface of (a) Ball mill $\text{STF}_{(x=1)}$ powder after 120 hr milling (X1000) (b) wet chemical $\text{STF}_{(x=1)}$ powder (X7500) and (c) High Temperature $\text{STF}_{(x=1)}$ powder after sintering at 1200 °C (X2000).

The pictures showed that the topography of this particle was completely different from the ball milled powder. The agglomeration of the powder particles can be obviously

seen. Figure 4.9 shows the EDX map of the ball mill and the high temperature solid state reaction powders that indicated homogenous distribution of the elements in the homogeneous solid solution powders. From the EDX analysis, the ratio of Fe/Ti for High Temperature solid state powders was closer to the ideal stoichiometry $(0.7/0.3)=2.34$. This ratio for wet chemical powders and ball milled powders were 2.51 and 1.98, respectively that can be explain by some impurities because of different preparation process or measurement error.

Figure 4.9. EDX X-ray map analysis from (a) STF (X=0.2) powder after 120 hr milling and ,(b) STF (X=0.8) High temperature solid state reaction.

4.2.2 Transmission Electron Microscopy

The TEM bright-field images and SAED patterns showed amorphous phase in the ball milled and wet chemical powders. Figure 4.10 shows TEM images and SAED for the

ball mill powder after 120 hr milling, wet chemical and high temperature solid state powders. The TEM results confirmed the crystallite size measured with XRD. The corresponding diffraction patterns in Figure 4.10 showed that the ball milled powder and wet chemical powder were a mixture of polycrystalline and amorphous phases but for the high temperature solid state powder (Figure 4.10.(c)) because of heating and sintering at a high temperature of 1200 °C for a long time (48 hr), only single crystalline phase was observed. Different ordination of atoms that implied different grain was also observed.

Figure 4.10 TEM bright-field images and SAED pattern (a) SFO ball milled powder after 120 hr milling (b) wet chemical powder and (c) SFO high temperature solid state powder.

4.3 Particle size and surface area measurement

To investigate the size distribution of the particles, the Malvern particle size analyzer was used. Figure 4.11.(a) shows the size distribution of ball mill; wet chemical and high temperature solid state powders and Figure 4.11.(b) compares the average particle size of this result for ball mill, wet chemical and high temperature solid state powders.

Figure 4.11 (a) Size distribution and (b) Average particle size of $STF_{x=1}$ for ball mill after 120 hr milling, wet chemical, High temperature solid state and High temperature solid state after 7 min Spex.

The measurement of the surface area of powders is based on calculating the amount of gas absorbed on the sample surface at low temperatures and then estimating the monolayer capacity using the “known” size of the adsorbed molecules. Nitrogen, at liquid nitrogen temperature, is the most common gas used, whereas krypton, at liquid nitrogen temperature, is used for samples with an area less than $1 \text{ m}^2/\text{g}$ [157]. The Brunauer-Emmett-Teller (BET) method [158] of measuring the specific surface area is

based on the above principle. The specific surface area (m^2/g) determined by this method includes both the external and internal (pores) surface areas.

To measure the surface area of powders, BET test was carried out at 50 K to compare the specific area of STF_x using the Micropore system (Autosorb-1-c, Quantachrome). Figure 4.12.(a) shows the surface area measurement of STF_1 powder at different milling time. It showed that with the increasing of milling time, the crystallite size decreased. However due to agglomeration after 15 min of spex milling, the surface area decreased when the crystallite size became fairly constant. Moreover the surface area of the 15 min spex powder was larger than the wet chemical powder and surface areas for the 15 and 30 min spex samples were larger than the ball milled powder. With increasing time of milling, the surface area initially decreased and then increased. This may be attributed to the occurrence of hard agglomeration with strong inter-particle bonds within each aggregate resulting from the dissipated heat energy of prolong milling [159, 160]. Figure 4.12.(b) shows the BET result for $\text{STF}_{x=1}$ powders synthesized by ball mill, wet chemical and high temperature solid state reaction process.

Figure 4.12 Specific Surface area (BET) plots for (a) surface area measurement of STF_1 powder at different milling time and (b) $\text{STF}_{x=1}$ ball mill, wet chemical and high temperature solid state reaction $\text{STF}_{x=1}$ powders.

Tables 4.5 and 4.6 present the surface area results (BET measurements) for $\text{STF}_x = (0 \sim 1)$. These results showed that with increasing iron content, the surface area of powder decreased due to the increasing grain growth of the particle and the samples were highly oxidized. Moreover these data also showed that the surface area and total pore volume of powders after 5 hr of normal ball milling increased. There are two different methods to measure the surface area of powder; 1- Normal isotherm or fast scan 2- Full isotherm that takes a longer time. From Full isotherm measurement we can obtain the total pore volume and pore size distribution using different model. The difference between the values of table 4.5 and 4.6 is due to the different measurement methods. In Full Isotherm method the value was measured using at least 20 point and hence more accurate.

Table 4.5 Variation of surface area of STF_x high temperature powders Normal isotherm.

Samples (STF_x)	Average Surface area (m^2/g)
0.2	5.343
0.4	5.019
0.6	4.056
0.8	3.097
1	2.203
1 (5 hrs milled)	10.085

Table 4.6 Variation of surface area and pore size of STF_x high temperature powder before and after millingthat measured by Full isotherm method.

Samples (STF _x)	Without milled			Milled		
	Average Surface area (Un milled) m ² /g	Total pore volume (cc/g)	Pore size distribution (Å)	Average Surface area (milled) m ² /g	Total pore volume (cc/g)	Pore size distribution (Å)
0.8	2.992	6.476e-03	16.686	9.167	2.350e-02	17.449
1	1.990	3.407e-03	16.722	8.992	2.463e-02	18.622

4.4 Optimization of reaction temperature of High temperature SrTi_(1-x)Fe_xO_(3-δ) powders

From The photocatalytic test (Chapter 8, section 8.2), SrFeO₃ (SFO) showed the best efficiency for photodegradation and decolorization of Methylene Blue. In next step we tried to find optimize reaction temperature for SrFeO₃ (SFO). To find the optimum calcination time and calcination temperature, the SrFeO_{3-δ} powder was calcined at different temperatures, from 700 °C to 1000 °C. For each sintering temperature step, one sample was annealed for 24 hours (Cycle 1) and another for 48 hours (Cycle 2). From Figure 4.13, the SFO powder prepared at 700 °C showed multiple phases including those of the three separate SrFeO₃, SrCO₃ and Fe₂O₃. With increasing time and temperature of sintering, the conditions facilitated the reactions kinetically and thermodynamically. To obtain pure single perovskite phase, the temperature of 900 °C and above must be chosen.

Figure 4.13 XRD spectra (20-100 Degree) for SFO from 700 °C to 1000 °C.

Table 4.7 presents the calculated crystallites size using Rietveld analysis for the first and second cycles of sintering. The particle size distribution measurement in Figure 4.14 also confirmed the results of XRD. With lower temperature of sintering from 1200 °C to ranges between 900-1000 °C the particle size of powder decreased.

The SEM micrographs in Figure 4.15 for the strontium ferrite particles showed clearly high grain growth with increasing temperature of sintering, especially for the powder at 1200 °C. This was due to its high tendency to release the stress and defects such as dislocation and point defects at higher temperature. These images also confirmed the obtained results of particle size analyzer.

Table 4.7 Crystallite size of powder sintered at different temperature by using Rietveld analyzing.

Sintering Temperature (°C)	Cycle one(24 hrs)	Cycle two (24 hrs)
1200	210 (nm)	234 (nm)
1000	156 (nm)	170 (nm)
900	139 (nm)	149 (nm)
800	137 (nm)	145 (nm)

Figure 4.14 The size and size distribution of SrFeO₃ nanoparticles at different temperatures of sintering.

Figure 4.16 shows the TEM images of SrFeO₃ nanoparticles. Selected area electron diffraction (SAED) patterns confirmed that strontium ferrite had crystallized. Figure 4.16.(b) presents the indexing of SrFeO₃ powder with [60] zone axes. These diffractions showed the single crystallite structure produced with the high temperature solid state reaction method.

Figure 4.15 SEM micrograph of the strontium ferrite particles at different sintering temperatures X10,000 (a) 900 °C, Cycle 1 (b) 900 °C, Cycle 2 (c) 1000 °C, Cycle1 (d) 1000 °C, Cycle 2 (e) 1200 °C, Cycle 1 (f) 1200 °C, Cycle 2.

Figure 4.16. (a) TEM micrographs of SrFeO₃ nanoparticles (b) SAED patterns could be indexed as strontium ferrite with [60] zone axis .

5 Surface Chemical Study, X-Ray Photoelectron Spectroscopy (XPS) and Ultra violet Photoelectron Spectroscopy (UPS)

5.1 Introduction

The perovskite-type oxides are well known among the metal oxide photocatalyst because perovskite structures have a very important characteristic which is their ability of partial substitution of cations at both A and B sites and the stability of mixed oxidation states or unusual oxidation states in the crystal structure. For example if the Cr cations are alternatively doped at the Sr^{2+} site rather than the Ti^{4+} site, different photo physical and photocatalytic properties might be obtained. A wide range of cations and valences can be accommodated in this simple crystal structure due to the susceptibility of partial substitution at both A and B sites, and so rendering perovskite to various and flexible chemical tailoring [89].

As a typical ABO_3 type perovskite, SrTiO_3 has been known as a photocatalyst capable of decomposing H_2O into H_2 and O_2 without applying an external bias potential [90, 91]. In recent years, many perovskites studied, and the results of these reports on the ABO_3 that contained transition metal ions (B) presented an interesting range of electrical properties. Perovskite structure material are used in a wide range of application such as catalysis [161, 162], photocatalysis [13], fuel cells [163], magneto-optics [164, 165] and in spin valves [166]. The stability of perovskite materials at high temperatures and in chemically aggressive atmospheres has made these materials such as SrTiO_3 and BaTiO_3 suitable as gas-sensor materials [167, 168]. Strontium Titanate Ferrite, STF_x , has a continuous solid state solution between strontium ferrite, SrFeO_3 and strontium titanate, SrTiO_3 . The existence of oxygen

vacancies in STF_x is unavoidable because in this structure iron atoms were replaced with titanium atoms and due to the difference in their preferential oxidation states (+4 for Ti and +3 for Fe), to maintain charge balance in the system, oxygen vacancies were formed [99]. STF_x has found vast applications in oxygen sensor [100, 119], hydrocarbon sensor [117], fuel cell [100, 120], oxygen separation membranes [169] and phase shifters in communication systems [121], however STF_x compound is still new and need more research to find more application for it.

As there is not enough surface study on the STF_x perovskite material, this chapter details the surface chemical states of STF_x samples characterized by XPS and UPS to elucidate the structure with different doping of iron in the SrTiO_3 perovskite structure.

5.2 Experimental

5.2.1 Materials synthesis

Strontium carbonates (SrCO_3 , 99.9%), iron oxide ($\alpha\text{-Fe}_2\text{O}_3$, 98.9%) and titanium dioxide (anatase TiO_2 , 99.9%) were obtained from Aldrich. The synthesis of STF_x powders ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1) were carried out with high temperature solid state reaction technique. First, strontium carbonate, iron oxide and titanium dioxide powders were prepared according to the x value, and then mixed manually in an agate mortar for 15 min. The mixture was calcinated at $1200\text{ }^\circ\text{C}$ for 24 hrs in oxygen ambient, with a flow rate of 150 sccm. Next, the calcinated powder was furnace cooled down to room temperature and grinded again manually in the agate mortar for 15 min. The ground powder was further calcinated at $1200\text{ }^\circ\text{C}$ for another 24 hrs and furnace cooled down to room temperature in oxygen ambient.

5.2.2 Materials Characterization

The surface chemical composition of the powders was monitored by X-ray Photoelectron Spectroscopy (XPS) measurements performed with a Kratos Axis ULTRA X-ray Photoelectron Spectrometer and an Mg K α anode (1253.6 eV photon energy, 15 kV, 300 W) at a take-off angle of 45°. Valence band UPS experiments were performed using He I (21.22) eV and Al K α (1486.6) eV photon lines. Binding energies were calibrated by measuring the Fermi step position and the Au 4f $_{7/2}$ core level of a clean gold film.

5.3 Results and Discussion

5.3.1 X-Ray Photoelectron Spectroscopy (XPS) Surface Chemical

Study

Figure 5.1 shows the survey XPS spectra of STF powders. Only the Sr, Ti, Fe, C and O elements were observed on the samples when the binding energy was below 1000 eV and these element peaks were used for the elements quantification analysis. The fitted curve for the metal peaks (Fe, Ti, Sr), O 1s peaks and C 1s peaks were depicted in Figure 5.1. The calibration of the binding energy scale was performed with the C 1s peak (BE = 285 eV) from the ubiquitous carbon contamination.

The spectral features of the STF_x series samples, for the O 1s, C 1s, Sr 3d $_{5/2}$, Fe2p $_{3/2}$ and Ti 2p peaks were summarized in Figures 5.2. and 5.3, respectively. Table 5.1 presents a summary of peak position and components.

Figure 5.1. The XPS spectra of $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_{(3-\delta)}$.

Table 5.1 Summarize of peak position and components.

Element		Position	Descriptions
O 1s	O 1s a	529.0	Oxygen lattice
	O 1s b	531.2	carbonates compounds
	O 1s c	532.9	water and hydroxide absorbed on the surface
Sr 3d	Sr 3d 5/2 a	130.82	$\text{SrO}_{(1-x)}$
	Sr 3d 5/2 b	131.9	Sr (Perovskite)
	Sr 3d 5/2c	133.80	SrCO_3
C 1s	C 1s a	285	atmospheric contamination
	C 1s b	286.1	CO like species (contaminated by hydrocarbons)
	C 1s c	289.1	carbonates
Fe 2p	Fe 2p 3/2 b	710.13	Fe^{3+}
	Fe 2p 3/2 c	711.8	Fe^{4+}

Deconvolution of the O 1s spectra yielded three peaks, namely O 1s a (529.0 eV), O 1s b (531.2 eV) and O 1s c (532.9 eV). From the literature, the peak at the 532.9 eV was probably due to the water and hydroxide absorbed on the surface [22, 170-172], while the peaks at 531.2 eV corresponded to carbonates compounds and chemical adsorption [45, 173-179].

Figure 5.2 The core level XPS spectra for STF for $x=0 \sim 1$ for (a) O 1s and (b) C 1s.

The main peaks at 529.0 eV corresponded to oxygen lattice [121, 169, 179].

Quantification analysis has shown that with increasing the iron content in STF _{x}

powder, the amount of the oxygen lattice decreased. This observation was attributed to the partial substitution of Fe with Ti, iron participated with mixed oxidation state of Fe^{3+} to Fe^{4+} and the formation of oxygen vacancy that consequently led to the reduction of the oxygen lattice. The ratio of O 1s presented in Table 5.2 showed that with increasing iron content, the ratio decreased that can be explained by the formation of oxygen vacancy with the Fe in Ti site. Figure 5.2(b) showed the detailed scan peak for C 1s. Three peaks were observed, namely C 1s a (285.0 eV), C 1s b (286.1 eV) and C 1s c (289.1 eV). The low binding energy peak at 285 eV with strong intensity was the result of the presence of adventitious carbon (C-H) [175, 179], due to atmospheric contamination present on the solid surface which was used as the calibration reference. The higher binding energy at 286.1 eV was possibly due to the CO like species (C–O) [180]. The well-defined peak at 289.1 eV was related to carbonates (O–C–O and/or C=O) [175, 179, 181] as a result of the perovskite thermal treatment.

Figure 5.3 The core level XPS spectra for STF for $x=0 \sim 1$ for (a) Sr 3d and (c) Fe 2p

The Sr3d XPS spectra, as shown in Figure. 5.3(a) showed a clear doublet structure. The Sr 3d peak was de-convoluted carefully into three pairs of peaks, namely Sr 3d (a), Sr 3d (b) and Sr 3d (c). The three Sr 3d 5/2 peaks were located at binding energies of 130.82, 131.9 and 133.80 respectively. The peak of Sr 3d (a) at 130.82 eV was observed only for STF₁ which was subscript to the Sr ions surrounded by vacancies in the oxygen-deficient perovskite structure, similar to that of SrO_(1-x). This phenomena could be explained by the dramatic increase of Fe³⁺ and Fe⁴⁺ in SrTi_(1-x)[Fe³⁺, Fe⁴⁺]_(x)O_(3-δ) perovskite structure[175, 182, 183].

Table 5.2 Atomic concentrations calculated from XPS results for STF powders with $x=0 \sim 1$.

Elements	Binding Energy (eV)	Atomic concentrations (%) for $\text{SrTi}_{(1-x)}\text{Fe}_x\text{O}_{(3-\delta)}$ @ different x					
		x=0	x= 0.2	x= 0.4	x= 0.6	x= 0.8	x= 1
Fe 2p a (Fe^{3+})	710.1	-	1.335	1.956	3.458	5.019	5.362
Fe 2p b (Fe^{4+})	711.8	-	0.472	0.789	1.677	3.866	4.194
Fe Satt	718.2	-	0.249	0.14	0.271	0.197	0.332
O 1s a	529.0	13.61	11.3	10.35	5.15	2.818	1.62
O 1s b	531.2	12.45	19.3	20.233	20.45	20.85	29.94
O 1s c	532.9	1.405	2.1	1.833	2.15	2.826	1.99
Ti 2p (Ti^{4+})	457.3	5.31	5.421	5.034	3.627	2.241	0
C 1s a	285	23.65	42.45	44.24	35.251	35.65	40.03
C 1s b	286.1	28.86	4.741	2.024	10.831	8.256	2.135
C 1s c	289.1	1.796	2.228	3.932	5.789	5.071	5.472
Sr 3d a	130.8	-	-	-	-	-	0.584
Sr 3d b	131.9	-	-	9.442	5.285	10.328	3.315
Sr 3d c	133.8	12.922	10.485	1.043	6.083	2.895	5.56
Total	-	100.003	100.081	101.016	100.022	100.017	100.034
Elements	Ratio						
Ti/Fe	-	2.637	1.745	0.671	0.247	0	
$\text{Fe}^{3+}/\text{Fe}^{4+}$	-	2.828	2.479	2.062	1.298	1.278	
Sr/(Ti+Fe)	2.434	1.402	1.324	1.256	1.168	1.002	

The peaks at 131.9 eV Sr 3d (b) observed for all samples corresponded to SrCO_3 and the peak at 133.80 eV, Sr 3d (c) observed corresponded to Sr (Perovskite) respectively (Figure 5.3(a)) [175, 178, 181, 184]. The Sr/Fe ratio was higher by more than 3-fold compared to the stoichiometric $\text{Sr/Fe} = 1$ value for STF_0 , and it decreased slightly with decreasing O content of the STF_x perovskite. This result indicated that Sr was segregated toward the surface of the samples.

The Fe 2p XPS region (Figure 5.3.(b)) showed a doublet, 2p_{3/2} and 2p_{1/2}. By deconvoluting the Fe 2p spectra, two components were obtained. The Gaussian fitting

of the peaks to the component of Fe^{3+} and Fe^{4+} was also indicated in the figure. The peaks at 710.13 eV (Fe 2p (a)) and 723.93 eV were similar to those reported for Fe 2p study and the shake-up contribution at about 718.2 eV were consistent with the presence of Fe(III) [185-188]. The fitting results and the ratio of Fe^{3+} and Fe^{4+} were presented in Table 5.2. It was obvious that iron in STF_x perovskite structure participated in mixture of Fe^{3+} and Fe^{4+} ($\text{SrTi}_{(1-x)}[\text{Fe}^{3+}, \text{Fe}^{4+}]_x\text{O}_{(3-\delta)}$) and with increasing iron dopant the amount of Fe^{3+} and Fe^{4+} increased significantly.

Bocquet *et al* investigated the electronic structure of the Fe^{4+} perovskite oxide SrFeO_3 by XPS, and they concluded that the large increase in charge at the Fe site led to a chemical shift to a higher binding energy [189]. The doublet peaks appeared at 711.8 eV (Fe 2p (b)) and 725.6 eV could be assigned to Fe^{4+} . Moreover with increasing amount of Fe^{4+} , the shape of satellite also changed. P.Mills *et al.* and other researchers presented that the position of satellite state was the key and finger print to detect the oxidation state of Fe. With changing oxidation state, the surface oxidation could also be changed. For $\alpha\text{-Fe}_2\text{O}_3$, shake up satellite peaks located at around 718.2 eV were approximately 8 eV higher than the Fe 2p_{3/2} peak, whereas the satellite peak for FeO was approximately 6 eV from Fe 2p_{3/2} peak. There was no satellite peak observed for Fe_3O_4 [79, 186].

Bocquet and *et al.* used a *p-d* charge-transfer cluster-model calculation to interpret the Fe 2p core levels. They defined the charge transfer energy Δ_{eff} with respect to the lowest multiplet levels of the d^4 and d^5L configurations and showed charge transfer energy Δ_{eff} was negative. They presented that the shape of satellite could be used to detect the oxidation state of Fe. For the Fe 2p core-levels XPS spectra, strong satellite

features were observed for the d^5 compounds with an apparently weaker satellite present for $SrFeO_3$. Similarly, the spectrum for $SrFeO_3$ was primarily composed of main peaks due to screened $\underline{cd}^5\underline{L}$ states and satellite structure from mixed $\underline{cd}^4$ and $\underline{cd}^6\underline{L}^2$ states .

The XPS spectra of Ti 2p was also deconvoluted with a pair peaks (Figure 5.4) at 457.3 eV and 462.8 eV that attributed to Ti 2p $3/2$ and Ti 2p $1/2$ respectively. They were separated from each other with 5.7 eV. These XPS studies have shown that titanium was involved in this compound as (+4) oxidation state.

5.3.2 Ultra violet Photoelectron Spectroscopy (UPS) Valance band Study

In this study, different series of UPS samples were prepared. The charge effect was reduced by using the finger point mask on the samples surface. The valence band UPS and core level XPS experiments were performed using He I (21.22) eV and Al K α (1486.6) eV photon lines. The binding energies were calibrated by measuring the Fermi step position and the Au 4f $7/2$ core level of a clean gold film.

Figure 5.4 The core level XPS spectra for STF with $x=0 \sim 1$ for Ti 2p.

The determination of the position of the valance band (E_{VB}) from the UPS data was done by using the intersection of the linear extrapolation of the leading edge of the E_{VB} spectrum with the base line. The relationship between the energy levels (E_{VB} , E_F , and E_{vac}) and the UPS spectrum of STF_x and Au were shown in Figure 5.5. The figure shows the scale of binding energy with the Fermi level of Au set at 0 V. The vacuum level (E_{vac}) should be located at 21.22 eV above the cutoff energy of the spectrum. The work functions of STO and Au based on this definition were estimated to be 4.32 and 5.1 eV, respectively. According to the spectrum a, the value of the valence band maximum (E_{VB}) was located at ca. 3.19, 2.91, 2.79, 2.39, 1.84 eV below the Fermi level (E_B) (0 eV) for $x=0, 0.2, 0.6, 0.8$ and 1 respectively, determined by fitting a straight line into the leading edge. The secondary electron onset (SO) on the left side

of the spectra was measured between 16.4, 16.9 eV, 17.2 eV for Au, STO and SFO respectively. The work function of SrTiO_3 was calculated to be $4.32 (\pm 0.1)$ eV by subtracting the secondary electron onset position of the He I UPS spectra from the excitation energy (21.2 eV) [146, 190-194].

A. Rothschild and et.al had reported that with increasing Fe dopant the UPS spectra, in the range of low binding energies (<25 eV), showed that the valence band of STF_x was broader than that for SrTiO_3 and extended closer to the conduction band edge, which corresponded to the reduction in the band-gap energy of these compositions accordingly [33, 102]. Table 5.3 presents the analyzed data and results of UPS measurement.

Figure 5.5 Ultraviolet photoelectron spectra (He I) for the surface of $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_{(3-\delta)}$.

Table 5. 3 The analyzed data and results of UPS measurement.

x in STF _x	E _{VB} [with respect to Fermi level] (eV)	E _{s,o} (eV)	E _{Vac} (eV)	E _{VB} [with respect to E _{Vac}] (eV)
0	3.19	16.4	-4.8	-7.79
0.2	2.91	16.48	-4.7	-7.63
0.6	2.79	16.71	-4.5	-7.28
0.8	2.39	16.8	-4.4	-6.79
1	1.84	16.9	-4.3	-6.14

5.3.3 Correlation between the band gap, work function, local structure and photocatalyst effect

Figure 5.6 shows a schematic energy diagram of a n-type semiconductor. The valence bands and conduction bands are separated by the band gap (E_g). In a non-degenerated semiconductor (having a moderate doping level), the Fermi level is located within the band gap. This means the work function is now different from the ionization energy (*energy difference between valence bands maximum (VBM) and vacuum level*). The Fermi level is a form of theoretical construct since there are no allowed electronic states within the band gap. This means the Fermi distribution needs to be considered as a statistical function that gives the probability of finding an electron in a given electronic state. The Fermi level refers to the point on the energy scale where the probability is just 50% [195, 196].

In photocatalyst material the position of conduction band and band gap energy both are more important than work function position. With a lower band gap material, the energy required to generate the electrons is lower. In the case for water splitting, the position of conduction band should be lower than the reduction potential of water otherwise the material is not able to reduce the water. Hence the band gap and conduction band are both important.

Work function of material can also affect the photocatalytic activity of material. The photocatalytic activity for the splitting of water increased significantly with a decrease in the work function (ϕ) of the samples, as the activity decreased in the following sequence : $STF_1 > STF_{0.8} > STF_{0.6} > STF_{0.4} > STF_{0.2} > STF_0$ (Figure 5.5). This observation suggested that the work function (ϕ) of the substrate plays a significant role in the electron transfer in photocatalyst material [197, 198].

Figure 5.6 Schematic energy diagram in an n-type semiconductor[93].

The substitution of iron by titanium increased the Ti (Fe)-O first shell disorder factor that can be explained by the increase in the oxygen vacancies. Since Oxygen vacancies /or defects act as electron traps, which could capture the photo induced electrons, thus effectively inhibit the recombination of the photo induced electrons and holes. The EXAFS and XANS are good supplementary equipment to explain the

catalyst and photocatalyst properties of material and many researchers use them in catalyst studies. In chapter 6, the local structure of STF samples has been studied comprehensively.

5.3 Conclusions

The $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_{(3-\delta)}$ (STF_x) powders for photocatalyst application have been prepared by high temperature solid state process. The XPS results showed that Sr ions were in 2+ oxidation state and there were existence of SrCO_3 on the surface of samples in addition to $\text{SrO}_{(1-x)}$ on the surface of $\text{STF}_{x=1}$. Moreover, the analysis showed that iron in STF_x perovskite structure participated in mixture of Fe^{3+} and Fe^{4+} ($\text{SrTi}_{(1-x)}[\text{Fe}^{3+}, \text{Fe}^{4+}]_{(x)}\text{O}_{(3-\delta)}$). With increasing iron dopant, the amount of Fe^{3+} and Fe^{4+} significantly increased. Oxygen vacancy was formed. Consequently, with increasing oxygen vacancy, the amount of oxygen lattice reduced. The valence band positions of STF were determined by UPS. The value of SrTiO_3 valence band position (E_{VB}) was reasonably consistent with the results of previous reported work. Moreover, the change in the band positions of UPS analysis were in good agreement with the modeling data that done by A. Rothschild and et.al. UPS results further showed that the Fermi level in the Fe-doped samples was located $4.82 (\pm 0.1)$ (for $\text{STF}_{x=1}$) - $4.32 (\pm 0.1)$ (for $\text{STF}_{x=0}$) eV above the E_{Vac} .

6 Local structure investigation around Fe and Ti in $\text{SrTi}_{(1-x)}\text{Fe}_x\text{O}_{3-\delta}$

6.1 Introduction

In terms of bandgap energy, with increasing iron concentration, it was suggested that the bandgap reduced from 3.17 eV for SrTiO_3 to 1.80 eV for SrFeO_3 [37, 199, 200] and this electronic structural variation might have effect on the photocatalytic properties of the material. In this chapter, the $\text{SrTi}_{(1-x)}\text{Fe}_x\text{O}_{(3-\delta)}$ material was further investigated for the local structure study and electronic properties using the X-ray absorption spectroscopy. The coordination chemistry of iron (titanium) was of particular interest. Information about the valence state and charge transfer of iron (titanium) was obtained from the chemical shift of the absorption spectra, while the pre-edge features of the X-ray absorption near edge structure (XANES) region were related to the d-electron configuration and local symmetry of iron (titanium). The extended X-ray absorption fine structure (EXAFS) region was used to probe local geometric structures up to several coordination shells around iron (titanium) ions, where the Fe–O (Ti–O) distance was of interest in connection with the valence state of iron. In this work, the Fe(Ti) K-edge X-ray absorption fine structure spectra were recorded at room temperature to investigate the local structures of Fe replaced $\text{SrTi}_{(1-x)}\text{Fe}_x\text{O}_{(3-\delta)}$ ($0 \leq x \leq 1$). The local environment around Fe (Ti) centers as well as the local distortion throughout the whole x series revealed by the X-ray absorption spectroscopy were explained in connection with the observed catalytic properties.

6.2 Experimental details

XAFS experiments at room temperature were carried out for the oxide samples and metal foils at the X-ray Demonstration and Development (XDD) beamline of

Singapore Synchrotron Light Source. The beamline provided a focused monochromatic X-ray source of 2.5 ~ 10 keV with a Si <111> monochromator. The experiments were carried out in transmission mode using two ion chambers which record the incident and transmitted X-ray intensities simultaneously. Each sample was ground into fine powders of 400 mesh, pressed into a pellet of 10 mm in diameter. The absorption spectra were recorded at room temperature as a function of photon energy at Ti and Fe K-edges. The data analysis was carried out using the WinXAS package [106]. The energies were calibrated using an Fe foil standard, assigning the first inflection point to 7112 (4966) eV for Fe (Ti)-edge absorption data. A smooth pre-edge background was removed from each averaged spectrum by fitting a first-order polynomial to the pre-edge region, a second-order polynomial to the post-edge region and subtracting this polynomial from the entire spectrum, with all data being normalized. A spline function was fitted to extract the EXAFS amplitude. The oscillations $\chi(k)$ were then obtained as a function of the photoelectron wave vector k ; and further, Fourier transforms weighted by k^3 over the range 3.1-13.1 $\text{\AA}^{-1}$ for Ti and 2.8-12.6 $\text{\AA}^{-1}$ for Fe. The first three shells of Fourier-transformed spectra was filtered out and fitted in the real space by the least square curve based on the single scattering theory [201]. The phase shift and backscattering amplitude were extracted from the crystallographic data of SrTiO_3 and SrFeO_3 , respectively. The inelastic factors, s_0^2 was fixed to 0.95 and 0.72, respectively for Ti and Fe edge data which were obtained by fitting to the standard references.

6.3 Results and Discussion

The coordination chemistry of iron (titanium) is of particular interest. Information about the pre-edge features of the X-ray absorption near edge structure (XANES) region was related to the d-electron configuration and local symmetry of iron (titanium). The extended X-ray absorption fine structure (EXAFS) region was used to probe local geometric structures up to several coordination shells around iron (titanium) ions, where the Fe–O (Ti–O) distance was of interest in connection with the valence state of iron. The Fe and Ti K-edge XANES spectra for the STF_x samples at various x (0, 0.2, 0.4, 0.6, 0.8 and 1) were shown in Figure 6.1 (a) and 6.1 (b), with the standard Fe and Ti foils presented. At the K-edge X-ray excitation, electrons of 1s orbitals were transferred to partially occupied or empty states (XANES region) nearby the Fermi level (3d and 4p-related orbitals). At higher energy, X-rays electrons jumped to the continuum (EXAFS region, where the outgoing electrons were scattered by neighboring atoms) [144, 202, 203]. The pre-edge peaks A and B, main peaks C and D in Figure 6.1 (a) were identified. The pre-edge peaks were related to a pure quadrupole origin due to the 1s→3d transitions in transitional metal oxides [204-206]. Under careful detail observation, the peak A for SrTiO₃ actually appeared as two peaks. As reported earlier [207], A₁ was a pure quadrupolar (E₂), A₂ is partially quadrupolar (and partially dipolar), B was pure dipolar (E₁) and shifted with increasing iron content distortion. Even in SrTiO₃, a high distortion in TiO₆ was observed [208]. A was lowest for the perfect octahedral TiO₆ (Oh symmetry) and was enhanced by a distortion to Oh due to the loss of centro-symmetry. It was suggested that the intensity of the peak B was proportional to the displacement of Ti atoms from

the center of the TiO_6 octahedra [205] but inversely related to the Ti-O bond length. The peak C was a 4p-related “shape resonance” in the continuum part of the spectrum and the peak D was attributed to more delocalized states [209, 210]. The XANES spectra showed almost no edge shift as a function of x but their intensity and shape changed systematically with x. Table 6.1 presents the atomic positions of Sr, Ti, Fe and O in the unit cell of SrTiO_3 and SrFeO_3 perovskites.

The spectra with low Fe content exhibited the lowest pre-edge peak A intensities in Figure 6.1.a. With increasing Fe contents, peak A was stronger and not resolved into two peaks, while B shifted slightly to higher energy.

Table 6.1 Atomic positions in the unit cell of SrTiO_3 and SrFeO_3 perovskites.

Site	Np	x	y	z	Atom
SrTiO ₃					
Sr1	1	0.00000	0.00000	0.00000	Sr
Ti1	1	0.50000	0.50000	0.50000	Ti
O1	3	0.00000	0.50000	0.50000	O ⁻²
SrFeO ₃					
Sr1	1	0.50000	0.50000	0.50000	Sr
Fe1	1	0.00000	0.00000	0.00000	Fe
O1	3	0.00000	0.00000	0.50000	O ⁻²

Figure 6.1 Ti K-edge (a) and Fe K-edge (b) XANES spectra of the $\text{SrTi}_{(1-x)}\text{Fe}_x\text{O}_3$ samples at $x=0, 0.2, 0.4, 0.6, 0.8, 1$. The inset in (a) is a zoomed plot of the pre-edge peaks.

The peak C also shifted slightly toward higher energy. Within the accuracy limit of XANES, it was not observable for any changes or splitting with the peak A in Figure 6.1.(b). This was due to the more closely packed FeO_6 clusters and highly symmetry because of the smaller atomic radius for Fe. With increasing Fe dopant, the intensities of B_1 and B_2 and their ratios changed continuously. No significant shift for the main peak was observed in Figure 6.1.b. After standard data reduction, the $\chi(\kappa) \kappa^3$ function was shown in Figure 6.2 (a) and its Fourier transforms in Figure 6.2 (b) contained the information about the coordination geometry around each Ti. Figures 6.2 (a) and 6.2 (b) show the Ti K-edge and Fe K-edge EXAFS spectra of the STF samples after background removal. The radial structure functions $F(r)$ of STF samples obtained from Fourier transformation of their $k^3\chi(k)$ are shown in Figures. 6.2 (a) and 6.2 (b). After standard data reduction, the $\chi(\kappa) \kappa^3$ function is shown in Figure 6.2 (a) and its Fourier transforms in Figure 6.2 (b) contain the information about the coordination geometry around each Ti. The first peak of the Fourier transform is due to the first Ti-

O shell. The second peak contains the contribution from Ti-8Sr and Ti-5Ti(Fe) and the third shell is Ti-5Ti (Fe).

Figure 6.2.(a) Ti K-edge EXAFS functions, $\chi(k) k^3$ of the $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ samples (x : 0, 0.2, 0.4, 0.6, 0.8, 1.0); (b) Fourier transforms of the EXAFS signals in (a), phase shifts were not corrected.

Two fitting models were applied which fit the first three shells, the coordination numbers (CN) were fixed, the first Ti-O shell was fitted by 4, 2 and 3, 3 respectively. The 4-2 model gave slightly better results and was presented as follows. The two-coordination fitting to the first peak in the Fourier-transform, the Ti-O coordination shows the effect of the Ti displacement in TiO_6 directly. The second peak is due to the eight Sr neighbors at the distance of $3.38 \text{ \AA}$, and the third peak is due to Ti or Fe atoms in adjacent unit cells at the distance of $3.90 \text{ \AA}$, contributing mainly from the linear Ti-O-Ti paths.

Using the 4-2 fitting model, two kinds of Ti-O coordination's are identified, assuming a typical Ti-O (4) (intra-bilayer, bond length R_1) and Ti-O(2) (inter-bilayer, bond length R_2), the Coordination number (CN) are set to 4 and 2, respectively. The fitted R_1 , R_2 , and the mean-square relative displacement or the Debye-Waller factors σ_1^2 and

σ_2^2 are reported in Table 6.2 as a function of x . The bond length of Ti-O(2) R_2 is much shorter for the $x=0.6$ and 0.8 two samples indicating a large distortion for these two samples in TiO_6 . An attempt to fit the $x=0$ sample with two Ti-O shell was not successful, meaning the TiO_6 in SrTiO_3 is relatively less distorted, and introducing Fe has induced a significant displacement of oxygen atoms in the inter-bilayer. Such local distortions can induce some additional energy band splitting near the Fermi level. In addition, the bond length change for the Ti-Ti (Fe) shell is not significant, the Ti-Ti and Ti-Fe are not distinguishable in this shell. Hence it may also contain some Ti-Fe component, but for simplicity, it was fit by only Ti-Ti shells. In the cubic phase of perovskites, the scattering intensity of the third peaks is much larger, this is from the “shadow effect” of the linear Ti-O-Ti(Fe) bond [211-213]. For Ti K-edge data in the STF_x samples when the Fe content of the samples increases, such as sample $\text{SrTi}_{0.2}\text{Fe}_{0.8}\text{O}_3$ and sample SrFeO_3 their shoulder peaks shift to low- R direction at about 0.12 nm. Moreover significant disorder in EXAFS leads to shells not being seen or having severely reduced amplitude to that expected and disorder effects affect the amplitude of the EXAFS [214]. As the Ti content decrease, the amplitude of the Radial distribution functions (RDF) shown in Figure 6.2 (b) becomes weaker and weaker (top to bottom in Figure 6.2 (b)). Comparing their structural disordering factor (σ^2) presented in Table 6.2, it is observed that the disordering of Ti coordination in STF samples increases with the Fe content.

The increase of the Ti (Fe)-O first shell disorder factors can explain by increasing the oxygen vacancy that is confirmed by XRD results data before. At the Fe K-edge absorption near edge, the $1s \rightarrow 3d$ quadrupole transition and $1s \rightarrow 4p$ dipole transition

followed by ligand to metal charge transfer (LMCT) process are shifted to lower energy with increase of the x value, which represents the Fe–O bond covalency decrease systematically [215]. The pre-edge features (Fe 1s→3d transitions) reveal an intensity increase with increasing x , suggesting an increase in the Fe valence state upon titanium substitution [144, 216]. Figure 6.3 (a) and 6.3 (b) presents the experimental Fe K-edge EXAFS signals of the $\chi(\kappa) \kappa^3$ functions and its Fourier transform. XAFS analyses of the Fe K-edge EXAFS spectra also support the XRD and XANES results. The Fourier transform of the $\chi(\kappa) \kappa^3$ (Figure 6.2 (b)) reveals a strong reduction of the Ti–O shell radius in accordance with the formation of Fe⁴⁺ proportional to x . Normally, this would be attributed to a decrease in coordination number. The main reason for this decrease in intensity in Figure 6.2 (b) and 6.3 (b) are most probably due to the formation of the Jahn-Teller Fe⁴⁺ ion (h.s. d⁴), which leads to a distorted FeO₆ octahedron associated with an anomalous increase in the Debye-Waller factor [144, 216]. Iron participated in SrFeO₃ structure with valance Fe⁴⁺ as well that observed previously by Bocquet et al. [217]. Due to the correlation observed for the EXAFS parameters s_0^2 , σ^2 and CN, a more reliable fit was performed by fixing CN = 6 for Fe–O, CN=8 for Fe–Sr and CN=6 for Fe–Fe(Ti) bonds in most stoichiometries. The exception is the $x=0.2$ sample, in which a two Fe–O shell must be adopted, this hints a maximum distortion for the $x=0.2$. Table 6.3 lists the coordination number (CN), bond length and Debye-Waller factors for Fe K-edge data in the STF _{x} samples (x : 0, 0.2, 0.4, 0.6, 0.8, and 1.0). From these data there are no any noticeable changes for $R_1(\text{Fe–O})$, 1.91~1.93 Å, and $\sigma^2(\text{Fe–O})$. It should be mentioned once again that the data for Fe–Fe should include both Fe–Fe and Fe–Ti (which is not distinguishable) coordination's.

Table 6.2 Coordination number (CN), the bond length and Debye-Waller factors at the Ti K-edge EXAFS of the $\text{SrTi}_{(1-x)}\text{Fe}_x\text{O}_3$ samples at $x = 0, 0.2, 0.4, 0.6$ and 0.8 . The error bars are 10% for σ^2 , 0.01 Å for Ti-O1 Ti-O2 and 0.02 Å for Ti-Sr and Ti-Ti.

$\text{SrTi}_{(1-x)}\text{Fe}_x\text{O}_3$	X = 0			X = 0.2			X = 0.4			X = 0.6			X = 0.8		
Bond Lengths	CN	R (Å)	σ^2 ($10^{-3}\text{\AA}^2$)	CN	R (Å)	σ^2 ($10^{-3}\text{\AA}^2$)	CN	R (Å)	σ^2 ($10^{-3}\text{\AA}^2$)	CN	R (Å)	σ^2 ($10^{-3}\text{\AA}^2$)	CN	R (Å)	σ^2 ($10^{-3}\text{\AA}^2$)
[Ti-O]₁	6	1.96	6.7	3	1.95	6	3	1.96	5.6	3	1.95	3.2	3	1.96	5.7
[Ti-O]₂	-	-	-	3	1.87	15	3	1.84	4.4	3	1.76	4.5	3	1.82	6.6
[Ti-Sr]	8	3.39	8.1	8	3.36	13	8	3.35	13	8	3.34	15	8	3.32	14
[Ti-Ti]	6	3.96	1.4	6	3.98	5.4	6	3.98	5.6	6	3.99	7.5	6	3.97	6.3

There is a linear relation between the Fe-O bond length and the iron valence number [218]. In iron oxides (CN=6), the Fe-O bond length reduces as Fe valance gets higher, such as in compounds FeO (2+, 2.10 Å), $\alpha\text{-Fe}_2\text{O}_3$ (3+, 2.00 Å), SrFeO_3 [4+, 1.90 Å] [211, 217, 218]. The shorter Fe-O distance listed in Table 6.3 also implies some tetravalent Fe may exist, consistent with the analysis by [219, 220]. Moreover valance of Ti is 4+ in TiO_6 and the Ti-O distance in STF is similar to other Ti 4+ oxides (TiO_2) thus with Fe replacement, Fe remains also a short Fe-O distance, meaning Fe is mostly 4+ (actually are mixing of the 3+ and +4). As presented in Table 6.2 and Table 6.3, with increasing iron dopant the $[\text{Ti}(\text{Fe})\text{-O}]_{\text{ave}}$ (measured by equation (1)) decreased and also there is some reports explaining that by increasing the bond length of [Ti-O] the consequent [Ti-O-Ti] increased that is due to the formation of titanium oxide crystal and this phenomenon affects the photo catalyst and photo degradation properties of material and its efficiency also decreased[221, 222]. Moreover oxygen vacancies /or defects act as electron traps, which could capture the photo induced

electrons and thus could effectively inhibit the recombination of the photo induced electrons and holes. Also, due to the substitution of Ti with Fe, lattice shrinkage was observed and the largest derivation from the Gaussian distribution in STF_x was from those samples with $x= 0.6$ and $x=0.8$. The substitution of iron by titanium increased the iron valence state, hence the formation of the Jahn-Teller Fe^{4+} ion [221, 222].

According to the obtained data (Figures 6.2 and 6.3, Tables 6.2 and 6.3), the iron and titanium surrounding is highly symmetric and does not depend on the oxide stoichiometry [223]. Figure 6.3 (a) and (b) shows a plot of all interatomic distances from the fitting results of EXAFS data as a function of x . The distances determined by EXAFS analysis exhibit a more detailed picture with different Ti-O and Fe-O distances for the same sample. The plotted distance for Ti-O and Fe-O is the average of [Ti (Fe) –O] of 1 and 2 that is measured by;

$$\text{Average } R = (CN_1 \cdot R_1 + CN_2 \cdot R_2) / (CN_1 + CN_2) \tag{6.1}$$

Table 6.3 Coordination number (CN), the bond length and Debye-Waller factors at Fe K-edge EXAFS of the $SrTi_{(1-x)}Fe_xO_3$ samples at $x = 0.2, 0.4, 0.6, 0.8$ and 1.0 . The error bars are 10% for σ^2 , 0.01 Å for Ti-O1 Ti-O2 and 0.02 Å for Ti-Sr and Ti-Ti.

$SrTi_{(1-x)}Fe_xO_3$	x = 0.2			x = 0.4			x = 0.6			x = 0.8			x = 1		
Bond Lengths	CN	R (Å)	σ^2 (10^{-3}Å^2)	CN	R (Å)	σ^2 (10^{-3}Å^2)	CN	R (Å)	σ^2 (10^{-3}Å^2)	CN	R (Å)	σ^2 (10^{-3}Å^2)	CN	R (Å)	σ^2 (10^{-3}Å^2)
[Fe-O]	4	1.93	8	-	-	-	-	-	-	-	-	-	-	-	-
[Fe-O]	2	1.72	6.9	6	1.92	7.8	6	1.90	7.7	6	1.90	7	6	1.91	6.6
[Fe-Sr]	8	3.35	12	8	3.37	8.6	8	3.34	7.9	8	3.33	7.9	8	3.30	9.3
[Fe-Fe]	6	3.93	6.8	6	3.92	2	6	3.90	1.4	6	3.91	1.1	6	3.92	2.3

In Figure 6.3 for the STF_x samples, the Ti-O distance remains essentially constant, at about 1.95 Å the same as in SrTiO_3 , while the Fe-O distances stay close to that in SrFeO_3 1.91 Å for large x and increase only for $x > 0.4$. Note that the first shell of the TiO_6 and FeO_6 is compactly stacked that changes little with x . The second shell for Ti-Sr and Fe-Sr, R reduces significantly with increasing x . In addition, in the third shell of Ti-Ti(Fe) and Fe-Fe(Ti), using R to estimate lattice parameters, the theoretical values are 3.90 Å for SrTiO_3 and 3.85 Å for SrFeO_3 . The uncertainties for these measurements were ± 0.01 Å for R1 and ± 0.02 Å for R2 and R3.

Figure 6.3.(a) experimental Fe K-edge EXAFS signals of the $\chi(k) \kappa^3$ functions and (b) Fourier transforms of the EXAFS functions for the $\text{SrTi}_{(1-x)}\text{Fe}_x\text{O}_3$ samples (x : 0, 0.2, 0.4, 0.6, 0.8, 1.0), phase shift was not corrected.

Clearly, the substitution of iron by titanium increased the oxygen vacancy. And as explained above oxygen vacancies/defects act as electron traps, which could capture the photo induced electrons and thus could effectively inhibit the recombination of the photo induced electrons and holes [224-226]. Furthermore, when these traps are close enough to the surface, the trapped electrons can react with oxygen. The iron doping generated more oxygen vacancies and /or defects, which could capture the photo

induced electrons and thus could effectively inhibit the recombination of the photo induced electrons and holes. EXAFS study also confirmed that with increasing the substitution of iron by titanium, the structure disorder of STF samples also increase that is related to producing the defects and oxygen vacancy. These data shows a good consistency with XRD, Rietveld analysis that presented in chapter 3 (Section 3.2.1.1) and XPS analysis. Moreover, defects could be regarded as another factor that affects the catalytic activity of STF. The amount of oxygen vacancy can examine by XRD or increase of the first shell disorder factors. The structure disorder of the sample could be regarded as another factor that affects the catalytic activity of STF and the sample with greater σ^2 would provide more oxygen vacancies and /or defects and suitable surface sites.

Figure 6.4 Composition dependence of the bond length in $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ samples (x: 0, 0.2, 0.4, 0.6, 0.8, 1.0) from the first three coordination shells. (a) Ti K-edge and (b) Fe K-edge.

6.4 Conclusions

The electronic properties and local structure of the perovskite STFx ($0 \leq x \leq 1$) systems have been probed by extended X-ray absorption fine structure (EXAFS) spectroscopy. The substitution of iron by titanium increased the Ti (Fe)-O first shell disorder factors that can be explained by the increase in the oxygen vacancies. Consequently, with increasing oxygen vacancy, the amount of oxygen lattice would reduce. This observation can be explained by the bond length of [Ti-O] and [Ti-O-Ti]. With increasing iron dopant the $[\text{Ti(Fe)-O}]_{\text{ave}}$ decreased and bond length of [Ti-O] the consequent [Ti-O-Ti] increased that is due to the formation of titanium oxide crystal and this phenomenon affects the photo catalyst and photo degradation properties of material and its efficiency also decreased. Moreover oxygen vacancies /or defects act as electron traps, which could capture the photo induced electrons and thus could effectively inhibit the recombination of the photo induced electrons and holes. Also due to the substitution of Ti with Fe, lattice shrinkage was observed and the largest derivation from the Gaussian distribution in STFx was from those samples with $x=0.6$ and $x=0.8$. The substitution of iron by titanium increased the iron valence state, hence the formation of the Jahn-Teller Fe⁴⁺ ion.

EXAFS analysis indicates that all samples have quite similar local structure. The peaks A and B (Ti K-edge) reveal an intensity increase with increasing x , suggesting an increase in the Fe valence state upon iron substitution. The Fe K-edge XANES spectra (peak C) of $\text{SrFe}_x\text{Ti}_{(1-x)}\text{O}_3$ are shifted to higher energies with increasing x , which is also an indication for an increase in the valence state of iron. The strong decrease of the intensity of the Fourier-transformed $\chi \times \kappa^3$ functions is probably due to an increase of the Debye-Waller factor arising from the production of Jahn-Teller

distorted Fe(IV) O₆ octahedrons, rather than a decrease of the oxygen coordination number. Results from these experiments indicate that Fe XANES can identify the presence of Fe(6) in a sample. It has been shown that, for the samples measured in this study, the Fe-O bond length is linearly related to the iron valence regardless of the Fe-O coordination number (consistent with valence-dependent ionic radii tables). From the XAFS spectra, the Fe-O, Fe-Sr and Fe-Fe bonding were observed around iron. The chemical state of iron was determined from the results of Fe-O bond-lengths. The average Fe-O bond length in the layer is smaller than that for Fe₂O₃ and FeO. This increase in the Fe-O bond-length is due to the increase in the Fe-valance state. The structure disorder of the sample could be regarded as another factor that affects the catalytic activity of STF and the sample with greater σ^2 would provide more oxygen vacancies and /or defects and suitable surface sites.

7 Band gap study

7.1 Introduction

To shift and improve the activity of photocatalyst material toward the visible light, the band gap of material plays a very important role. The smaller band gap of the material allows for more light absorption by the catalyst, therefore increasing the activity. The development of photocatalyst that yielded high reactivity under visible light would allow the main part of the solar spectrum and even interior lighting to be used. When considering whether visible-light activity could be introduced by doping, the following requirements must be met [70]:

1. Doping should produce states in the band gap that absorb visible light;
2. The conduction band minimum should be higher than the H_2/H_2O level to ensure its photo reduction activity;
3. The new impurity states should overlap sufficiently with the band states of titanium dioxide to transfer photo excited carriers to reactive sites at the catalyst surface within their lifetime.

For measuring the band gap of material, most researchers used the UV-Visible spectra and then measure the transmittion or diffuse reflectance mode for the thin film and powder, respectively. After this step, the Kubelka – Munk model was used to extrapolate the linear part to estimate the band gap of material. However there were some limitations for using this model. Kubelka-Munk model was applicable for low absorbance material although the color of our compounds was almost dark and most of the light was absorbed by the surface of the powder. Thus this method was not applicable for our material. Moreover the narrow band gap was not enough to obtaining good photocatalyst properties, and the position of conduction band was also

important. In this chapter, first we reported the use of the photo-voltaic method to measure the position of conduction band and then combined with the position of valance band obtained from the UPS data to deduce the value of the band gap for our samples.

7.1.1 Determination of conduction band position

TiO₂ photocatalyst, which was first introduced in 1930, is a substance that can change the rate of reaction under the effect of irradiation without changing in amount and properties after the reaction. Under irradiation, a light quantum with energy in excess of the semiconductor band gap, electrons which were initially in the “valence band” can jump to the “conduction band”. As a consequence, holes (h⁺) were left in valence band and the photogenerated electrons (e⁻) in conduction band (equation 7.1).

These holes and electrons can be recombined or undergo photocatalytic reaction. There are two kinds of processes involved in photocatalytic reaction: oxidation process and reduction process.

Reduction process: In this process, electrons from semiconductors surface are transferred to the adsorbates (electron acceptors). Common electron acceptor is O₂, an easy reductant. Oxygen adsorbed on photocatalyst surface receives one electron to form superoxide anion radical [229]. Superoxide can self – dismutase to oxygen molecule and hydrogen peroxide or react with H⁺ to form hydrogenpeoxyl (HO₂•). H₂O₂ can be reduced to form hydroxyl radical OH•.

Oxidation process: in the oxidation process, adsorbates are electron donors. Hole in the valence band take electrons from the adsorbates, most frequently is H_2O . H_2O

Oxidation mechanism: On the other hand, holes at the TiO_2 surface can oxidize adsorbed water or hydroxide ions to produce hydroxyl radicals [230]. Positive holes can oxidize water to yield $\text{OH}^\bullet$ and H^+ .

These radicals, belonging to the oxygen reactive species group, are strong reagents; it has ability to decompose persistent organic pollutants. Besides, photogenerated electrons and holes can react with pollutants directly to decompose them. Photocatalytic activity of semiconductors is driven by the potential difference between valence band/conduction band and redox couple in interest. The energy at the bottom of conduction band determines the reduction ability while the energy at the top of valence band decides the oxidizing ability. Conduction band energy and valence band energy positions determine whether the electrons and holes can take part in, photocatalytic reactions. An effective photocatalyst must possess a conduction band whose energy E_{cb} is more negative than the redox potential of an acceptor and a valence band whose energy E_{vb} is more negative than the redox potential of a donor.

For this system, the common electron acceptor is oxygen O_2 while common electron donor is water. The relative positions of conduction/valence bands of several common semiconductors are shown in Figure 7.1. Figure 7.1 also shows the redox potential for the formation of some oxygen reactive species.

Figure 7.1 Conduction band (top) and valence band (bottom) energy positions for common semiconductors @ pH=0. The values noted on the right axes are the redox potentials for certain common redox couples of interest in water purification [231, 232].

It has long been known that rutile has narrower band gap than anatase, but its photocatalytic activities is much lower. There were many explanations for this phenomenon, such as anatase has indirect band gap while rutile has direct one, hence the recombination rate between holes and photogenerated electrons in rutile form was higher than in anatase form [233]. Banerjee et al. considered optical absorption band gap was the reason make anatase to have higher photocatalytic activity [233]. The wider band gap of anatase led to lower effective mass of photoelectrons, meaning

higher mobility. In his study, Tanaka explained that because of higher Fermi energy level, anatase has higher degree of hydroxylation [234].

Because the difference between the redox potential of a particular reaction and the potential of the valence/conduction band is the driving force of the reaction, determining conduction band/valence band position is a key factor to judge whether the catalyst is good or not. There are several ways determine the conduction band position. One traditional way was to use the Mott- Schottky plot. However, it was difficult to apply this method due to the changes in charge separation due to size and inter particle interactions. Laser flash photolysis was another way to measure the conduction band position [235]. A laser flash photolysis studied of the reduction of methyl viologen by conduction band electrons of TiO_2 and Fe-Ti oxide photocatalysts. This method employed a pulse of laser to excite the generation of electrons and holes. Methyl viologen act as an electron scavenger. The concentration of MV^+ was measured by spectrophotometric method. There are two different methods to measure the conduction band position:

- I. Photo Voltage measurement
- II. Photo-current measurement

The principal of both measurements are same except that in the first method, voltage measurement was used to find the position of conduction band and in the second case current measurement was employed to achieve to this goal.

7.1.2 Photoelectrical quantification of conduction band position

Studies found in literature [236-238] have suggested a couple of related techniques that combined photo-current or photo-voltage measurements along with the use of a pH independent redox couple in order to estimate the position of the conduction band.

In this study, the photo-voltage technique as elaborated by Roy et al [237] was used to find the position of the conduction band for our $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_3$. Without going into the details of the physics, the basic rationale and methodology was described briefly here for the benefit of the readers. The position of the Fermi level and conduction band of a semiconductor oxide in contact with an aqueous solution is dependent on the pH of the aqueous solution. The exact nature of this dependence is a function of the material. The ability of a photoelectron to participate in a photo reduction of a species depends on the relative positions of the photoelectron Fermi level and the redox potential of the reduction reaction being considered. Certain redox couples such as methyl viologen $[\text{MV}^{2+}/\text{MV}^+]$ are pH independent. Thus the combination of a pH dependent oxide conduction band and a pH independent redox couple provides a way to estimate the position of the semiconductor oxide conduction band by varying the pH of the aqueous solution containing the oxide and methyl viologen. Figure 7.2 presents the relative positions of energy bands of semiconductor at different pH.

Figure 7.2 Relative positions of energy bands of semiconductor and E_0 , the Fermi level of the electron acceptor at different pH.

At low pH the quasi-Fermi level potential is more positive than the redox potential of

an electron acceptor (E_0). Then the excited electron from the conduction band is not able to reduce MV^{2+} but becomes possible at $pH \geq pH_0$, when $E_f \leq E^\circ$. The quasi-Fermi level potential depends on the pH [237].

The fundamental and basic of the methyl viologen experiment was summarized in table 7.1.

Table 7.1 The Effect of relative positions of energy bands of semiconductor at different pH

$pH < pH_0$	$E_f < E_0$	No photogenerated electrons
$pH = pH_0$	$E_f = E_0$	Onset of photo-voltage (MV^{2+} is reduced)
$pH > pH_0$	$E_f > E_0$	E.m.f (E) increase, $[MV^+]$ increase, lead to the formation of blue color

- pH_0 is the pH at which Femi level is in equilibrium with redox potential of MV^{2+}

In this study, we determined the position of conduction band based on the measurement of photo-voltage resulted from irradiating photocatalyst suspension in the presence of an electron acceptor (methyl viologen MV^{2+}). When exposure to light, photogenerated electrons were formed. These electrons were trapped by the methyl viologen. A working electrode was used to collect the photogenerated charge of the semiconductor particles. Methyl viologen MV^{2+} was suitable for this measurement because of its well-known redox potential, which was independent of pH. It was also a stable chemical; and not took part in the photochemical and chemical reactions. Methyl viologen underwent one electron reduction to form MV^+ , a stable intermediate.

This reaction is highly reversible and has redox potential of -0.45 vs. NHE. Because oxygen – a good electron acceptor – can act as competing reagent, the solution was deoxygenated before used.

7.2 Experimental setup

The experiment was conducted by using KNO_3 (0.1M) as the electrolyte and to control the pH HCl and NaOH were used. The suspension (containing the powder photocatalyst (0.15 g in 100 ml)) was deaerated by bubbling N_2 gas through it for 1 hour. Since oxygen can scavenge the electrons much better than the methyl viologen, thus the experiment was performed by excluding oxygen from the system. Then 0.012 g methyl viologen dichloride was added to the solution and the suspension was degased for a further 30 minutes. Figure 7.3 presents the schematic of the experimental setup of methyl viologen experiment.

Figure 7.3 a) Laboratory set-up for quasi-Fermi level potential determination: 1- suspension of catalyst, 2-magnetic stirrer, 3-reference electrode (Ag/AgCl), 4-working electrode (Pt), 5- pH electrode, 6-nitrogen inlet Schematic of experimental setup used to measure photo-voltage generated when methyl viologen is reduced and b) Schematic diagram of electrochemical photocell: 1- n-type TiO_2 electrode; 2- platinum black counter electrode; 3- ionically conducting separator; 4-load resistance; and 5-voltmeter [237].

The measurement of photo-voltage was developed by irradiating the suspension with visible light in the presence of an electron acceptor (methyl viologen MV^{2+}) (open circuit potential measurement). Photogenerated charge of semiconductor particles was collected by an inert Au electrode (WE) with big surface area (1 in^2). A saturated calomel electrode (Ag/AgCl) was immersed as the reference. In an irradiated semiconductor suspension, photo-voltage or photo-current was enhanced by adding a small amount of electron trapping agent (in this case MV^{2+}). When irradiated under light, a non-equilibrium population of e_{CB}^- and h_{VB}^+ was generated, thereby splitting the Fermi level into 2 quasi Fermi levels, one for the hole (VB) and one for the electrons (CB), $E_f(e^-)$. The photogenerated electrons at conduction band were trapped by MV^{2+} to form MV^+ (equation 7.7).

7.3 Results and Discussion

Stable photo-voltages were recorded about 30 min after changing the pH value. The value of pH_0 was estimated by plotting the photo-voltage data vs pH value. Once the methyl viologen transformed from oxidized to reduced form, the color changed from colorless to blue. The changing of the color functioned as an additional qualitative indicator for the present of the occurrence of the methyl viologen reduction reaction. The method was based on voltage measurements (Roy, 1995) [236] and Current measurement (Bard 1983) [239] between these electrodes upon irradiation as a function of pH (Bard 1983). The obtained pH_0 values were converted to the E_{fb} at pH_0 or any pH by the equation 7.8 [236].

$$E_{fb} = -0.445 + 0.059 (pH_0 - pH) \quad (7.8)$$

Figure 7.4 (b)-(d) presents the data of the photo voltage measurement for P25, STF_{0.8} and STF₁.

Figure 7.4 a) Schematic of photo voltage setup and dependences of photo-voltage (V vs Ag/AgCl) on pH value of electrolyte for: b) P25 (TiO₂), c) STF_{0.8} and d) STF₁

Under Visible illumination a steadily increasing current was observed, that was related with the forming of the blue methyl viologen radical cation (MV⁺). When the light was illuminated, the anodic current continued and decayed slowly to zero as MV⁺ was oxidized at the electrode. Table 7.2 summarizes the result of photo voltage and photo current.

Figure 7.5.(a) presents the Photo-current vs. time plot. When the catalyst suspension was illuminated, the anodic photocurrents were produced at an inert metal electrode (collector electrode) immersed in the suspension. This current raised for a short period

of time, achieving a maximum of 6 μA in 1.5 min. The anodic photo-current resulted from the production of electron-hole ($e-h^+$) pairs followed by reduction of holes by reaction with acetate and collection of electrons at the electrode. The current was limited by the accumulation of electrons on the particles which increased the rate of $e-h^+$ recombination. When the light was removed, the anodic current persisted and decayed slowly to zero as MV^+ was oxidized at the electrode. During this decay, the blue color of MV^+ diminished; at zero current only colorless MV^{2+} was apparent. For oxide semiconductors, E_F depends upon the pH of the contacting solution. Indeed, the rate of photo-current increased during illumination, $\Delta i / \Delta t$, was found to depend on the pH of the catalyst suspension containing MV^{2+} . As the pH of the suspension was increased by incremental addition of 1.0 M NaOH solution, $\Delta i / \Delta t$ increased significantly and in the end reached a plateau at very high pH values (pH > 9 (depend on the composition of catalyst)). Using the extrapolation curve the value of pH_0 can be estimated as shown on Figure 7.5.(b).

Figure 7.5. (a) Photo-current vs. time for stirred STF_1 suspension @ adjusted pH = 5.4 photocell containing MV^{2+} , light on; 250 s. (b) Dependence of rate of the change of photo-current with time ($\Delta i / \Delta t$) on pH for stirred STF_1 suspension photocell.

Table 7.2 The results of conduction band position measurements by photo voltage and photo-current method.

Samples	Position of CB	Position of CB	Position of CB
	@ pH =0 (by Photo voltage method)	@ pH = 7 (by Photo voltage method)	@ pH =0 (by Photo-current method)
P25	- 0.111	- 0.525	N.A
SrTi _(1-x) Fe _(x) O ₃	- 0.058	- 0.4715	N.A
SrFeO ₃	- 0.029	- 0.4420	- 0.088

7.4 Conclusions

The photo-voltage and photo-current results suggested that the conduction band position became more negative for STF_x by changing the x. Figure 7.6 summarizes the conduction band and valence band positions obtained for the STF_x samples. Note that the photo-voltage experiment provided the conduction band positions only and the position of valence band was measured in the previous chapter by UPS measurement.

Figure 7.6 Conduction band and valence band positions for P25 and STF_x .

8 Photocatalysis properties and Methylene Blue degradation test

8.1 Experimental setup

The photocatalytic activity of the nanoparticles was evaluated by measuring the decomposition of methylene blue at 650 nm. The experiment of photocatalytic reaction was conducted in a 50 mL cell culture vessel with continuous magnetic stirring. The as-prepared SFO was used as photocatalyst, and the mixture of only DI water with Methylene blue (MB, 0.0313 M for 10.8 $\mu\text{mol/L}$) was used as a control sample. Moreover all the data were compared with results using Degussa P25 particle under the same conditions.

8.2 Results and Discussion

There were some reports on the effect of particle size on photocatalytic properties of TiO_2 nano powders [207]. The particle size of the powders directly affected the surface area and surface reaction of the powders. Figure 8.1.(a) presents the typical absorbance of MB under visible light illumination from 0 to 12 hours. Strontium ferrite powders with different particle size and time of milling were chosen to investigate the photocatalytic activity of the nanopowders and sampling was done for 0, 1, 2, 3, 5, 7, 10 and 12 hours.

To investigate the effect of surface area on photocatalytic properties, high temperature solid state powders were milled (described in Chapter 4) for different times. From The photocatalytic test, SrFeO_3 (SFO) showed the best efficiency for photodegradation and decolorization of Methylene Blue (8.1.(b)) so we focus in this composition. Figure 8.2 shows a plot of C/C_0 versus time for all the experiments of photocatalytic decomposition, where C_0 was the initial concentration of methylene blue. The results demonstrated that degradation was faster in the solution with finer powder, which can

be ascribed to the increase in surface area and the number of active sites on the finer powder. From Figure 8.2 all powders showed the ability to degrade methylene blue after prolonged exposure time. All powders performed better than the P25 powder. Thus, it can be concluded that the SFO powder works as a photocatalytic material. The high temperature SrFeO_3 sample after 5 hours milling showed best performance due to minimum crystallite size and maximum surface area and showed the best photo degradation reaction in methylene blue solution.

Figure 8.1 (a). Absorbance of methylene blue under visible illumination from 0 to 12 h (b) Methylene blue degradation by high temperature STF_x ($x= 0-1$) powder with different composition.

Figure 8.2.(a) also shows that the performance of high temperature SrFeO_3 sample after 5 hours milling was not much different compared with the sample milled up to 30 hours and 50 hours. This can be explained by Figure 8.2.(b), which shows that the crystallite size of high temperature SrFeO_3 powder reached a minimum at 4 to 5 hours ball milling.

Figure 8.2. (a) Methylene blue degradation by high temperature SFO powder with different milling time and (b) The size and size distribution of SrFeO₃ nanoparticles before and after milling.

Therefore, the optimal ball milling time for the high temperature SrFeO₃ powder was set to 5 hours. Beyond 5 hours, the photocatalytic performance of high temperature sintering SrFeO₃ powder did not improve any further.

8.3 Kinetic modeling

Based on literature reports, the chemical kinetic of photocatalytic dye oxidation in liquid systems can be described by a first-order model with respect to the dye concentration. Using this hypothesis, the reaction rate for the second order surface decomposition of methylene blue can be written in terms of the Langmuir–Hinshelwood kinetics [240, 241]. The Langmuir–Hinshelwood model can be written as

$$r = k \frac{K[C]}{1 + K[C_0]} = k_{obs}[C] , \quad (8.1)$$

$$\frac{1}{k_{obs}} = \frac{1}{kK} + \frac{C_0}{k}, \quad (8.2)$$

where C_0 is the initial concentration of methylene blue (MB) (ppm), K is the Langmuir – Hinshelwood adsorption equilibrium constant (ppm⁻¹), k is the second order rate constant of surface reaction (ppm min⁻¹), and k_{obs} is the pseudo-first-order rate constant (min⁻¹) that satisfies

$$-\frac{dC}{dt} = k_{obs} C_0 \quad (8.3)$$

giving

$$-\ln\left(\frac{C}{C_0}\right) = k_{obs} t. \quad (8.4)$$

For the case of methylene blue (MB) the Langmuir-Hinshelwood kinetics can be given by

$$r = -\frac{d[MB]}{dt} = -\frac{kK[MB]}{1 + K[MB]_0} \quad (8.5)$$

where r is the rate of dye mineralization, k is the rate constant, $[MB]$ is the dye concentration, and K is the adsorption coefficient. The implicit solution for equation 8.5 is

$$\ln\left(\frac{[MB]}{[MB]_0}\right) + K([MB] - [MB]_0) = -kKt. \quad (8.6)$$

Equation 8.6 can be solved explicitly for t by using discrete changes in $[MB]$ from the initial concentration to a zero reference point. The model presented in Equation 8.6 yielded an exact solution for the degradation of methylene blue. However, when the concentration was in the scale of millimoles, an apparent first-order model can be assumed [220], such that

$$r = -\frac{d[MB]}{dt} = k'[MB] = kK[MB] \quad (8.7)$$

Integration results in either

$$[MB] = [MB]_o e^{-k't} \quad (8.8)$$

$$\ln\left(\frac{[MB]_o}{[MB]}\right) = -kKt = -k't, \quad (8.9)$$

where k' is in units of time^{-1} . The assumption of a pseudo-first order model was used in several studies to characterize the effect of different experimental conditions on the degradation rate [221].

Figure 8.3 shows the results of methylene blue degradation by SFO powder under visible light illumination. The semi log data plot did not produce a single straight line, hence did not fit a simple first-order reaction model for the entire period of visible illumination examined. This plot presented three linear regions that can be explained by a series of reaction mechanism. Figure 8.3 suggests a series of reaction mechanism for photocatalytic degradation of organic dyes, described by

In the first stage of reaction, the methylene blue was absorbed by the surface of the powder; It means first some amount of Methylene blue were absorbed by surface of powder and then the reaction between our material and Methylene blue started from there. Next, the organic dyes were degraded into intermediate products. The reaction rate for this step C_D was described by equation 8.11. After this step, the intermediate products, CI were transformed in to colorless products, with a reaction rate given by

equation 8.12. Finally, the surface of the powder particles was saturated by intermediate and colorless products and the reaction rate decreased .

Figure 8.3. (a) Data plot of methylene blue degradation by SFO powder under visible light illumination (b) schematic of series of reactions.

If the consumption reactions of the dye and intermediate are both first-order, then CI can be described with respect to time by

$$\frac{d[C_D]}{dt} = -k_2 C_D \Rightarrow C_D = C_{D(0)} \exp(-k_2 t) , \quad (8.11)$$

$$\frac{d[CI]}{dt} = k_2 C_D - k_3 C_I \Rightarrow C_I = \left(\frac{k_2 C_D}{k_3 - k_2} \right) ((\exp(-k_2 t) - \exp(-k_3 t))) . \quad (8.12)$$

Table 8.1 presents the reaction rate at each step calculated from the slopes of a straight line obtained by plotting $-\ln(C/C_0)$ versus reaction time (Figure 8.3). The results show that the Step 1, Step 2 and Step 3 for P25 were constant, which can be explained by the fact that P25 works under UV- light and was not sensitive to visible light. For the milled powder (for more than 3 hours) the slope of Step 3 was smaller than Step 2 due to saturation of the powder surface. The reaction rate of this step was lower than step

2 for the case of 0 and 1 hour milled powder because the surface of powder was lower. The reaction rate of first step (Step 1) was not as high as that for the 3 hour milled powder; hence the saturation case in step three was negligible. This table also confirmed that the optimized time for milling was 5 hour to achieve optimum reaction rate.

Table 8.1 Kinetic rate constants of methylene blue (MB) at various ball-mill times.

Samples	$k_{\text{Step 1}} (\text{hr}^{-1})$	$k_{\text{Step 2}} (\text{hr}^{-1})$	$k_{\text{Step 3}} (\text{hr}^{-1})$
P25	0.03	0.0281	0.0271
0 hr milled	0.061	0.2548	0.4958
1 hr milled	0.191	0.5019	0.7699
3 hr milled	0.3147	1.0195	0.246
5 hr milled	0.4727	0.8791	0.2623
30 hr milled	0.515	0.9057	0.2062
50 hr milled	0.4344	0.9025	0.2056

8.4 Product analysis and identification using HPLC–MS studies

To obtain a better insight into the catalytic mechanism of the SrFeO_3 powders with Methylene blue (MB), the degradation of Methylene blue, under both dark and light conditions was measured. 10 mg of SrFeO_3 powders were dispersed in DI water and added to the MB solution with 10 ppm concentration. The initial pH value of the SrFeO_3 and MB solution at both dark and light conditions were 9.35 and 9.15 respectively. For this experiment a precise continuous setup was used to investigate the Methylene blue degradation and by products in situ. Figure 8.4 presents the Methylene blue degradation for the dark and light conditions.

As shown in Figure 8.4, a degradation of Methylene blue in dark condition was observed. This can be explained as the self-degradation of Methylene blue at basic pH values. The slope of the curve in light condition increased, compared with the two

dark conditions. This higher rate can be explained by the increase in the degradation of Methylene blue in the presence of light. In addition the slope for the light condition was not exactly linear and can be explained by the three different steps including (initiation, propagation and termination) in the following section (Figure 8.4).

Figure 8.4 Methylene blue degradation by high temperature SFO powder in light and dark region

The chromatographic separation of the dye solution initially and during the photocatalytic process were recorded and monitored. To show that the degradation of Methylene blue occurred in three steps, several sampling in dark and light conditions were made and the by-product of the reactions analyzed using the HPLC equipment. The gradient HPLC separation was coupled with the ion trap mass spectrometer. The degradation of the dye was captured by the qualitative analysis of the samples studied by HPLC before and after photocatalytic degradation. Further analysis of the product formation was done by mass spectroscopic (MS) studies of the degradation intermediate products and the results were shown in Figure 8.5. Many peaks of

different intensities were observed in addition to the peak of Methylene Blue dye, which indicated the variation in the composition and concentration of the degradation products. By studying some of these intermediate masses and predicting their structure by the cleavage of one or more of the methyl groups substituent on the amine groups, that led to the production of intermediate products, it was found that there was agreement in their masses with the intermediates formed. For instance, the formation of azure B and thionin (Figure 8.5) through the demethylation cleavage during the photocatalytic degradation has been reported in the literature [221]. From the HPLC peak area calculations, it was found that Methylene blue structure broke into the azure B and then cleavage to thionin. As expected Methylene blue structure degraded even in the dark condition (Figure 8.5.(b).2). However the slope of part under light in comparison with the two parts under dark was higher and can be explained by the increase in the degradation of Methylene blue in the presence of light. Moreover the rate of producing the Azure B increased when the light was turned on (Figure 8.5.(c).2) and after further exposure to light decreased because at the same time this intermediate product started to breakdown and produced the thionin.

8.5 Conclusions

In this work, we have successfully prepared photocatalytic strontium ferrite particles using a high temperature solid state reaction method. Determining the optimal processing condition required adjustment of ball milling time. The single phase nano materials showed better photocatalytic degradation of methylene blue in the visible light compared to P25. The improved performance of samples milled

for 5 h relative to samples milled for more or less time was attributed to the optimum particle size, providing large reaction area.

Figure 8.5. (a) HPLC peaks for Methylene blue (284) Azure B (270) and Thionin (227) and Mass spectra of the major detected degradation intermediates (b) for Methylene blue peak (c) Azure B (d) Thionin and (2) it's related area under curves.

9 Conclusions and Recommendations

9.1. Conclusions

This research has successfully met all the tasks defined in Section 1.3, through which the four objectives set in Chapter 1 have been fulfilled. The contribution of the work undertaken by the author can be summarized as follows:

- In this study, the preparation of nanostructured metal oxide $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_{(3-\delta)}$ materials, characterization of materials, and photocatalyst properties have been systematically investigated. The nanostructures $\text{SrTi}_{(1-x)}\text{Fe}_{(x)}\text{O}_{(3-\delta)}$ materials have been successfully synthesized by high energy ball milling, wet chemical and high temperature solid state reaction techniques. As explained in section 4.1.2 the content of amorphous can affect the photocatalyst activity of powder [23], therefore after preparing all powders, the high temperature solid oxide method was chosen as the preparation method. Micro structure study was performed by XRD and TEM and the crystal structure, lattice parameter, crystallite size, grain boundaries and dislocations of powder have been described.
- In order to enhance the surface and structural properties of this metal oxide various structural characterization techniques have been used. The surface chemistry of powder was investigated systematically by using X-ray Photoelectron Spectroscopy (XPS) and the valence band structure study were performed by using UPS (Ultra violet Photoelectron Spectroscopy (UPS)). XPS results showed that iron in STF_x perovskite structure participated in mixture of Fe^{3+} and Fe^{4+} ($\text{SrTi}_{(1-x)}[\text{Fe}^{3+}, \text{Fe}^{4+}]_{(x)}\text{O}_{(3-\delta)}$). In this state with increase in the iron dopant, the amount of Fe^{3+} and Fe^{4+} significantly increased and oxygen

vacancy was formed consequently. With increasing the oxygen vacancy, the amount of oxygen lattice reduced. The valence band positions of STF were determined by UPS. The value of SrTiO_3 valence band position (E_{VB}) was reasonably consistent with the results of previous reported works. Moreover, the change in the band positions of UPS analysis was in good agreement with the modeling data done by A. Rothschild and et.al. UPS results further showed that the Fermi level in the Fe-doped samples was located $4.82 (\pm 0.1)$ (for STF $x=1$) - $4.32 (\pm 0.1)$ (for STF $x=0$) eV above the E_{Vac} .

- The local structure around Fe and Ti in the STF_x perovskite structure was investigated by the X-ray absorption spectroscopy. This analysis was a useful method to investigate the local structural and electronic properties of these compounds. The coordination chemistry of iron (titanium) was of particular interest. In this work, the Fe(Ti) K-edge X-ray absorption fine structure spectra were recorded at room temperature to investigate the local structures of Fe replaced $\text{SrTi}_{(1-x)}\text{Fe}_x\text{O}_{(3-\delta)}$ ($0 \leq x \leq 1$). The local environment around Fe (Ti) centers as well as the local distortion throughout the whole x series, revealed by the X-ray absorption spectroscopy, were explained in connection with the observed catalytic properties. EXAFS analysis indicated that all samples have quite similar local structure. For the samples measured in this study, the Fe-O bondlength was linearly related to the iron valence regardless of the Fe-O coordination number (consistent with valence-dependent ionic radii tables). From the XAFS spectra, the Fe-O, Fe-Sr and Fe-Fe bonding were observed around iron. The chemical state of iron was determined from the results of Fe-O bond-lengths. The average Fe-O bondlength in the layer was smaller than

that for Fe_2O_3 and FeO . This increase in the Fe-O bond-length was due to the increase in the Fe-valance state.

- The band gap of STF_x material was successfully studied by measuring the position of the valence band using the UPS measurement together with the position of the conduction band carried out using the photo-voltage and photo-current study. The photo-voltage and photo-current results suggested that the conduction band position become more negative for STF_x . These studies reveal that the band gap of SFO and $\text{STF}_{0.8}$ were 1.8 and 2.6 respectively.
- Catalyst performances of STF_x material were successfully compared and measured by slurry and bed reactor setup. In both cases the degradation of Methylene Blue was successfully measured. The results of this study revealed that STF_x showed good photocatalyst properties and has potential for more studies in water treatment, water splitting and photocatalyst field.

9.2. Recommendations for Future Research

Based on the work reported in this thesis there are several areas which can be considered for future research.

1. Further improvement of the synthesized material to enhance their photocatalytic performance, including using heterogeneous approach such as the core-shell structure. By using the core-shell method, the new heterojunction with lower band gap can be produced and the photocatalyst properties of STF_x powders improved. Figure 9.1 presents a TEM images of core-shell $\text{SrFeO}_3\text{-TiO}_2$ and $\text{TiO}_2 / \text{SiO}_2 - \text{SrFeO}_3$ that were obtained in our preliminary study.

Figure 9.1 TEM micrograph of (a), (b) Titania shell (10% v/v) on SrFeO_3 nano particle (c) SAED could be index as SrFeO_3 and titania (ring pattern) (d) $\text{SiO}_2/\text{TiO}_2$ nano particle after SrFeO_3 coating.

2. More detail study on the photocatalyst properties using different method including study of OH radical using Cytc C electrode. The coated electrode could then be calibrated using Xanthineoxidase. As the life time of OH radical is too short (femtosecond) the Cytc C electrode could be used to measure the super oxide radical. In this method thiol can be first coated on the surface of gold electrode and then followed by cyt c. Next the electrode is calibrated by using Xanthineoxidase. During photocatalyst reaction some superoxide and OH radical are produced in the solution. The superoxide is measured using the enzyme electrode and then used the (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) compound. This is a kind of scavenger and the concentration before

and after visible irradiation can be analyzed using HPLC- Mass Spec and finally the OH radical can be obtained indirectly.

There are several ways to enhance binding ability of electrode surface to protein: adsorption, gel trapping and making self – assembled monolayer (SAM). SAM is the method in which hydrocarbon chains with thiol group at one end and a carboxylic or amine group at the other end are used. It is based on chemisorption of thiol compounds on gold surface. The role of Di(N-succinimidyl) 3,3'-dithiodipropionate (DTSP) as linker is illustrated in figure 9.2.

Figure 9.2. Scheme of preparing DTSP-protein electrode [242].

Electrodes modified with SAMs can response to SO, however, they are not sensitive. They can response to many interferes such as hydrogen peroxide and ascorbic acid. Another problem with DTSP modified electrode is DTSP can trap Xanthineoxidase enzyme (the enzyme used for generating SO). Therefore, to increase the sensitivity and selectivity of biosensor, a redox protein, in this case, cyt c is employed. Cyt c is well-studied in electrochemistry and spectro electrochemistry. The summary of electron transfer pathway is shown in figure 9.3.

Figure 9.3 Electron transfer underlying cyt c-biosensor.

Figure 9.4 presents some of initial data obtained in our preliminary study done at UIUC University. This work could allow for the creation of novel method to measure and investigate the photocatalyst properties of catalyst in future.

Figure 9.4 a) CV of cyt c electrod in 0.05 M H₂SO₄ solution b)calibration curve of electrode by Xanthineoxidase c) results of superoxide measurment in presense of visible light (blue) and dark condition (blak).

3. Our preliminary study on the SrTi_(1-x)Fe_(x)O_{3-δ} (STF_x (x=0 ~ 1)) powders reveals promising information and it is desired to go further in the photo catalysis study using other dyes and non-dye based organics to fully test the synthesized nano-structure materials as well as to extend to anti-bacterial study for biological degradation. Moreover because this material has enough potential for water treatment and air purification application more study on the catalyst life and separation of STF powder in water treatment application are also suggested.

Author's publications

- 1- **M.Ghaffari** , P.Y.Tan, M.E.Oruc, O.K.Tan, MS Tse ,M.Shannon ,*“Effect of ball milling on the characteristics of SrFeO₃ nano powder for visible light photocatalytic applications and its reaction kinetics”*, Catalysis Today, Volume 161, Issue 1, 17 March 2011, Pages 70-77 .
- 2- **M.Ghaffari**, H.Hui, M.Shannon, O.K.Tan and A.Irannejad,*“ Preparation, Surface State and Band Structure Studies of SrTi_(1-x)Fe_(x)O_(3-δ) (x=0 ~ 1) Perovskite-Type Oxides by X-ray and Ultraviolet Photoelectron Spectroscopic”* Journal of Surface science, Volume 606, Issues 5–6, March 2012, Pages 670–677.
- 3- **M. Ghaffari**, H.Hui, O.K.Tan *“Synthesis and visible light photocatalytic properties of SrTi_(1-x)Fe_xO_(3-δ) powder for indoor decontamination”* Journal of powder technology, *In Press, Accepted Manuscript*.
- 4- **M. Ghaffari**, T. Liu, O. K. Tan and B.Agnieszka, *"Preparation and Characterization of SrTi_(1-x)Fe_xO₃ and investigation of Effect of Local structure and X-ray absorption characteristics (EXAFS) of Fe (Ti) K-edge of SrTi_(1-x)Fe_xO₃ on its photocatalyst properties "* Journal of Photochemistry and photobiology, under review.
- 5- **M.Ghaffari**, O.K.Tan, P.Y.Tan, *“Preparation of SrTi_(1-x)Fe_xO_(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 (SPEA6).

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APPENDIX A. PHOTO REACTOR SETUP

This appendix provides the detail of the photocatalyst test and photocatalyst reactor. The photocatalyst properties of STF samples investigated by measuring degradation of methylene blue in visible light. Figures A.1 – A.9 in this appendix briefly describe the different parts of photo reactor setup. Further details, data and discussion are available in chapter 3 and chapter 9.

Photocatalyst system

Figure A.1 Setup for photochemical testing of the photocatalysts.

Figure A.2 Schematic flowchart of photochemical testing setup.

Part 1: solution

Figure A.3 Schematic flowchart of solution part of photochemical testing setup.

Figure A.4 Schematic flowchart of pump part of photochemical testing setup.

Figure A.5 Schematic flowchart of photo reactor part of photochemical testing setup.

Figure A.6 Schematic flowchart of details part of photo reactor.

Figure A.7 Schematic flowchart of Z cell part of photochemical testing setup.

Part 5: Light source

Figure A.8 Schematic flowchart of light source.

Part 6: Spectrophotometer

Figure A.9 Setup for photochemical testing of Spectrophotometer.