Perovskite-metal-oxide-based advanced oxidation technology for water treatment application

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**PEROVSKITE-METAL-OXIDE BASED ADVANCED
OXIDATION TECHNOLOGY FOR WATER TREATMENT
APPLICATION**

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SCHOOL OF ELECTRICAL AND ELECTRONIC ENGINEERING
2014**

Perovskite-Metal-Oxide-Based Advanced Oxidation Technology for Water Treatment Application

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A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2014

Statement of Originality

I hereby certify that the works enclosed in this thesis is the results of original research and have not been submitted to any other universities or institutions for a higher degree.

Date

Leiw Ming Yian

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Summary

The development of cost-effective advanced technologies for water treatment and wastewater recycling is highly desirable to ensure the adequacy of clean water supply and safe discharge as well as prevent further worsening of water scarcity. In recent years, intense research has been devoted to develop advanced oxidation technologies (AOTs), which rely on the generation of reactive species to degrade a wide range of pollutants. However, the current AOTs often involved chemically and energetically intensive processes, which are undesirable to be integrated for a cost-effective, large-scale system for water treatment and wastewater recycling.

In this project, Strontium Ferrite ($\text{SrFeO}_{3-\delta}$, SFO) based sub-micron sized particles with perovskite crystalline structure were studied as a potential alternative material for the development of novel bi-functional AOT with or without the need of external light stimulant under ambient condition to achieve a low cost and green water treatment system.

The SFO metal oxides with single perovskite structure were synthesized by a combination of high temperature solid state reaction and high-energy ball milling process. The milled SFO metal oxide was systematically characterized to investigate the crystalline structure and the surface properties. The synthesized SFO metal oxides were investigated for the oxidative degradation of two toxic and carcinogenic man-made model pollutants in water that have attracted increasing attention and efforts for

their proper treatment in the water supply and ecosystem, namely the Bisphenol A (BPA) and Acid Orange 8 (AO8). High degradation efficiency of these pollutants at high concentration in water was achieved using the milled SFO metal oxide particles dispersed inside a simple reactor after reacting for some times under dark ambient condition and without the use of other chemical. Superoxide anion radicals were indirectly identified, by the use of suitable scavengers in a series of further study, to be the predominant reactive oxidative species responsible for the dark oxidative degradation of the pollutants. The superoxide anion radicals were likely formed through interaction between the adsorbed oxygen molecules and the surface oxygen vacancies on the surfaces of the milled SFO metal oxide particles. Based on these results, a possible BPA degradation pathway was proposed and illustrated.

Furthermore, repeatability tests showed that the milled SFO metal oxide could be reused for at least four AO8 degradation cycles with comparable good degradation efficiency. During the repeated tests, the milled SFO metal oxide was found to exhibit decomposition into strontium carbonate due to carbon dioxide poisoning.

To improve the structural stability of milled SFO metal oxide, iron atoms were replaced with titanium atoms to form the solid solution Strontium Titanate Ferrite ($\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, STF_x) metal oxides with various Ti molar ratio to the total (Ti + Fe) composition in the range of 0 to 100 %. With increasing titanium content, the structural stability of milled STF_x metal oxides was greatly enhanced. However, the substitution of iron atoms by titanium atoms reduced the amount of surface oxygen vacancy on milled STF_x metal oxides and thus the amount of active oxidative species, which in turn suppressed the oxidative activity of milled STF_x metal oxides. When more than 80 % of iron atoms were replaced by titanium atoms, the surface charge

state of milled STFx metal oxides was found to change from positive to negative, leading to poorer adsorption and hence lower degradation of the anionic BPA and AO8 pollutants. There was a tradeoff between oxidative activity and structural stability for the milled STFx metal oxides.

In summary, this research project demonstrated the potential of both perovskite SFO and STFx metal oxides as alternative materials for the development of novel bi-functional AOT and provided scientific insights to the physiochemical properties of metal oxides required when designing a robust advanced oxidation process (AOP) for water treatment.

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List of Abbreviations

Chemical Names

BiVO_4	Bismuth vanadate
Bi_2WO_6	Bismuth tungstate
C	Carbon
CCl_4	Carbon tetrachloride
CeO_2	Cerium (IV) oxide
Co	Cobalt
CO_3^{2-}	Carbonate anion
COD	Chemical oxygen demand
Fe^{2+}	Ferrous ion or Fe (II) ion
Fe^{3+}	Ferric ion or Fe (III) ion
Fe^{4+}	Tetravalent iron ion or Fe (IV) ion
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	Iron (III) chloride, hexahydrate
Fe_2O_3	Iron (III) oxide
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Ferrous sulfate heptahydrate
Hg	Mercury
$\text{HO}_2^\bullet$	Hydroperoxyl radical
H^+	Hydrogen ion
H_2O_2	Hydrogen peroxide
KOH	Potassium hydroxide
KBr	Potassium bromide
KBrO_3	Potassium bromate
NaOH	Sodium hydroxide
NaN_3	Sodium azide
NO	Nitrogen monoxide
O^-	Monatomic oxygen ions
O	Oxygen

O_2^-	Diatomic superoxide
$O_2^{\bullet -}$	Superoxide anion radical
O_2^{2-}	Peroxide species
O_3	Ozone
1O_2	Singlet oxygen
$OH^\bullet$	Hydroxyl radical
Pt	Platinum
SnO_2	Tin (IV) oxide
Sr	Strontium
Sr^{2+}	Divalent strontium ion
$SrCO_3$	Strontium carbonate
$SrFeO_{3-\delta}$	Strontium ferrite
$SrTi_{1-x}Fe_xO_{3-\delta}$	Strontium titanate ferrite
$SrTiO_3$	Strontium titanate
Ti	Titanium
Ti^{4+}	Tetravalent titanium ion
TiO_2	Titanium (IV) oxide
W	Tungsten
WC	Tungsten carbide
Xe	Xenon
ZnO	Zinc oxide
ZnS	Zinc sulfide

Physical Variables

C	Concentration
C_o	Initial concentration
E_g	Bandgap energy
λ	Wavelength
P	Pressure
P_o	Initial pressure

Abbreviations

AO8	Acid Orange 8
AOPs	Advanced oxidation processes

AOTs	Advanced oxidation technologies
AP	Acetophenone
B. E.	Binding energy
BET	Brunauer-Emmett-Teller
BPA	Bisphenol A
BPA ⁻	Bisphenolate ion
DMSO	Dimethyl sulfoxide
DPPH	2,2-diphenyl-1-picrylhydrazyl
FTIR	Fourier transform infrared
FWHM	Full width at half maximum
HPLC	High performance liquid chromatography
HQ	Hydroquinone
IC	Ion chromatography
LED	Light emitting diode
O _{latt}	Lattice oxygen
<i>p</i> -BQ	<i>p</i> -Benzoquinone
<i>p</i> -HAP	<i>p</i> -hydroxyacetophenone
<i>p</i> -HBA	<i>p</i> -hydroxybenzaldehyde
<i>p</i> -HMEP	<i>p</i> -(1-hydroxy-1-methyl-ethyl)phenol
<i>p</i> -IPeP	<i>p</i> -isopropenylphenol
<i>p</i> -IPP	<i>p</i> -isopropylphenol
PP	2-phenyl-2-propanol
RB	Rhodamine B
ROS	Reactive oxidative species
SEM	Scanning electron microscopy
SFO	Strontium ferrite
STF	Strontium titanate ferrite
STF _x	Strontium titanate ferrite -- iron ratio $x = \text{Fe}/(\text{Ti} + \text{Fe})$
STF20	$\text{SrTi}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
STO	Strontium titanate
TOC	Total organic carbon
UV-Vis	Ultraviolet-visible
VLA	Visible-light-activated
XPS	X-ray photoelectron spectroscopy

XRD	X-ray Diffraction
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Chapter 1 : Introduction

1.1 Motivations

Water is one of the most important natural resources for all living organisms on Earth and plays a key role in determining the life quality of the human population. Due to the rapid industrial development and population growth, the world is currently facing ever-increasing demand for clean water supply. However, only less than 1% of fresh water on the earth is readily accessible [1]. With around 4 billion people lacking access to safe and sanitized water supply and 2 million people killed annually by water-related diseases [2], water scarcity has become one of the top ten global challenges. Such dire situation urges the society to seek for various economical, robust and environmental-friendly solutions to produce more viable water resources for the human population.

Recently, recycling industrial or municipal wastewater has become an attractive option to cater to the overwhelming water demand while reducing discharged effluent to the environment. By using various advanced wastewater treatment technologies, raw sewage water can be converted into clean water suitable for further applications such as agricultural irrigation, equipment cooling and process use in electronic and

power generation industries. A well-known example is the NEWater production process initiated in Singapore to supplement the national water supply, in which ultra-clean and potable water is reclaimed from used water by employing dual-membrane (ultrafiltration and reverse osmosis) and ultraviolet technologies.

Despite being capable of producing high quality water, membrane separation technology remains less than ideal due to its high operation and maintenance costs. Furthermore, it functions like other conventional physical treatment technologies (coagulation/flocculation, sedimentation, membrane filtration and adsorption), whereby water pollutants such as chlorinated organic compounds, endocrine disrupting compounds, synthetic organic chemicals, etc. are transformed into other phases rather than completely destroyed. Consequently, large amount of concentrated suspended solids and sludge are generated which in turn resulted in membrane fouling and poorer performance. For that, further tedious and expensive post-treatment is required to remove the secondary pollutants and re-generate the membrane. This pushes the society to look for more economical and robust solutions to be incorporated into the next generation of water treatment and wastewater recycling systems.

Various physical, chemical and biological technologies have been developed over recent years to treat water and recycle wastewater. Among them, the chemical approach involving advanced oxidation processes (AOPs) has received great attention due to its high efficiency in generating reactive oxidative species (ROS) such as hydroxyl radical ($\text{OH}^\bullet$), superoxide anion radical ($\text{O}_2^{\bullet-}$), ozone, hydrogen peroxide, hydroperoxyl radical ($\text{HO}_2^\bullet$), and singlet oxygen ($^1\text{O}_2$), to oxidize a wide range of organic pollutants into carbon dioxide, water and inorganic ions [3-7]. AOPs can be

categorized into two main groups, namely dark oxidation and photo oxidation. Thus far, the most commonly adopted dark oxidation method to treat emerging water pollutants is ozonation. However, ozonation is inefficient in oxidizing organic pollutants completely into carbon dioxide, water and inorganic ions [8]. Furthermore, it is a chemically intensive process which produces carcinogenic and toxic bromate ions [9]. Fenton process is another dark oxidation method, which involves the use of one or more oxidants (usually hydrogen peroxide and oxygen) and a catalyst (a metal salt or oxide, usually iron) to generate ROS [3]. Homogeneous Fenton process which involves all reactants in dissolved phase, requires strong acidic operating condition to prevent precipitation of Fe (II) and Fe (III) [3]. Although heterogeneous Fenton process has been reported recently to be able to treat organic pollutants at a wider pH range, this process is only effective with the use of ultrasonic or chelating agents [3, 10]. On the other hand, organic pollutants can also be efficiently destroyed under sunlight illumination by photo oxidation process such as photocatalysis [4, 5], but photocatalyst becomes inactive in the absence of light illumination. Therefore, it is important to explore on other material alternatives which can function as a robust oxidant in dark condition without the use of external stimulants while achieving high oxidation efficiency.

Perovskite (ABO_3) mixed oxides have been demonstrated to be an effective heterogeneous catalyst for oxidation of organic compounds [11, 12]. Recently, SFO, a perovskite material, was demonstrated to possess redox behavior [13] and catalytic activity to oxidize organic compounds such as toluene and methane [14, 15]. Despite SFO being studied as a photocatalyst [16, 17] due to its narrow bandgap (1.9 eV) [18], the capability of SFO to degrade water pollutants in dark has yet to be fully explored.

Hence, in this project, perovskite SFO metal oxide, prepared by a combination of high temperature solid state reaction and high-energy ball milling process, was firstly explored as an alternative material for the development of dark AOT targeted for water treatment application. The capability of the milled SFO metal oxide to oxidize two different types of man-made model pollutants, namely BPA (endocrine disruptor) and AO8 (anionic synthetic azo dye) under dark and room temperature conditions was investigated and the results discussed in this thesis. The structural stability of milled SFO oxide after oxidative degradation reaction was further improved by substituting the iron atoms with titanium atoms to form the solid solution perovskite STF metal oxide containing various amounts of Ti atoms with respect to the iron atoms. The effect of titanium content in the total (Ti + Fe) composition on the physicochemical properties, oxidative degradation efficiencies and structural stability of a series of solid solutions STFx metal oxides was also studied and presented in this thesis.

1.2 Objectives

The main focus of this thesis is to explore on the SFO metal oxide with perovskite crystalline structure as a potential alternative material for the development of novel AOT which is effective and efficient under dark and room temperature condition for water treatment application. To achieve this goal, several sub-objectives are outlined as following:

- To synthesize submicron-sized perovskite SFO metal oxide with repeatable particle size distribution in the range of 100 nm to 750 nm and large effective surface area using a low-cost, highly scalable and facile process involving high temperature solid state reaction and high-energy ball milling process, as well as

to characterize their physicochemical properties, which play critical roles in the oxidative degradation reaction of the target pollutants.

- To investigate the oxidative degradation of BPA under dark ambient condition as well as to identify the intermediate byproducts and responsible ROS for the degradation of BPA so as to deduce a possible degradation pathway of BPA over the milled SFO metal oxide.
- To study the oxidative degradation of AO8 over the milled SFO metal oxide, under dark ambient condition as well as to identify the intermediate byproducts and responsible ROS for the degradation of AO8.
- To investigate the effect of external visible light stimulant on the oxidative degradation of BPA and AO8 over the milled SFO metal oxide.
- To evaluate the reusability of the milled SFO metal oxide for the degradation of AO8 under dark ambient condition and to examine the structural stability of the metal oxide after oxidative degradation reaction.
- To enhance the structural stability of the milled SFO metal oxide by substituting iron atoms with titanium atoms and to study the effects of titanium content on the physicochemical properties, oxidative activities, and structural stability of milled STFx metal oxides.

1.3 Major Contributions of the Thesis

First of all, the submicron size milled SFO metal oxide particles (< 500 nm) with single perovskite phase and uniform particle size were successfully synthesized through a low-cost, highly scalable and facile process involving a combination of high temperature solid state reaction and high-energy ball milling process. The surface

properties of SFO metal oxides such as surface elemental oxidation states, surface area and surface charge, were studied systematically using XPS, BET and zeta potential analysis respectively.

The application of the milled SFO metal oxide for effective and efficient breakdown of high concentration of BPA and AO8 in aqueous solutions under dark ambient condition was demonstrated through the identification and elimination of intermediate byproducts. These results were highly reproducible. Furthermore, the milled SFO metal oxide was found to be capable in oxidizing BPA into carbon dioxide, as validated by the high total organic carbon (TOC) removal efficiency.

Further efforts were devoted to understand the mechanism of oxidative degradation of the target pollutants under dark ambient condition. The presence and role of ROS were elucidated indirectly by using suitable scavengers, such as Dimethyl Sulfoxide (DMSO), Benzoquinone (BQ) and Sodium Azide (NaN_3). $\text{O}_2^{\bullet-}$ was identified as the predominant ROS for oxidative degradation of the target pollutants. Based on the identified intermediate byproducts and responsible ROS, a possible degradation pathway of BPA over the milled SFO metal oxide under dark ambient condition was proposed.

Another major contribution of this thesis was to examine the reusability of the milled SFO metal oxide for the AO8 degradation under dark ambient condition, which was imperative for achieving a low cost water treatment system. Comparable good results were demonstrated among four consecutive cycles of AO8 degradation. However, the milled SFO metal oxide was found to decompose into strontium carbonate after the oxidative degradation reaction due to carbon dioxide poisoning.

To tackle the stability issue of the SFO metal oxide, the iron atoms of the perovskite SFO metal oxide was substituted with titanium atoms to form STF metal oxide so as to enhance its structural stability. The titanium content was varied from 0 to 100 %, leading to the formation of a series of solid solution STFx metal oxides. The physicochemical properties of STFx metal oxides were investigated extensively using various characterization techniques. The replacement of iron atoms with titanium atoms showed no negative impact on the crystallinity of STFx metal oxides. Interestingly, the STFx metal oxides with increasing titanium content were found to possess smaller particle size with higher BET specific surface area. Despite improved structural stability with titanium substitution, both BPA and AO8 degradation efficiencies of the STFx metal oxides under dark ambient condition decreased with increasing titanium content. The poorer oxidative degradation efficiency of these STFx metal oxides was attributed to the decrease in oxygen vacancies, which were crucial in producing the responsible $O_2^{\cdot -}$ oxidizing species.

This project can be summarized as the pioneer work on discovering and investigating the potential of perovskite SFO-based metal oxide as an alternative material for AOT to degrade and oxidize organic water pollutants effectively and efficiently without any external stimulants. Nonetheless, the enhanced oxidative degradation activity under stimulated visible light illumination showed promising photocatalytic effect, demonstrating the potential of SFO and STF metal oxide based system as a novel bi-functional AOT suitable for water treatment.

1.4 Organization of the Thesis

The thesis is organized into seven chapters as following:

Chapter 1 presents the introduction, which consists of motivations and objectives for this research project as well as major contributions and organization of this thesis.

Chapter 2 reviews several commonly adopted advanced oxidation processes for water treatment. Properties of target pollutants, BPA and AO8, and their degradation through AOPs are also illustrated.

Chapter 3 covers the properties, synthesis methods and applications of SFO metal oxides. It also outlines the synthesis process and the various material characterization techniques for the in-house SFO metal oxides.

Chapter 4 presents the oxidative degradation of BPA aqueous solution with dispersion of SFO metal oxide particles under dark ambient condition. Influences of solid loading of the milled SFO metal oxide and the identification of intermediate byproducts and the ROS responsible for the degradation of BPA are discussed. A possible BPA degradation pathway is proposed. The visible-light enabled photocatalytic oxidative activity of milled SFO metal oxide is confirmed.

Chapter 5 presents the oxidative degradation of AO8 aqueous solution with dispersion of milled SFO metal oxide particles under dark ambient condition. Influences of solid loading of the milled SFO metal oxide and the identification of intermediate byproducts and the ROS responsible for the degradation of AO8 are discussed. The reusability and structural stability of milled SFO oxide for AO8 degradation is discussed. The visible-light enabled photocatalytic oxidative activity of milled SFO metal oxide is confirmed.

Chapter 6 details the improvement on the structural stability of milled SFO metal oxide via the substitution of iron with titanium in the perovskite structure.

Physicochemical properties characterization, oxidative degradation efficiency and structural stability of a series of STF_x oxides are described.

Chapter 7 concludes the thesis and proposes a future direction of this research project.

Chapter 2 : Review of Advanced Oxidation Processes (AOPs) for Degradation of BPA and AO8

2.1 Advanced Oxidation Processes (AOPs) for Water Treatment Application

Advanced Oxidation Processes (AOPs) are processes involving the production and utilization of highly reactive oxidizing species for the destruction of complex and persistent chemicals in the effluent water [3, 4]. Numerous reactive oxidizing species such as hydroxyl radical, ozone, hydrogen peroxide, superoxide anion radical, hydroperoxyl radical, and etc., have been shown to be responsible in AOPs [3-7]. Amongst which, the hydroxyl radical, one of the most powerful oxidizing species with an oxidation potential of 2.80 V [5], can attack most organic and many inorganic solutes in an extremely fast and nonspecific manner. Nonetheless, several other oxidizing species have been reported to outperform the hydroxyl radical during the AOPs. Styliadi and coworkers found that superoxide anion radicals were the predominant reactive species during the photocatalytic degradation of Acid Orange 7

using TiO_2 [19]. Wang and Lim also found that BPA was mainly oxidized by superoxide anion radicals, which were generated by the CN-codoped (carbon-nitrogen-codoped) TiO_2 photocatalyst [20].

AOPs can be classified into two main categories, which are dark oxidation and photo oxidation (light-driven) AOPs. The dark oxidation processes include Fenton and Fenton-like processes, ozonation, and ultrasound process. On the other hand, UV-based, photo-Fenton and photo-Fenton-related processes as well as heterogeneous photocatalysis are examples of photo oxidation processes. AOPs can operate individually and in synergy with each other to form a hybrid system. It should also be noted that there are other oxidation technologies such as wet air oxidation and supercritical water oxidation, being developed to treat model pollutants and actual wastewaters at high concentrations. However, these technologies are not discussed here because they tend to require high energy consumption and high pressure equipment, which oppose the objectives of this research work.

2.1.1 Dark Oxidation Processes

2.1.1.1 Fenton and Fenton-like Processes

The Fenton processes are based on the coupling of oxidizing agents such as hydrogen peroxide (H_2O_2) and oxygen with a catalyst, usually ferrous iron, Fe^{2+} to produce free radicals such as hydroxyl radicals, hydroperoxyl radicals, $\text{HO}_2^\bullet$ and its conjugate base, $\text{O}_2^\bullet$ [21-23]. When ferrous iron is replaced by ferric iron, Fe^{3+} , it is called Fenton-like reagent [21]. Iron is a favorable choice of catalyst because it is highly abundant and non-toxic [3, 23]. The removal of water pollutant for both Fenton and Fenton-like

processes, which are evaluated in terms of chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC) and color removal, are highly dependent on the reaction pH, dosages of Fenton reagents and temperature [24]. The conventional Fenton process is only efficient at pH 2-4 with three predominant species such as $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2$, abbreviated as Fe^{2+} , FeOH^+ , and $\text{Fe}(\text{OH})_2$ respectively [22]. Below pH 2, $(\text{Fe}(\text{H}_2\text{O})_6)^{3+}$ is the main species and it has poor interaction with H_2O_2 to produce free radicals thereby suppressing the oxidation process [21, 25]. Furthermore, hydrogen ions act as scavengers of hydroxyl radicals at very low pH [25]. At $\text{pH} > 4$, precipitation of ferric oxyhydroxides inhibits the regeneration of ferrous ions and thus, reduces the catalytic activity [3, 21]. Therefore, an acid-resistant reactor is required to prevent equipment corrosion. Neutralization of the discharge from the Fenton reactor is also needed and is achieved through pH adjustment, thus incurring additional chemical cost. Besides the requirement of strict pH control, the Fenton and Fenton-like processes remains problematic with the formation of undesirable iron sludge, which requires appropriate post-treatment [22, 24].

2.1.1.2 Ozonation Process

Ozone is commonly used for disinfection purpose owing to its anti-bactericidal property [26, 27]. During the wastewater treatment process, ozone is usually injected into the effluent in its gaseous form. Due to the low solubility of ozone in the aqueous solutions [25, 28], the resulting high gas-liquid mass transfer resistance greatly hampers the overall efficacy of the ozonation process. Although ozone is an electrophile with high selectivity, the use of ozone alone exhibits lower reaction rate compared to other processes based on the free radicals [29, 30]. When ozone is used

with H_2O_2 , free radicals can be generated and thus shorten the treatment time [31-33]. Although ozonation works well in a pH range of 7-8, it is an expensive process and has other drawbacks such as causing the formation of highly toxic bromate through oxidation of bromide ions, which exist in natural and fresh water [25, 34, 35].

2.1.1.3 Ultrasound Process

Ultrasonication of water at frequency ranging from 20 kHz to 1 MHz causes formation, growth, and sudden collapse of micro bubbles, which is a phenomenon of acoustic cavitation [3, 36]. The cavitation induces short-term high temperature and pressure, leading to the thermal dissociation of water molecules into free radicals that speed up AOPs. The cavitation can also destroy the contaminants through pyrolysis route. Although ultrasound process is proven to be technically feasible to treat various kind of chemical pollutants in water [37-39], its high operating cost remains to be the primary challenge for efficient large-scale operation [34, 40].

2.1.2 Photo Oxidation Processes

2.1.2.1 UV-Related Processes

In UV photolysis, the target contaminants must be able to absorb the incident UV irradiation to undergo degradation through their excited states [6]. However, the industrial applications of UV photolysis process are limited by its ability to treat effluents with low concentration of contaminants and low turbidity as well as the long reaction time for complete photo-dissociation [3]. To shorten the reaction time, the generation of hydroxyl radicals is enhanced by coupling the use of UV irradiation with H_2O_2 and/or ozone [3, 31]. But these processes are pH-dependent and an excess

H_2O_2 can act as scavenger of hydroxyl radicals, causing adverse impact on the degradation rate [29].

2.1.2.2 Photo-Fenton and Related Processes

UV light irradiation improves the efficiency of both dark Fenton and Fenton-like processes by enhancing the regeneration rate of Fe^{2+} from photolysis of Fe^{3+} complex for continuous source of free radicals [29, 31]. The photo-Fenton processes are further improved by complexing Fe^{3+} with oxalate because the ferrioxalate complex is highly photoreactive and has a broader light absorption spectrum up to 500 nm [41, 42]. Nonetheless, similar to the dark Fenton system, such processes also require strict pH control and post-treatment of sludge. To overcome the costly removal process of iron sludge, heterogeneous photo-Fenton and photo-Fenton-like processes have been developed for use in environmental remediation by depositing iron catalyst on different supporting substrates such as Nafion membrane, zeolite, pillar and laponite clay. [43-47]. However, the pH-dependency of those heterogeneous systems remained unsolved. Although the Fe-ZSM-5 produced by fixing iron catalyst on zeolite allowed the heterogeneous system to operate under a milder pH condition (i.e. pH 5-7) and ease the catalyst removal through filtration, it tends to require an additional input of thermal energy for higher oxidation efficiency [48, 49].

2.1.2.3 Heterogeneous Photocatalysis

Heterogeneous photocatalysis can be defined as an acceleration of a chemical reaction by irradiation in the presence of a semiconductor catalyst. When the semiconductor is illuminated with light with photo energy greater than or equal to its bandgap energy, the photogenerated electron will be ejected from the valence band to the conduction

band, leaving behind a hole in the valence band. The created electron-hole pair migrates to the photocatalyst surface and initiates a chain of complex redox reactions to produce reactive species. Figure 2-1 shows the photocatalytic mechanism for the degradation of water pollutant over TiO_2 , whereby the photo-induced electron is scavenged by oxygen molecules to form superoxide anion radicals and the remaining hole oxidizes water molecules and hydroxyl ions to form hydroxyl radicals [4, 5].

Figure 2-1 Schematic of TiO_2 photocatalytic mechanism with the presence of pollutant (P) [4].

The first generation of photocatalysts includes TiO_2 , ZnO , Fe_2O_3 , WO_3 , CdS , ZnS and SrTiO_3 [7, 50]. Among them, TiO_2 is the most popular candidate and has been commercialized as it is low-cost, non-toxic, and stable with high photoactivity [5, 7, 21]. However, it can only absorb 5 % energy of the solar spectrum due to its wide bandgap (3.0 eV and 3.2 eV for rutile and anatase respectively), limiting the utilization of the abundant solar energy for its activation [5]. SrTiO_3 is another UV-driven photocatalyst while other semiconductor photocatalysts have stability-related issue [7]. Substantial efforts have been devoted to develop the second generation

(visible-light-activated, VLA) photocatalysts through modification of TiO_2 with metal and non-metal doping, dye photosensitization, coupling of semiconductors, and synthesis of new materials such as BiVO_4 , Bi_2WO_6 , and CeO_2 [51-60]. However, some of these techniques contain major drawbacks which include limited doping concentration, increased recombination rate of charge carriers and poor photostability [61, 62]. Furthermore, the photocatalyst is inactive without proper photo-energy excitation. For instance, VLA photocatalyst dependent on sunlight activation loses its functionality during night fall, without the use external light source.

2.2 Target Contaminants

In this project, Bisphenol A and Acid Orange 8 were chosen as model pollutants to study the capabilities of both SFO and STF_x metal oxide particles for water treatment application. Both organic compounds are man-made and possess harmful natures. BPA can be found in surface water, drinking water, and wastewater [63, 64] while AO8 is commonly found in wastewater [65]. Their properties and applications as well as negative impacts on the aqueous environment and living organisms are covered in detailed. Furthermore, their degradations through AOPs as reported in the literature are also reviewed critically.

2.2.1 Bisphenol A (BPA)

Bisphenol A (BPA) is a non-volatile organic compound with a chemical formula of $\text{C}_{15}\text{H}_{16}\text{O}_2$. The chemical structure of BPA is depicted in Figure 2-2. It is moderately soluble in water (0.53-1.31 mM at pH 7) and forms a colorless solution [63]. BPA is

used extensively in the production of polycarbonate and epoxy resins. The polycarbonate plastic is a high performance, strong and durable light-weight material that is used to make a wide variety of daily products, such as housings for electrical and electronic products, food and beverage containers--plastic bottles and cups, optical media and toys, architectural glazing and floorings, safety glasses and helmets, biomedical devices and equipment and automotive lighting covers and protections. Epoxy resins have vast applications as protective coatings such as the metal food and beverage cans to prevent contents from spoilage and extend shelf-life, marine protective coatings, powder coatings on many items and equipment, civil engineering applications and adhesives. Other applications of BPA can be found in flame retardants, antioxidants, stabilizers and high performance resins such as unsaturated polyester and polysulfone. In 2008, 5.2 million metric tons of BPA were produced annually worldwide [66].

Figure 2-2 Chemical structure of BPA.

BPA is known to be toxic (in the range of 4-44 μM for freshwater and marine species) and carcinogenic in nature, while causing detrimental impact on living organisms by disrupting the estrogenic endocrine pathway [67, 68]. The chemical has come under scrutiny in recent years for possibly disrupting hormone systems, potentially leading to miscarriage, behavioral and developmental problems in children, and other health concerns. Some countries are considering to ban the use of BPA in some of the daily

products such as baby bottles and toddler's cups but so far no confirmed legislation has been passed to limit the use of BPA. Major routes of BPA entering the aquatic environment are via manufacturing facilities, wastewater treatment plant discharge and landfill leachate [63, 68]. In 2010, the US Environmental Protection Agency reported that more than 1 million pounds of BPA was released to the environment annually [69]. Yamamoto, et al. also reported that the concentration of BPA in hazardous waste landfill leachates in Japan was in a range of 0.006-75 μM [70]. The increasing presence of harmful BPA in the environment has thus caused it to be labeled as an emerging pollutant that needs to be removed.

2.2.1.1 Application of AOPs for BPA Degradation

Table 2-1 and Table 2-2 summarize the reported removal of highly concentrated BPA ($\geq 44 \mu\text{M}$, upper limit of toxicity for freshwater and marine species) from water through dark and photo-induced AOPs respectively. Although BPA can absorb UV, direct photolysis of BPA through UV irradiation is inefficient for its complete removal. Neamtu and Frimmel [71] reported that only 7.3 % and 8.8 % of BPA molecules were removed from pure water and wastewater effluent respectively after 15 minutes of UV irradiation ($\lambda = 254 \text{ nm}$). By adding H_2O_2 , the removal efficiency was increased to 35 % (pure water) and 28 % (wastewater) with a reduction in the estrogenic activity of BPA. Another indirect photolysis of BPA was through the coupling of UV irradiation with ozonation, whereby complete degradation of BPA could be achieved within a shorter reaction time [72].

Among the photo-induced AOPs, heterogeneous photocatalysis is gaining more attention owing to its potential to render oxidation of pollutants into CO_2 , water and inorganic ions. Ohko and coworkers reported that complete oxidation of BPA were

achieved after 15 hours and 20 hours respectively in the presence of TiO_2 powder under artificial UV irradiation from a Hg-Xe lamp [73]. They also reported that the estrogenic activity of BPA was reduced to $< 1\%$ in 4 hours. Approximately 3-6 times improvement on the complete oxidation of BPA at pH 3 was attained by platinizing TiO_2 with optimal Pt loading of 0.2-1.0 wt % [74]. However, the oxidation process was greatly hampered at pH 10 due to the inhibited adsorption of BPA on the negatively-charged surface of Pt- TiO_2 and the presence of carbonate ions, which were hydroxyl radical scavengers. Kaneco, et al. demonstrated the use of solar irradiation as an alternative to the energy-intensive and expensive artificial light sources for the oxidation of BPA [75]. However, oxidation of BPA completely into carbon dioxide under comparable reaction duration required much higher loading of TiO_2 . Another visible light-activated semiconductor, namely $\text{Bi}_4\text{Nb}_{0.1}\text{Ta}_{0.9}\text{O}_8\text{I}$ was developed by Hu, et al. and it was shown to have 99 % of BPA and TOC removal efficiencies after 16 hours [76]. To ease the separation of photocatalyst powder from the treated solution, TiO_2 powder was combined with zeolite sheets to form paper-like composite [77]. However, the TiO_2 -zeolite composite sheets were less efficient as compared to TiO_2 powder form.

Besides the synergetic effect of UV/ O_3 , ozonation can act alone to degrade BPA in dark condition via either direct oxidation by O_3 or indirect oxidation by hydroxyl radicals, which are formed through decomposition of O_3 in alkaline medium. Deborde, et al. investigated the direct oxidation of BPA by O_3 in the presence of a strong hydroxyl radical scavenger, namely ter-butanol [78]. Complete degradation of BPA into five major intermediates such as catechol, orthoquinone, muconic acid derivative, benzoquinone and 2-(4-hydroxyphenyl)-propan-2-ol at pH 6.5 was achieved after 24 hours. Higher ozone consumption was needed for complete degradation of those

intermediates into smaller acids and aldehydes. To shorten the reaction time, addition of other chemicals such as bicarbonate ions was necessary [79]. However, when acted alone, ozonation was inefficient in completely oxidizing these intermediates due to its low TOC removal rate [8].

Another dark AOP involves the use of Fenton and Fenton-like reagents. Homogeneous Fenton treatment of BPA was strongly dependent on pH and initial concentration of Fe(II) and H₂O₂ [80]. Higher BPA degradation efficiency could only be achieved in the presence of higher concentration of homogeneous Fenton reagents under acidic condition, i.e. pH 3-4 to prevent precipitation of Fe (II) and Fe (III) [81]. Heterogeneous Fenton process with the aids of chelating agents has been proposed to extend the operating pH range. Wang and coworkers studied the effects of different chelating agents on the degradation of BPA under dark condition using their BiFeO₃-H₂O₂ system [82]. They observed that the BPA degradation rate was accelerated in the pH range of 5-9 by adding proper ligands such as ethylenediaminetetraacetic acid and 2,2-diphenyl-1-picryl-hydrazyl. However, dark Fenton and Fenton-like processes are inefficient for complete oxidation of BPA. Photo-illumination such as UV irradiation is required to shorten the reaction duration and to achieve higher oxidation efficiency [10, 81].

Recently, ultrasonication had been adopted to treat BPA and complete degradation of BPA and intermediates were achieved in 90 minutes and 2 hours respectively under the optimal condition: 300 kHz and 80 W with oxygen as saturating gas [83]. However, more than 50 % of COD and 80 % of TOC remained in the solution even after a long treatment time (9 hours) due to the accumulation of recalcitrant aliphatic acids toward ultrasound irradiation. Similar observation was found by Inoue and

coworkers for their ultrasonic system operating at 404 kHz and 41.5 W, whereby BPA was totally degraded in 2 hours with 20.2 % TOC removal in 10 hours [84].

Table 2-1 Dark AOPs for degradation of BPA.

Dark Oxidation	Medium	BPA Concentration	Process Conditions	Performance	Intermediates	Ref. (Yr)
Fenton and Fenton-Like Processes	Milli-Q ultrapure water	110 μ M	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 5\text{-}9 \mu\text{M}$; $\text{H}_2\text{O}_2 = 206 \mu\text{M}$; pH 4-6.5; 25 ± 5 $^\circ\text{C}$.	Highest efficiency at pH 4 with ~96 % BPA degradation in 50 min by 9 μM $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.	N. A.	[80] (2010)
	Distilled pilot plant feedwater	50 μ M	$\text{Fe(II)} = 50 \mu\text{M}$; $\text{H}_2\text{O}_2 = 1 \text{ mM}$; pH 3.	50 % BPA degradation in 1.9 min; 90 % phenolic intermediates degradation in 39 min; 15 % TOC removal in 18 min.	Benzaldehyde, phenol, 1-hezanol-2-ethly, <i>p</i> -isopropenylphenol, 4-hydroxyacetophenone, 4,4'-dihydroxybenzophenone, ethanone,1-(4-cyclohezyphenyl), 4,4'-isopropylidenedi-phenol, and carboxylic acids; toxicity increased during early stage and decreased afterward.	[81] (2010)
	Double distilled water	100 μ M	1.6 mM BiFeO_3 ; $\text{H}_2\text{O}_2 = 10 \text{ mM}$; ligand = 250 μM ; DPPH = 5 μM ; pH 5; 2 h; 30 $^\circ\text{C}$.	Blank (20.4 % BPA degradation) < Modified with proper ligand: tartaric acid < formic acid < glycine < nitrilotriacetic acid < ethylenediamin-etetraacetic acid (91.2 %).	N. A.	[82] (2011)
Ozonation	Water	100 μ M	$\text{O}_3 = 6 \text{ mM}$; 80 min.	100% BPA degradation.	N. A.	[72] (2005)
	Milli-Q purified water	100 μ M	$\text{O}_3 = 15\text{-}550 \mu\text{M}$; tert-butanol = 83 mM; pH 6.5; 24 h; 20 ± 2 $^\circ\text{C}$.	100% BPA degradation by 400 μM O_3 ; 100 % major intermediates degradation into smaller acids and aldehydes by $\geq 570 \mu\text{M}$ O_3 .	Catechol, orthoquinone, muconic acid derivative, benzoquinone and 2-(4-hydroxyphenyl)-propan-2-ol, acids, and aldehydes.	[78] (2008)
	Deionized water	57 μ M	$\text{O}_3 = 513 \mu\text{M}$; pH 7; bicarbonate = 2 mM; 14 min; 22 ± 1 $^\circ\text{C}$.	77 % BPA degradation.	N. A.	[79] (2009)
Ultrasonication	Deionized water	118 μ M	300 kHz; 80W; 20 ± 1 $^\circ\text{C}$.	100% BPA degradation in 90 min; 100% intermediates degradation of intermediates in 2 h; 50 % COD and 21 % TOC removal in 9 h.	Monohydroxylated-4-isopropenylphenol, 4-isopropenylphenol, 4-hydroxyacetophenone, dihydroxylated BPA, quinone of dihydroxylated BPA, monohydroxylated BPA, quinone of monohydroxylated BPA, and aliphatic acids.	[83] (2008)
	Air-saturated aqueous solution	500 μ M	404 kHz; 11.4, 29 and 41.5 W; 25 $^\circ\text{C}$.	At 11.4, 29 and 41.5 W, 100% BPA degradation in 10, 3 and 2 h; 12.4, 15.4 and 20.2 % TOC removal in 10 h; addition of 4 mM of FeSO_4 at 29 W increased TOC removal to 50.2 %.	Formaldehyde, formic and propionic acids, 3-hydroxybisphenol A, benzoquinone, phenol, catechol, hydroquinone, 2-(4-hydroxyphenyl)-2-propanol, and 4-hydroxyacetophenone.	[84] (2008)
	Deionized water	300 μ M	300 kHz; 80 W; pH 8.5; 21 $^\circ\text{C}$; 15 min.	55 % BPA degradation; negligible effect with 12-500 mg/L bicarbonate ion.	N. A.	[85] (2010)

Table 2-2 Photo AOPs for degradation of BPA.

Photo Oxidation	Medium	BPA Concentration	Process Conditions	Performance	Intermediates	Ref. (Yr)
Photo-Fenton and Related Processes	Doubly distilled water	44 μM	High-pressure Hg lamp (125 W, ≥ 365 nm); Fe(III) = 10 μM ; oxalate = 120 μM ; pH 3.5 $\pm$ 0.05; 28 $^{\circ}\text{C}$.	38 % BPA degradation in 80 min; 23.9 % oxidation into CO_2 in 160 min.	BPA-o-catechol and BPA-o-quinone.	[86] (2004)
	Demine-ralized water	44 μM	Xe lamp (990 W, 320-410 nm, 0.5 mWcm^{-2}); Fe(II) = 4-40 μM ; H_2O_2 = 40-400 μM ; pH 2-4.5; 25 $\pm$ 1 $^{\circ}\text{C}$.	100 % BPA degradation by 40 μM Fe(II) and 400 μM H_2O_2 at pH 4 in 9 min with 63 % TOC removal and 54 % oxidation into CO_2 in 24 h.	4-hydroxyacetophenone, 4-isopropylphenol, <i>p</i> -hydroquinone, phenol, 4-isopropenyl-phenol, 4-(1-hydroxy-1-methyl-ethyl)-phenol, methyl-benzofurans, <i>p</i> -quinone, 3-(4-hydroxyphenyl)-3-methyl-2-oxobutanoic and simple acids.	[10] (2004)
	Distilled pilot plant feedwater	50 μM	Solar irradiation (30 Wm^{-2} UV dose); Fe(II) = 50 μM ; H_2O_2 = 1 mM; pH 3.	50 % BPA degradation in 1.2 min; 90 % phenolic intermediates degradation in 11 min; TOC removal: 15 % in 2.7 min and 75 % in 47 min.	N. A.; toxicity increased at the early stage of BPA degradation before decreased afterward.	[81] (2010)
			Fe(III) = 50 μM ; oxalic acid = 1 mM; pH 3 and 6.5	50 % BPA degradation: pH 3 (2.2 min) > pH 6.5 (2.4 min) > no oxalic acid, pH 3 (34 min) > no oxalic acid, pH 6 (infinite); 90 % phenolic intermediates degradation: pH 3 (165 min) > pH 6.5 (> 200 min) > no oxalic acid, pH 3 (> 200 min); 50 % TOC removal: pH 3 (44 min) > pH 6.5 (>> 50 min) > no oxalic acid, pH 3 (>> 50 min).	N. A.	
			$\alpha\text{-Fe}_2\text{O}_3$ = 626 μM ; oxalic acid = 1 mM; pH 6.5	50 % BPA degradation in 61 min; 90 % phenolic intermediates degradation in > 200 min; 50 % TOC removal in >> 50 min.	N. A.	
UV/Ozonation	Water	100 μM	Low-pressure Hg lamp (15 W); O_3 = 5.6 mM; 75 min.	100 % BPA degradation.	N. A.	[72] (2005)
		400 μM	O_3 = 8.5 mM; 218 min.	100 % BPA degradation.	N. A.	
UV/ H_2O_2	Milli-Q pure surface and wastewater	520 μM	UV immersed low-pressure Hg lamp (15 W, 254 nm); H_2O_2 = 550 μM ; pH 6.7; 25 $^{\circ}\text{C}$.	Pure water (35 % BPA degradation) > wastewater (28 %) in 15 min; 62 % BPA degradation in both media in 2 h.	Phenol, 1,4-dihydroxylbenzene, 1,4-benzoquinone, and aliphatic acids; decrease in estrogenic activity.	[71] (2006)

Table 2-2 (cont.)

Photo Oxidation	Medium	BPA Concen-tration	Process Conditions	Performance	Intermediates	Ref. (Yr)
Heterogeneous Photocatalysis	Doubly distilled water	175 μ M	Hg-Xe lamp (200 W, < 365 nm, 10 mW/cm ²); 12.5 mM TiO ₂ .	> 99 % BPA degradation in 15 h; 100 % oxidation of intermediates into CO ₂ in 20 h.	3-(4-hydroxyphenyl)-3-methyl-2-oxobutanoic acid, 4-hydroxyacetophenone, 4-vinyl-phenol. Decreased estrogenic activity (< 1 %) in 4 h.	[73] (2001)
	Deionized water	100 μ M	Hg-Xe lamp (< 365nm, 2 mW/cm ²); 2 g/L TiO ₂ powder/composite TiO ₂ -zeolite sheet; 24 h.	100 % and ~75 % BPA degradation by TiO ₂ powder and composite TiO ₂ -zeolite (2:1) sheet respectively.	N. A.	[77] (2003)
	Aqueous solution	100 μ M	Hg lamp (75 W, 360 nm, 2.5 mW/cm ²); 25 mM TiO ₂ ; pH 4.4.	100 % BPA degradation with 90 % TOC removal in 2 h; 90 % oxidation into CO ₂ in 4 h.	4-isopropylphenol, OHC(CH ₃) ₂ C ₆ H ₄ OH, CH ₂ =CHC(OH)CHCH=CH ₂ , OHC-CH ₂ -C(OH)=CH-CH=CH-C(CH ₃) ₂ , simple acids.	[87] (2003)
	Ultrapure water	440 μ M	Sunlight (> 300 nm, 0-1.7 mW/cm ²); 0-250 mM TiO ₂ ; pH 2-10; 10-70 °C.	~100 % BPA degradation in 6 h at optimal condition: 125 mM TiO ₂ , 1.3 mW/cm ² , pH 6, 30 °C; 100 % TOC removal and oxidation into CO ₂ in 11 h.	<i>p</i> -hydroxyacetophenone, phenol, <i>p</i> -hydro-quinone, <i>p</i> -isopropenylphenol, <i>p</i> -hydroxy-benzaldehyde, <i>p</i> -hydroxyphenyl-2-propanol, methylbenzofuran, <i>p</i> -hydroxybenzoic acid, and aliphatic acids.	[75] (2004)
	Milli-Q ultrapure water	88 μ M	Fluorescent black light blue lamp (20 W, 355 nm); ~1.3 mM pure and platinized TiO ₂ (optimal Pt = 0.2-1.0 wt %); pH = 3, 10; continuous air bubble (50 ml/min); 120 min.	Pt-TiO ₂ had higher efficiency (3-6 times) than pure TiO ₂ ; 100% BPA oxidation into CO ₂ by Pt-TiO ₂ at pH 3; 20 – 30% at pH 10 despite 100 % BPA degradation.	Detected intermediates were unidentified; at pH 3, more toxic intermediates formed at the beginning of BPA degradation followed by gradual decrease in toxicity; at pH 10, intermediates were less toxic than BPA.	[74] (2004)
	Milli-Q ultrapure water	88 μ M	Medium-pressure Hg lamp (300W, 365 nm); 6.3 mM (optimal) 3D mesoporous TiO ₂ microspheres; 60 min.	99.7 % and 98.5 % BPA degradation by TiO ₂ 3D _{M1} and TiO ₂ 3D _{M2} respectively.	<i>p</i> -isopropenylphenol, demethylated, mono and dihydroxylated derivatives, and aliphatic acids.	[88] (2010)
	Deionized water	88 μ M	Xe lamp (300 W, > 420 nm); pH 6.7; 16 h; 1.6 mM Bi ₄ Nb _{0.1} Ta _{0.9} O ₈ I;	99 % BPA and TOC removal.	Absent due to complete oxidation.	[76] (2012)

2.2.1.2 Mechanism and Pathway of BPA Degradation via AOPs

Figure 2-3 Degradation pathway of BPA by photo-Fenton process [10].

Figure 2-3 illustrates the degradation of BPA through photo-Fenton process, as suggested by Katsumata, et al. [10]. Upon the initial attack by hydroxyl radicals, the phenyl groups of BPA were ruptured to produce *p*-isopropylphenol (*p*-IPP), hydroquinone (HQ), *p*-(1-hydroxy-1-methyl-ethyl)phenol (*p*-HMEP) and phenol. Dehydration of *p*-HMEP resulted in the formation of *p*-isopropenylphenol (*p*-IPeP),

which was further oxidized by H_2O_2 to generate *p*-hydroxyacetophenone (*p*-HAP). HQ and phenol were produced following the further attack of *p*-IPP, *p*-HMEP, *p*-IPeP, and *p*-HAP by hydroxyl radicals. Phenol was converted to methylbenzofurans by propenyl radicals, which were originated from *p*-IPeP; while HQ was further oxidized to *p*-BQ (*p*-benzoquinone). Finally, the aromatic rings of those intermediates were opened via oxidation reaction, leading to the formation of aliphatic acids and evolution of carbon dioxide gas.

Another hydroxyl radical based TiO_2 -UV photocatalysis system with two possible BPA degradation pathways was proposed by Fukahori et al., as shown in Figure 2-4 [77]. One of the pathways involved the elimination of water after BPA hydroxylation or abstraction of a hydrogen atom from one of the phenolic hydroxyl groups of BPA, leading to the formation of phenoxyl radicals. Phenoxyl radicals were subsequently converted to quinone-like compounds and oxidized to *p*-IPeP (or *p*-HMS) and *p*-BQ before being converted into *p*-HAP and HQ respectively. Another pathway followed the oxidation of hydroxylated BPA, whereby one of its phenolic aromatic rings was cleaved to form *p*-hydroxybenzaldehyde (*p*-HBA), *p*-HBA acid, *p*-IPeP, and *p*-HAP. Since larger accumulation of HQ was observed, this in turn signified that the former pathway was more predominant over the ring-rupturing pathway. Although their recommended pathways were different from that suggested by Katsumata, et al., similar final products such as aliphatic acids and carbon dioxide were found upon the ring opening of those single-aromatic intermediates eventually.

Figure 2-4 Degradation pathway of BPA by TiO_2 – UV photocatalysis [77].

On the other hand, Deborde, et al. reported the direct oxidation of BPA into five major (B_1 - B_5) and two minor (b_2 & b_3) intermediate products by ozone after 24 hours, as depicted in Figure 2-5 [78]. The five major oxidation products, namely

hydroxylated BPA, *p*-BQ, *p*-HMEP, orthoquinone and muconic acid derivatives, were formed through the reaction between ozone and aromatic rings of BPA by electrophilic substitution; whereas both minor products were formed through secondary reactions between the major oxidation products.

Figure 2-5 Degradation pathway of BPA via ozonation process [78].

Figure 2-5 (cont.).

Despite different mechanisms and pathways involved during the degradation of BPA through heterogeneous photocatalysis, photo-Fenton process, and ozonation, similar intermediate products have been generated during the degradation process, including hydroxylated BPA, muconic acid derivatives, *p*-HMEP, *p*-HAP, HQ, and *p*-BQ.

2.2.2 Acid Orange 8 (AO8)

Azo dye is the largest class of synthetic dye, which accounts for 60-70 % of total annual dye production (more than 7×10^5 metric tons annually) [89]. It has been widely used in different industries, such as textile, paper, leather, paint, cosmetic, pharmaceutical, food and photochemical cell industries. Acid Orange 8 (AO8) is an anionic azo dye with a chemical formula of $C_{17}H_{13}N_2NaO_4S$.

Figure 2-6 Chemical structure of AO8.

Figure 2-6 shows the chemical structure of AO8, which consists of an azo group ($-N=N-$) linking a naphthalene ring and benzene ring at both ends. With reference to the azo group, the naphthalene ring has a hydroxyl group at the ortho position; while the aromatic ring has a sulphonic group and a methyl group at para and ortho position respectively. The conjugation of hydroxyl group and azo-linkage results in a prototropic equilibrium, which is generally known as azo-hydrazone tautomerism (a reaction which involves intramolecule migration of hydrogen atom/proton followed by interchange of a single bond and an adjacent double bond), as shown in Eq. 2-1 [90].

In aqueous solution, AO8 preferably exists in hydrazone form owing to the stabilizing effect of intramolecular hydrogen bonding between one of the nitrogen atoms and

hydrogen of the nearby hydroxyl group [90]. The dominant hydrazone form and minority azo tautomer tend to absorb light with wavelength between 475-510 nm and 400-440 nm respectively [91]. AO8 has a high solubility in water due to the existence of sulfonic, SO_3^- group [92]. Furthermore, the azo dye is also strongly resistant to aerobic and visible light degradation due to its complex structure and synthetic origin [92]. The widely used water soluble sulfonated azo dyes generally enter the environment through wastewater discharges because 15 % of the total production is lost during the dyeing process [89]. The presence of very low concentration of dyes in the effluent is highly visible, causing problematic aesthetic effect. Sulfonated azo dyes can interfere with aquatic life by obstructing penetration of sunlight for photosynthesis and affecting chemical oxygen demand. Furthermore, many azo dyes and their breakdown products are toxic and potentially carcinogenic and mutagenic [93].

2.2.2.1 Application of AOPs for AO8 Degradation

Table 2-3 summarizes the application of AOPs, including ultrasonication, Fenton-based processes, UV/ H_2O_2 process and photocatalysis, for the degradation of AO8. Among those AOPs, photocatalysis is the most commonly adopted technique for the study of AO8 degradation since 2003 [94-97]. Saquib and Muneer studied the degradation of AO8 using their UV irradiated TiO_2 photocatalytic suspension system [96]. They found that complete oxidation of AO8 was dependent on the type of TiO_2 material, TiO_2 and AO8 concentrations, pH and presence of electron acceptors such as H_2O_2 and KBrO_3 . For instance, commercial TiO_2 photocatalyst, P25 (12.5 mM) outperformed its counterparts such as UV100, PC500 and TTP by generating hydroxyl radicals and superoxide anion radicals to degrade 250 μM of AO8 at pH 9 at

a rate of 7 $\mu\text{M}/\text{min}$. Furthermore, increased degradation efficiency was observed with the addition of electron scavengers in the order of H_2O_2 (10 mM) > KBrO_3 (5 mM) due to generation of more hydroxyl radicals. Khataee and coworkers also carried out photocatalytic degradation of AO8 using PC500 TiO_2 as photocatalyst in which the oxide particles were immobilized on six pieces of glass plates [94]. The azo linkage of AO8 was found to be the most active site for oxidation attack by hydroxyl radicals and was converted into two amino groups (R-NH_2) in the process. Successive attack by $\text{H}^\bullet$ radicals on those amino groups led to evolution of ammonium ions and nitrogen gas.

Mehta and Surana had done a comparative study of AO8 degradation between TiO_2 photocatalysis and photo-Fenton process [97]. They found that the degradation performance of both systems was dependent on dye concentration, photocatalyst loading /Fenton reagent concentration, H_2O_2 and pH. At optimal condition, photo-Fenton reagent was more efficient than TiO_2 . A detailed study on the AO8 degradation through different Fenton-related processes was conducted by Abo-Farha. The degradation efficiency was found in the order of photo-Fenton > photo-Fenton-like > Fenton > Fenton-like under similar reaction condition [98]. Besides dark-Fenton-related processes, another dark AOP, namely ultrasonication was used to degrade AO8 by Özen, et al. in which the AO8 decoloration rate was enhanced with increased acidity [99]. By means of density functional theory calculations, they found that the adduct formation occurred through the attack of hydroxyl radicals to the carbon atom bearing the azo linkage instead of nitrogen atom for AO8. Furthermore, the AO8 degradation efficiency could be accelerated in the presence of CCl_4 through accumulation of reactive chlorine species and prevention of hydroxyl radical from

recombining with atomic hydrogen, but decelerated with the addition of t-butyl alcohol [100].

Table 2-3 AOPs for degradation of AO8.

AOP	Medium	AO8 Concen- tration	Process Conditions	Performance	Intermediates	Ref. (Yr)
Fenton and Fenton-Like Process	Aqueous solution	10-100 μM	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} / \text{FeCl}_3 \cdot 6\text{H}_2\text{O} = 5\text{-}100 \text{ } \mu\text{M}$, $\text{H}_2\text{O}_2 = 2\text{-}50 \text{ mM}$; pH = 2-6; RT.	Fenton (36 %, $\sim 1.5 \times 10^2/\text{s}$) > Fenton-like (28 %; $\sim 1 \times 10^2/\text{s}$) at 10 mM AO8; 10 μM $\text{Fe}^{2+}/\text{Fe}^{3+}$; 10 mM H_2O_2 ; pH = 3.	N. A.	[98] (2010)
Ultrasonication	Ultrapure deionized water	40 μM	300 kHz; 25 W; pH = 3, 5.95; $20 \pm 0.5 \text{ } ^\circ\text{C}$; 60 min; Ar bubbling (1 L/min).	$9.8 \times 10^{-4}/\text{s}$ at pH 3 > $8.5 \times 10^{-4}/\text{s}$ at pH 5.95.	N. A.	[99] (2005)
	Milli-Q water	30 μM	300 kHz; 25 W; 105-5200 μM CCl_4 ; 105-1050 μM t-butyl alcohol; pH = 6.34; $20 \pm 2 \text{ } ^\circ\text{C}$; 30 min; Ar bubbling.	In the presence of 2070 μM CCl_4 : 99.5 % ($4.1 \times 10^{-3}/\text{s}$) decoloration, 39 % and 68 % decay of UV254 and UV 312 bands respectively. Inhibitive effect of t-butyl alcohol regardless of its concentration.	N. A.	[100] (2009)
UV/ H_2O_2	Deionized water	50 μM	Low-pressure Hg lamp (15 W, 257.3 nm); $\text{H}_2\text{O}_2 = 78.4 \text{ mM}$; pH = 4.5-5.5; 15 min.	Pseudo-first order decoloration kinetic ($3.4 \times 10^{-3}/\text{s}$).	N. A.	[101] (2003)
Photo-Fenton and Related Process	Aqueous solution	10-100 μM	High-pressure Hg lamp (400 WMB7V); $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} / \text{FeCl}_3 \cdot 6\text{H}_2\text{O} = 5\text{-}100 \text{ } \mu\text{M}$; $\text{H}_2\text{O}_2 = 2\text{-}50 \text{ mM}$; pH = 2-6; RT; 1 h.	Photo-Fenton (99.5%, $\sim 1.8 \times 10^3/\text{s}$) > Photo-Fenton-like (97%; $\sim 1 \times 10^3/\text{s}$) at 10 mM AO8; 10 μM $\text{Fe}^{2+}/\text{Fe}^{3+}$; 10 mM H_2O_2 ; pH = 3.	N. A.	[98] (2010)
	Double distilled water	10-80 μM	W lamp (2x200 W); $\text{FeSO}_4 = 5\text{-}40 \text{ } \mu\text{M}$; $\text{H}_2\text{O}_2 = 19.4\text{-}31 \text{ mM}$; pH 1.5-5; continuous O_2 bubbling; 3 h.	Optimal condition: 30 μM AO8, 30 μM FeSO_4 , $\text{H}_2\text{O}_2 = 29.1 \text{ mM}$ pH 3.5 ($\sim 10.3 \times 10^5/\text{s}$).	N. A.	[97] (2012)
Photocatalysis	Double distilled water	120-500 μM	Medium-pressure Hg lamp (125 W); $\text{TiO}_2 = 6.3\text{-}62.6 \text{ mM}$; pH = 3-11; continuous O_2 purge; 1.5 h.	Highest oxidation rate by 25 mM P25 at pH 9.	N. A.	[96] (2003)
	Milli-Q water	20-60 μM	Iron alogenide lamps (250W, 315-400 nm, $4.5 \times 10^{-8} \text{ Einstein s}^{-1}\text{cm}^{-2}$); $\text{TiO}_2 = 1.25\text{-}3.5 \text{ mM}$; pH = 6; $35 \pm 1 \text{ } ^\circ\text{C}$.	Pseudo-first order rate constant of $3.93 \times 10^{-4}/\text{s}$ at optimal condition: 20 μM AO8, 1.25 mM TiO_2 .	N. A.	[95] (2003)
	Deionized water	82.6 μM	UV lamp (15 W, 365 nm); immobilized TiO_2 (PC500, 3 coatings) on 6 glass plates (5 cmx28 cm each); pH 6.86.	Nearly complete degradation in 210 min; 94.47 % TOC removal in 6 h.	Evolution of 18.1 mM of NH_4^+ in 6 h.	[94] (2009)
	Double distilled water	10-80 μM	W lamp (2x200 W); $\text{TiO}_2 = 12.5\text{-}50.1 \text{ mM}$; pH 6.5-9.5; continuous O_2 bubbling; 3 h.	Optimal condition: 30 μM AO8, 37.6 mM TiO_2 , pH 9 ($\sim 7 \times 10^5/\text{s}$).	N. A.	[97] (2012)

Chapter 3 : Strontium Ferrite (SFO) Metal Oxide Synthesis and Material Characterization

3.1 Introduction

This chapter covers the background of the perovskite SFO metal oxide including the properties and applications of the material as well as pros and cons of the currently available synthesis methods for SFO metal oxide particles. The synthesis method of the SFO metal oxide developed in this research project is described in detail. Lastly, a thorough discussion is included for the material characterizations of the in-house SFO metal oxide.

3.2 SFO Metal Oxide Crystalline Structure

Strontium Ferrite ($\text{SrFeO}_{3-\delta}$, in short SFO) is a perovskite-type metal oxide, with iron ions in an unusual higher oxidation state of +4. Perovskite-type metal oxides have crystal structure resembling that of calcium titanate, with the general formula of ABO_3 (A: divalent cation such as alkaline-earth or rare-earth element; B: tetravalent cation such as transition metal). Figure 3-1 shows the cubic perovskite structure,

whereby the larger A-site cation is 12-fold coordinated while the smaller B-site cation is 6-fold coordinated with the oxygen anions. Alternatively, the A cation is located at the center of the cube while the B cation is in the center of the octahedron. The corner sharing BO_6 octahedron forms the skeleton of the perovskite structure [11]. Such structure is unique for being able to host a high concentration of defects after substitution of its cation sites without disrupting its basic framework [102, 103].

Figure 3-1 ABO_3 perovskite structure [104].

Stoichiometric composition of SFO metal oxide can only be achieved under high oxygen pressure [105]. Therefore, it is inherently nonstoichiometric and exhibits a mixture of equilibrium compositions ($0 \leq \delta \leq 0.50$) over a wide range of oxygen partial pressures and temperatures. These compositions can be categorized into four structurally distinct phases depending on the oxygen vacancy density (δ), including cubic at $\delta = 0-0.12$ [106], tetragonal at $\delta = 0.16-0.24$ [107], orthorhombic at $\delta = 0.25$ [106, 108], and orthorhombic brownmillerite at $\delta = 0.50$ [106, 107].

Figure 3-2 Phase diagram of SFO_x as a function of oxygen content, x ($2.5 \leq x \leq 3.0$) and temperature, whereby the black circles indicate the transition temperatures determined by DTA [106].

As shown in Figure 3-2, Takeda and coworkers revealed that oxygen vacancies in SFO with different structural phases could undergo transition at different temperatures at a constant oxygen pressure [106]. For example, for the Br+C-P to C-P transition, the temperature ranged from approximately 500 °C to 830 °C when oxygen vacancies increased from approximately 0.38 to 0.50. As shown in Eq. (3-1), creation of an oxygen vacancy leads to the formation of two Fe^{3+} ions in order to maintain charge balance of the SFO system [13, 109].

Furthermore, Fe^{4+} ion is known to be an unstable species that is reduced to Fe^{3+} easily to attain a more stable form [110]. Therefore, the co-existence of mixed oxidation

states of +4 and +3 for iron cations is common in the SFO system as confirmed by Mössbauer spectroscopy studies [106, 107, 109]. The ratio between Fe^{3+} and Fe^{4+} also plays a crucial role in the magnetic and electrical properties of the SFO system. Stoichiometric SrFeO_3 is an anti-ferromagnetic metallic conductor while $\text{SrFeO}_{2.5}$ is an anti-ferromagnetic insulator [111, 112]. In addition, the redox property of SFO is highly dependent on the oxidation states of the iron cation because A-site cation (Sr^{2+}) is not involved in the redox reaction [13].

3.2.1 SFO Applications

The presence of two iron cation oxidation states and flexible accommodation of highly mobile oxygen vacancies at high temperature render the perovskite SFO metal oxide to possess interesting electronic, magnetic, transport, and redox properties, making it a promising candidate material for numerous applications [15, 113]. In 1979, Shin and coworkers were the first to demonstrate the excellent catalytic activity of the oxygen-deficient SFO to decompose nitrogen monoxide (NO) into nitrogen and oxygen [114, 115]. The team proposed a mechanism for the decomposition reaction and highlighted the role of Fe^{3+} ions and oxygen vacancies in the dissociation of NO molecules. The heterogeneous catalytic role of the oxygen-deficient SFO was further extended to oxidation of hydrocarbons such as methane, ethane and toluene into synthesis gas [14, 15, 116, 117]. Owing to its high oxygen ion mobility, SFO was explored as oxygen conductors for partial oxidation reactors and pressure-driven oxygen generators as well as oxygen separation membrane [118, 119]. This interesting property of the SFO also renders it to be suitable for chemical sensors [120].

The application of SFO has been further extended in the area of photocatalysis due to its narrow bandgap (1.9 eV). The photocatalytic activity of SFO was first demonstrated by Yang and coworkers in 2006, whereby 91 % of Methyl Orange was degraded within 2 hours of UV irradiation in a suspension reactor [17]. The photocatalytic property of SFO was attributed to the active FeO_6 octahedra and the changeable valence of Fe^{4+} ions with potential oxidizing ability under UV irradiation. In their work, it was noted that during photocatalytic reaction, SFO tend to be decomposed due to the interaction of strontium with the carbon dioxide released from the photodegradation of Methyl Orange. Furthermore, harmful UV irradiation was also needed as the excitation energy source, despite the small bandgap energy of SFO at 1.9 eV (equivalent $\lambda = 653$ nm). One year later, Jia, et al. studied the photocatalytic degradation of phenol over SFO under UV irradiation [121]. Although the SFO photocatalyst was reported to be able to absorb visible light more easily, its photocatalytic degradation rate was slow with only 39 % of phenol degraded after 4 hours of reaction time. The visible-light-activated SFO photocatalyst was first demonstrated in the previous work done by our team in 2010 [16]. As shown in Figure 3-3, Methylene Blue was completely degraded within 6 hours by the SFO photocatalyst synthesized through high temperature solid state reaction and subsequent 3 hours of high-energy ball milling process under visible light illumination from fluorescent tubes. Some intermediate byproducts such as Azure B and Thionin were identified, signifying the breakdown of Methylene Blue through demethylation cleavage. Besides that, a relatively slow degradation of Methylene Blue over the SFO was also observed in dark condition. However, no detailed investigation had been performed for the dark activity of the SFO metal oxide particles.

Figure 3-3 (a) Degradation of Methylene Blue with the formation of intermediate compounds such as (b) Azure B and (c) Thionine over the SFO photocatalyst [16].

3.2.2 Review of Synthesis Methods for SFO Metal Oxide Particles

3.2.2.1 Solid State Reaction

In the early studies of the SFO system, the conventional high temperature solid state reaction was commonly adopted to synthesize the SFO metal oxide [106, 107, 109, 112]. This technique still remained popular in recent research works [16, 122, 123], whereby the dry starting solid materials such as strontium carbonate and iron (III)

oxide were thoroughly mixed in a stoichiometric molar ratio and then annealed at high temperature from 950-1400 °C in different ambient to achieve a desirable oxygen composition. The high temperature solid state reaction is preferred for its simplicity, reproducibility, availability of high-grade starting solid materials, and feasibility for scale up production of highly crystalline single phase perovskite SFO metal oxide. However, such process usually produces oxide with large aggregated particles in the micron range with low surface area.

3.2.2.2 Co-precipitation

Highly crystalline SFO metal oxide can be synthesized via co-precipitation from metal-carrying precursor salts in an aqueous sol containing complexing agents and additives. The precipitation is initiated by basification of the sol with either sodium hydroxide or ammonium hydroxide under constant stirring. Then, the precipitate is filtered, washed, and dried prior to calcination at high temperature (≥ 900 °C). The final crystalline structure and crystallite size of the SFO metal oxides obtained from the sol prepared by mixing metal-nitrates in oxalic acid and tetraethylammonium hydroxide was reported to be sensitive to the calcination temperature [113]. Furthermore, when strontium carbonate and iron (III) oxide were used as the metal-carrying precursors with the addition of hydrogen peroxide, secondary phase would be formed in the final product [124]. Since this method also requires high temperature thermal treatment to achieve good crystallinity, the resulted metal oxides also tended to have large particle size and low surface area.

3.2.2.3 Sol-gel Route

Another wet chemistry route to make SFO metal oxide is through the sol-gel route. Metal-nitrates are usually adopted as the precursors to prepare a water-based sol with complexing agents such as citrate acid [13, 14, 17], oxalic acid [119], and glycine [125]. The sol is then polymerized into gel form under heating condition before subjected to two steps calcination at lower temperature 450-600 °C for removal of organic precursors, followed by thermal treatment at higher temperature (800-900 °C) to produce single phase product with good homogeneity. Nonetheless, this method is not suitable for mass production of SFO metal oxide.

3.2.2.4 Templating Method

With the use of additives such as ethylene glycol, L-lysine, and sucrose, citrate acid-assisted poly(methyl methacrylate)-templating method allowed the formation of SFO in three-dimensionally ordered macroporous structure with high surface area of 34-61 m²/g [15]. Although the calcination temperature could be lowered to 750 °C, the resulted oxide has poorer crystallinity and contains strontium carbonate impurity, which was formed through the interaction of strontium and carbon dioxide released during the oxidation of the template. The low throughput is another drawback of this technique.

3.3 In-house Synthesis of SFO Metal Oxide

In this project, it was aimed to devise a simple synthesis routine to produce SFO metal oxide particles with large surface area and uniform particle size in large quantity.

Although the conventional high temperature solid state reaction is a simple process, such method tends to synthesize powder with large aggregated particle size and irregular morphology. Smaller particle size is usually favored for application involving surface-mediated process, such as catalysis and heterogeneous oxidation, to achieve larger active surface area for improved reaction rate. In a recent pioneer work done by our team, the particle and crystallite sizes of the high temperature-synthesized SFO metal oxide have been greatly reduced through high-energy ball milling [16].

Previously, our group had carried out a thorough study regarding the effect of milling duration on the SFO metal oxide using a tungsten carbide (WC) milling media [16]. After 3 hours of milling, micrometer-sized crystallite of the SFO oxide was found to decrease significantly to 18 nm. Furthermore, the particle size distribution was narrowed from a range of 130-1150 nm to 130-600 nm. However, extended milling duration up to 50 hours only reduced the crystallite size slightly and showed insignificant effect on the particle size distribution. Furthermore, a short milling duration was desirable to minimize tungsten carbide contamination from the milling media. Therefore, the milling duration for the high-temperature-synthesized SFO powder was set as 3 hours in the current research work.

Figure 3-4 illustrated the synthesis route of the SFO metal oxide particles, which involves a combination of high temperature solid state reaction and high-energy ball milling process. Starting materials for the synthesis of the SFO metal oxide included strontium carbonate (SrCO_3 , 99.9+ % purity) purchased from Sigma-Aldrich and iron (III) oxide ($\alpha\text{-Fe}_2\text{O}_3$, hematite, 99.945 % purity) supplied by Alfa Aesar. Ethanol of reagent grade was obtained from Merck. The starting materials with stoichiometric

quantity were homogenized through wet milling in ethanol at 150 rpm for 6 hours by using agate milling media. The wet mixture was dried at 100 °C in an oven for 12 hours. Then, the dry mixture was placed in an alumina crucible and annealed at 1200 °C for 24 hours in oxygen ambient for two cycles in a Carbolite bottom loading furnace. Intermittent grinding using agate mortar was carried out in between the two annealing cycles for re-mixing purpose. The obtained SFO powders were then subjected to 3 hours of high-energy ball milling in a Retsch PM400 Planetary Ball Mill system, as shown in Figure 3-5. Tungsten carbide (93 wt % of WC and 6 wt % of Co) vial and balls were chosen as the grinding media. The vial had a volume of 250 ml with an inner diameter of 75 mm while the balls had a diameter of 20 mm. The ball-to-powder weight ratio was set at 20:1. Milling was conducted in 5 cycles, in which each cycle involved 25 min of milling at a speed of 200 rpm followed by 5 min of pausing to prevent overheating of the milling system. The as-synthesized SFO metal oxide particles were then directly used for characterization of their physicochemical properties.

Figure 3-4 Flow chart for the synthesis of the SFO metal oxide particles.

Figure 3-5 Retsch PM400 Planetary Ball Mill system.

3.4 Material Characterization

This section focuses on the characterization of the surface properties of the SFO metal oxide including its surface elemental oxidation state, specific surface area and surface charge through XPS, BET and zeta potential measurements. A brief discussion on physical properties such as crystallography, crystallite size and morphology of the metal oxide is also included.

3.4.1 Physical Property of SFO Metal Oxide

3.4.1.1 Crystallography and Crystallite Study

The non-destructive X-ray diffraction technique was employed to identify the crystalline structure and phase of the SFO metal oxide using the Shimadzu XRD-6000 diffractometer. The X-ray source was copper *K α 1* radiation with a wavelength of

1.5418 Å and was generated by bombarding a copper target with the electron beam at 40 kV and 40 mA. The SFO metal oxide samples were scanned with a scan rate of 1.5 ° per minute and step size of 0.01 ° from 20 ° to 70 °. The crystallite size was calculated from the full width at half maximum (FWHM) of the most intense (110) reflection peak by using the Scherrer equation, as shown in Eq. (3-2), in which K is the Scherrer constant, usually taken as 0.9 while λ is the wavelength of the X-ray radiation and β is the FWHM of the diffraction peak (in radians) located at 2θ .

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

Figure 3-6(a) shows the XRD pattern of the as-formed SFO metal oxide after high temperature reaction. All diffraction peaks can be indexed to the perovskite phase of $\text{SrFeO}_{3-\delta}$ (JCPDS PDF #34-0638) [15]. The absence of any traces ascribed to the starting materials ascertained that they were successfully incorporated into the perovskite structure of the as-formed SFO metal oxide. The single perovskite phase was well-preserved after 3 hours of high-energy ball milling, as shown in Figure 3-6(b). Furthermore, no noticeable shift of the diffraction peaks can be seen from the XRD pattern, signifying that a short milling process caused negligible impact on the crystal structure of the SFO metal oxide. In addition, the absence of diffraction peaks belonging to tungsten carbide confirmed that the milled SFO metal oxide was free of contamination originated from the milling media. After milling, all diffraction peaks experienced a reduction in intensity due to peak broadening, which in turn indicated a reduction of the corresponding crystallite size. The calculated crystallite size of the as-formed SFO metal oxide before milling was 60 nm. It was reduced to 14.6 nm after 3 hours of milling. The reduction of crystallite size was resulted from fragmentation of the SFO particles induced by the impacts created in between the balls and inner

wall of the vial as well as by ball-to-ball collisions during the mechanical milling process.

Figure 3-6 XRD patterns of (a) as-formed SFO metal oxide after high temperature reaction and (b) milled SFO metal oxide after high-energy ball milling. Crystallite size: As-formed -- 60 nm; milled – 14.6 nm.

3.4.1.2 Morphology Study

The morphology of the SFO metal oxide was observed with the LEO 1550 Gemini scanning electron microscope (SEM). The SEM was operating at the e-beam accelerating voltage of 5 kV and the working distance of 8 mm. The samples were prepared by dispersing the metal oxide particles in ethanol with 30 minutes of ultrasonic agitation before dropping the dispersion onto clean silicon wafer pieces

with thin silicon dioxide layer maintained at 60 °C to assist the evaporation of the ethanol.

Figure 3-7 depicts the SEM micrographs of the as-formed and milled SFO metal oxides. From Figure 3-7(a), it can be seen that the as-formed metal oxide consists of large micron-sized irregular shape aggregated particles, which is a common observation for material prepared via the conventional high temperature solid state reaction route. During the subsequent high-energy ball milling process, the repeated ball-particle-ball collisions generated high-energy impacts to flatten and fracture the SFO metal oxide particles, creating new surfaces with high density of dislocations and other structural defects. The deformation and fracturing of the SFO particles caused a significant decrease in the particles size to < 500 nm, as revealed in Figure 3-7(b). Furthermore, the milled SFO metal oxide particles were found to have a relatively uniform shape with rougher surface as compared to the as-formed counterpart. It should be noted that the reduction in the aggregated particle size was in line with the reduction of the crystallite size from 60 nm to 14.6 nm after milling as determined by XRD in Figure 3-6. The presence of relatively larger aggregates could be due to mild agglomeration of the milled SFO metal oxide particles in the ethanol dispersant during sample preparation.

Figure 3-7 SEM micrograph of (a) as-formed and (b) milled SFO metal oxides under magnification of 5,000 X and 10,000 X respectively.

3.4.2 Surface Property of SFO Metal Oxide

3.4.2.1 Surface Elemental Chemical State and Composition

The surface elemental chemical state and composition of the SFO metal oxide were characterized through X-ray Photoelectron Spectroscopy (XPS). The surface analysis was conducted in ultra-high vacuum (1×10^{-8} mbar) in a Kratos AXIS spectrometer with pass energy of 40 eV. Monochromatic Al K α (1486.71 eV) radiation was used as the X-ray source. Charge neutralizer was turned on throughout the scanning to minimize charging effect on the samples. Curve fitting was performed through the Lorentzian-Gaussian method (LG (30)) with Shirley background subtraction. C 1s peak from ubiquitous carbon contamination of the sample at 285 eV was taken as the binding energy (B. E.) reference.

Table 3-1 Surface elemental binding energy and atomic concentration of as-formed and milled SFO metal oxides.

Description	Label	B. E. (eV)	Atomic Concentration (%)	
			As-formed	Milled
C-H	a	285.0 $\pm$ 0.0	25.66	24.74
C-O	b	286.0 $\pm$ 0.1	2.88	4.44
CO ₃ ²⁻	c	289.7 $\pm$ 0.0	6.48	8.00
O _{latt, I}	a	528.1 $\pm$ 0.0	3.07	3.05
O _{latt, II}	b	529.4 $\pm$ 0.1	13.54	11.73
Adsorbed O ⁻ /O ₂ ⁻ /O ₂ ²⁻	c	530.4 $\pm$ 0.0	1.90	2.75
CO ₃ ²⁻	d	531.3 $\pm$ 0.1	24.50	24.03
Adsorbed H ₂ O	e	532.8 $\pm$ 0.2	3.19	1.81
Fe ³⁺	3/2a	709.8 $\pm$ 0.0	2.83	2.24
Fe ⁴⁺	3/2b	711.5 $\pm$ 0.0	2.10	1.85
Satellite of Fe ³⁺	3/2c	717.8 $\pm$ 0.0	0.54	0.46
Orbital splitting (Fe ³⁺)	1/2a	723.5 $\pm$ 0.1	1.41	1.11
Orbital splitting (Fe ⁴⁺)	1/2b	725.1 $\pm$ 0.1	1.04	0.92
Orbital splitting (Fe ³⁺ satellite)	1/2c	731.6 $\pm$ 0.0	0.27	0.23
Sr-O _I	5/2a	132.2 $\pm$ 0.1	1.86	1.82
Orbital splitting (Sr-O _I)	3/2a	133.7 $\pm$ 0.1	1.24	1.21
Sr-O _{II}	5/2b	133.0 $\pm$ 0.1	0.60	1.03
Orbital splitting (Sr-O _{II})	3/2b	134.8 $\pm$ 0.0	0.40	0.69
SrCO ₃	5/2c	133.9 $\pm$ 0.0	3.90	4.73
Orbital splitting (SrCO ₃)	3/2c	135.6 $\pm$ 0.0	2.59	3.15

Figure 3-8 XPS spectra of (a) C 1s, (b) O 1s, (c) Fe 2p, and (d) Sr 3d of (i) as-formed and (ii) milled SFO metal oxides.

Table 3-1 summarizes the surface elemental binding energy and atomic concentration of both as-formed and milled SFO metal oxides. Figure 3-8(a) reveals that the C 1s core level spectra of both SFO metal oxides contain three components at 285 eV (label a), 286.0 ± 0.1 eV (label b) and 289.7 eV (label c) respectively. The former two components were attributed to C-H and C-O of hydrocarbon contaminants; while the latter was attributed to the carbonate species (CO_3^{2-}) [14, 126, 127]. Formation of surface carbonate species had been commonly seen in strontium-based metal oxides due to the interaction between the surface strontium cations and carbon dioxide in the ambient atmosphere [14, 127, 128]. Furthermore, no strontium carbonate was observed in the XRD pattern of both SFO metal oxides (in Figure 3-6). Therefore, the observed surface carbonate species were unlikely originated from the strontium carbonate starting material, instead it was probably formed on the surface of the SFO metal oxide particles during the exposure to the ambient carbon dioxide.

The O 1s core level spectra of both SFO metal oxides could be de-convoluted into five components (in Figure 3-8(b)). The components at 529.4 ± 0.1 eV (label b), 530.4 eV (label c), 531.3 ± 0.1 eV (label d), and 532.8 ± 0.2 eV (label e) could be assigned to lattice oxygen (O_{latt}), adsorbed $\text{O}^-/\text{O}_2^-/\text{O}_2^{2-}$, surface carbonate, and adsorbed water molecules respectively [15, 128]. The as-formed SFO metal oxide had a relatively larger amount of lattice oxygen (13.54 %) as compared to its milled counterpart (11.73 %), reflecting more oxygen vacancies were formed in the milled SFO metal oxide. SFO is inherently a non-stoichiometric oxide due to the presence of mixed Fe^{3+} and Fe^{4+} , oxygen vacancies are formed to maintain its charge balance [14, 106, 125]. The mechanical milling caused bond breaking and release of oxygen from the lattice structure, therefore, further inducing the formation of oxygen vacancies [129, 130]. It had been reported that oxygen molecules were adsorbed directly at the

oxygen vacancies, followed by dissociation into mono-atomic oxygen ions (O^-) or reduction to diatomic superoxide (O_2^-) and peroxide species (O_2^{2-}) [131, 132]. This explained the larger amount of adsorbed oxygen species on the surface of the milled SFO metal oxide (2.75 %) than that of as-formed metal oxide (1.90 %). The adsorbed oxygen species at the oxygen vacancies had been reported to play crucial roles in the oxidation of organic compounds [15, 133]. The fifth component located at a lower B. E. of 528.1 eV (label a) was likely due to the presence of another oxygen lattice type in both metal oxides, and thus, it was named as $O_{latt, I}$.

From Figure 3-8(c), the Fe 2p spectra consist of three spin-orbit Fe $2p_{3/2}$ -Fe $2p_{1/2}$ doublet pairs. The energy separation of each doublet pair was about 13.7 eV. In a stoichiometric SFO, iron should have an oxidation state of +4. However, Fe^{4+} is known to be an unstable species which could be easily reduced to Fe^{3+} . Ji and coworkers had observed the co-existence of Fe^{4+} and Fe^{3+} in their SFO [15]. Therefore, the first doublet pair at 709.8 eV (label 3/2 a) and 723.5 ± 0.1 eV (label 1/2 a) could be assigned to Fe^{3+} ; while the second pair at 711.5 eV (label 3/2 b) and 725.1 ± 0.1 eV (label 1/2 b) to Fe^{4+} . The presence of Fe^{3+} was further confirmed by its characteristic shake-up satellite positions at 717.8 eV (label 3/2 c) and 731.6 eV (label 1/2 c), which were about 8 eV above its main doublet pair [127, 134].

Each of the Sr 3d core level spectra in Figure 3-8(d) is made of three overlapping spin-orbit Sr $3d_{5/2}$ -Sr $3d_{3/2}$ doublet pairs. The doublet pair at 133.7 ± 0.1 eV (label 5/2 b) and 134.8 eV (label 3/2 b) could be assigned to the lattice strontium cations bound to oxygen anions [14, 135]. Another doublet pair at 133.9 (label 5/2 c) and 135.6 eV (label 3/2 c) was due to $SrCO_3$ [14, 127], which were formed through carbonation of surface strontium and ambient carbon dioxide. The third doublet pair was found to

appear at a lower B. E. of 132.2 ± 0.1 eV (label 5/2 a) and 133.7 ± 0.1 eV (label 3/2 a). Since the atomic concentration of this doublet pair was nearly identical to that of the $O_{\text{latt, I}}$, therefore, formation of another type of Sr-O bonding was believed to occur in the perovskite structure.

3.4.2.2 Specific Surface Area

Heterogeneous oxidation of environmental pollutants involves a surface chemical reaction, whereby pollutant is first adsorbed onto the surface of oxidant through electrostatic attraction and then oxidized by the reactive oxidizing agent. Therefore, oxidant with a larger specific surface area is desirable for higher adsorption and faster oxidation of adsorbed pollutants. In this project, high-energy ball milling process for a short duration was used with the aim of increasing the surface area of the SFO metal oxide through particle fragmentation and creation of surface defects and vacancies.

The specific surface area of the SFO metal oxide was determined by a multipoint Brunauer-Emmett-Teller (BET) method based on physical gas adsorption on a solid surface. The measurement was carried out using a Quantachrome Autosorb-1 system. The metal oxides were degassed at $200\text{ }^{\circ}\text{C}$ for 21 hours under vacuum to remove all pre-adsorbed compounds on their surface prior to the nitrogen adsorption at liquid nitrogen temperature (77 K). The BET specific surface area was determined by using multi adsorption data points from the range of $0.05 < P/P_0 < 0.3$, whereby a linear relationship of the BET equation was maintained. Eq. (3-3) shows the BET specific surface area formula, in which S_t is total surface area, w is sample weight, V_m is monolayer capacity, N is Avogadro's number (6.022×10^{23}), A_m is adsorbate cross

sectional area (0.162 nm^2 for nitrogen), M_v is molar volume of monolayer, s is slope and i is intercept of linear plot of $1/[W(P/P_0)-1]$ against P/P_0 .

$$\text{Surface Area} = \frac{S_t}{w} = \frac{V_m N A_m / M_v}{w} = \frac{[1/(s+i)] N A_m / M_v}{w} \quad (3-3)$$

Figures 3-9(a) and 3-9(b) exhibit the nitrogen adsorption-desorption isotherm of both as-formed and milled SFO metal oxides respectively. Through the multipoint BET analysis, the specific surface area of both as-formed and milled SFO metal oxides was determined as $1.5 \text{ m}^2/\text{g}$ and $4.1 \text{ m}^2/\text{g}$ respectively. The larger surface area was attributed to particle size reduction and surface roughening of the milled SFO metal oxide, as shown in Figure 3-7(b).

Figure 3-9 Nitrogen adsorption-desorption isotherm of (a) as-formed and (b) milled SFO metal oxides.

3.4.2.3 Surface Charge Analysis

Adsorption of pollutant onto the surface of oxidant such as SFO metal oxide involves the electrostatic attraction force. Oxidant with surface charge opposite to the pollutant is crucial for effective adsorption of pollutant onto its surface. Otherwise, pH value of the mixture has to be adjusted to a favorable condition so that the oxidant and the pollutant would have opposing surface charges. For effective degradation of the pollutants, it is essential to identify the surface charge of an oxidant in the reaction medium. Thus far, no method can directly determine the surface charge of a material. However, zeta potential method has proven to be a useful option for deducing surface charge. Zeta potential is the electrical potential of an interfacial region between a substance and its dispersion environment. There are two main factors that govern the electrical potential, namely surface charge density of the substance and ionic composition of its dispersant. When the ionic composition of dispersant is kept constant, the zeta potential is dependent on the surface charge density of the substance. Since the target pollutants to be studied in this project were soluble in aqueous environment, hence water was used as the dispersant to study the surface charge of the SFO metal oxide particles. Zeta potential analysis (using the Malvern Nano ZetaSizer, model ZEN3600 fitted with a 633 nm red laser, as shown in Figure 3-10) of the aqueous dispersion of the SFO metal oxide particles was conducted to study the surface charge of SFO metal oxides in water. Malvern Dispersive Technology Software version 5.10 was used to convert the measured electrophoretic mobility (rate of migration of the particle in an electric field) to the zeta potential by the application of Henry equation using Smoluchowski approximation, whereby $f(K_a)$ is 1.5 as aqueous medium was selected as dispersant. Eq. (3-4) shows the Henry equation, in which U_E is electrophoretic mobility, z is zeta potential, ϵ is dielectric constant, η is

viscosity and $f(K_a)$ is Henry's function. A positive zeta potential signifies a positively-charged surface while a negative value for negatively-charged surface.

$$U_E = \frac{2\epsilon z f(K_a)}{3\eta} \quad (3-4)$$

Figure 3-10 Malvern Nano ZetaSizer, model ZEN3600.

Figure 3-11 presents the zeta potential distribution (number of detected photon vs. zeta potential) of the as-formed and milled SFO metal oxide particles in water.

Figure 3-11 Zeta potential distribution of (a) as-formed and (b) milled SFO metal oxides in water.

Figure 3-11 (cont.)

The zeta potential distribution of the as-formed SFO metal oxide was mainly in the negative value region while that of the milled SFO metal oxide was entirely localized in the positive value region. The mean values of the zeta potential of aqueous dispersion of as-formed and milled SFO metal oxides were extracted to be - 6 mV and + 36 mV respectively. From the sign of the mean zeta potential, it can be interpreted that as-formed had negatively-charged surfaces and milled SFO metal oxides had positively-charged surfaces when dispersed in water. The positively-charged surface of milled SFO metal oxide was believed to be originated from cationic surface defects such as unfilled oxygen vacancies [136, 137], created during the high-energy ball milling process. Since most natural materials are negatively-charged [138], the positively-charged surface of the milled SFO metal oxide can promote effective adsorption of anionic pollutants through electrostatic attraction for efficient oxidative activity.

3.5 Summary

The physical characterization and a detailed study of surface properties of in-house SFO metal oxide particles synthesized through a combination of high temperature solid state reaction and high-energy ball milling process was presented in this chapter. The particle size of as-formed SFO metal oxide was greatly reduced to sub-micrometers with only 3 hours of milling, while preserving the single perovskite structure. The particle size reduction and surface roughening of the milled SFO metal oxide led to an increase in specific surface area. Furthermore, the high-energy ball milling was found to be beneficial in creating more oxygen vacancies on the surface of milled SFO metal oxide through bond breaking and oxygen escape. More surface oxygen vacancies favored higher adsorption of oxygen molecules for the formation of adsorbed oxygen species such as O^- , O_2^- , and O_2^{2-} , which had been reported to be active species in the oxidation of organic compounds. In addition, the milling treatment induced cationic surface defects, which reversed the surface charge of the SFO metal oxide from negative to positive. Positively-charged surface of the milled SFO metal oxide could promote better adsorption of most anionic materials through electrostatic attraction for efficient oxidative activity.

Chapter 4 : Advanced Oxidative Degradation of Bisphenol A (BPA) over SFO Metal Oxide

4.1 Introduction

BPA is used extensively in the production of polycarbonate and epoxy resins for vast applications such as making plastic bottles, food and beverage can linings, protective coatings and adhesives. However, BPA is known to be a toxic and carcinogenic chemical. Furthermore, it is widely known as an endocrine disruptor, rendering it to be labeled as an emerging environmental pollutant. Current AOPs for the degradation of BPA are usually energy and chemical intensive processes. This project aimed to explore the potential of the in-house synthesized SFO metal oxides for the degradation of BPA without the use of any additional chemicals or any external stimulants such as photo irradiation. In other words, the SFO should work under dark ambient condition. This is believed to be the first to report the use of SFO metal oxide particles, synthesized with high temperature solid state reaction followed by subsequent short time high-energy ball milling to produce well-formed perovskite crystalline structure with uniform particle size distribution and large enough surface areas for effective oxidative degradation of BPA and potential for cost effective AOP application.

In this chapter, the study of self-degradation of BPA under dark ambient condition is first presented. This is followed by a comparative study of BPA degradation over as-formed (labeled as unmilled) and milled SFO metal oxides. Further discussion regarding the complete oxidation of BPA is then described. Detailed studies on the identification of intermediate byproducts formed during the oxidation of BPA, which were either present in the treated solution or being adsorbed on the surface of the milled SFO metal oxide, are then followed. In addition, the investigation for the responsible reactive oxidative species (ROS) for the oxidative degradation of BPA over the milled SFO metal oxide under dark ambient condition is evaluated with the aids of relevant ROS scavengers. Based on the identified intermediate byproducts and predominant ROS, a possible degradation pathway of BPA is proposed. Finally, the effect of visible light illumination on the degradation of BPA over the milled SFO metal oxide is discussed.

4.2 Experimental Setup and Characterization

Figure 4-1 shows the schematic of a simple experimental setup of the oxidative degradation test, which contains only an enclosed glass reactor and aquatic magnetic stirrer. Unless specified, the oxidative degradation of BPA was carried out in a batch reactor under dark ambient (room temperature) condition. The initial BPA concentration was set at 440 μM . BPA solution was set at 50 mL.

Figure 4-1 Schematic of experimental setup for oxidative degradation test.

For the study on self-degradation of the target pollutants, two control samples were prepared and subjected to similar experimental condition. The first control sample was blank aqueous solution containing the target water pollutant at its natural pH value. The second control sample was adjusted using 1 M NaOH solution to the pH value of 11.5. The latter sample was essential to simulate the pH value of 11.5 of the target pollutant solution upon the addition of the SFO metal oxide.

To study the degradation of BPA over the SFO metal oxide, the dispersion of SFO metal oxide particles in the BPA solution was stirred continuously throughout the experiment duration. Approximately 4.5 mL of the treated solution was sampled at designated time intervals, centrifuged and filtered through 0.45 μm syringe filter to remove the SFO metal oxide particles. The supernatant was collected and analyzed using UV-Vis spectroscopy to determine the temporal concentration of the BPA in the solution. The UV-Vis absorbance spectra between 200 nm to 400 nm were recorded on a Shimadzu UV2400 UV-Vis spectrophotometer. Figure 4-2 shows the typical absorption spectrum of BPA aqueous solution. A distinctive characteristic absorption

peak of BPA at the wavelength of 276 nm is attributed to the π - π^* electronic transition of aromatic ring in the BPA molecule. As shown in Figure 4-3, the absorbance at this characteristic wavelength is proportional to the concentration of BPA in the solution. For the study of degradation of BPA over the SFO metal oxide, the normalized absorbance for samples measured at different times with respect to the initial value of absorbance (at $t = 0$ hour) at this wavelength was used to report as temporal normalized concentration of BPA (denoted as C/C_o) in the treated solution for the evaluation of BPA removal or degradation efficiency. For clearer elaboration, the BPA removal or degradation efficiency is defined as $(C_o - C)/C_o * 100\%$, whereby C_o is the initial pollutant concentration while C is the temporal pollutant concentration [139, 140].

Figure 4-2 UV-Vis absorption spectrum of BPA aqueous solution.

Figure 4-3 Absorbance at 276 nm vs. concentration of BPA aqueous solution.

The remaining TOC in all samples was monitored using a Shimadzu ASI-V TOC analyzer. About 20 mL samples were needed for the measurement. The TOC concentrations were determined using a calibration curve obtained with reference to a TOC standard solution. The formation of intermediate byproducts during the degradation of BPA over the milled SFO metal oxide was identified through HPLC analysis. HPLC measurements for the treated BPA solution and standard chemical solution were conducted using an Inertsil ODS-3 column and a series 200 UV/Vis detector at 225 nm. Mobile phase consisting of acetonitrile/water (70/30 v/v) as carrier was used at a flow rate of 1 mL min⁻¹. The assignment of HPLC peaks in all samples was done by matching their retention times with that of the standard solutions containing one of the seven chemicals reported to be the intermediate compounds formed during the degradation of BPA by other advanced oxidation processes [10, 20, 73, 77]. These compounds include 2-phenyl-2-propanol (PP), *p*-isopropylphenol (*p*-

IPP), acetophenone (AP), *p*-hydroxyacetophenone (*p*-HAP), *p*-hydroxybenzaldehyde (*p*-HBA), *p*-HBA acid and hydroquinone (HQ).

Fourier transform infrared (FTIR) was employed to examine the adsorption of BPA molecules on the surface of the milled SFO metal oxide particles. The metal oxide was recollected after the experiment and dried at 66 °C for 12 hours to remove excess water molecules. Samples were prepared by mixing the SFO metal oxide with KBr powder (purchased from Fisher Chemical) at a weight ratio of 1:100 in an agate mortar and then pressed into pellet form. Absorbance spectra of these sample pellets were recorded on a Shimadzu IRPrestige-21 FTIR spectrometer. Each FTIR spectrum was obtained with an average of 45 scans conducted in ambient condition, from 1000 cm^{-1} to 1400 cm^{-1} with a step size of 4 cm^{-1} and corrected against the spectrum of pure KBr as background.

The investigations on the presence and role of responsible ROS for the oxidative degradation of BPA over the milled SFO metal oxide under dark ambient condition were carried out by adding controlled quantity of the appropriate ROS scavengers into the BPA solution during the degradation experiments. These scavengers included Dimethyl Sulfoxide (DMSO), Benzoquinone (BQ) and Sodium Azide (NaN_3) for the ROS hydroxyl radical ($\text{OH}^\bullet$), superoxide anion radical ($\text{O}_2^{\bullet-}$) and singlet oxygen ($^1\text{O}_2$) respectively. About 0.4 mM of the ROS scavenger was added into the test mixture at the beginning of the experiment.

To study the effect of visible light illumination on the oxidative degradation of BPA over the SFO metal oxide, the experimental setup containing the mixture of metal oxide and pollutant was illuminated with a UHP-Mic-LED-White light source. The visible light illumination intensity was set at 100,000 Lux, which simulated the

intensity of a direct sunlight. Figure 4-4 shows the power density spectrum of a UHP-Mic-LED-White light source, which only contains emission in a wavelength range of 400 – 700 nm. LED was chosen as the external source of energy to reduce electrical energy consumption and heat generation.

Figure 4-4 Power density spectrum of UHP-Mic-LED-White light source [141].

4.3 Self-Degradation of BPA under Dark Ambient Condition

A blank BPA aqueous solution was found to have a natural pH value of 5.5. Upon addition of the milled SFO metal oxide, the pH value of the aqueous mixture would usually increase to 11.5 spontaneously. Therefore, two blank BPA aqueous solutions with an initial pH value of 5.5 and 11.5 (adjusted by 1M NaOH solution) respectively were prepared as control samples. Figures 4-5 depicts the normalized BPA

concentrations of the aqueous solution as a function of time for both control samples under dark ambient condition. The BPA concentration in the aqueous solution at its natural pH value showed negligible degradation of the organic compound throughout the experiment of 8 hours. On the other hand, the BPA concentration was noticed to drop by about 17 % for the basic control sample after the first hour and remained constant for the remaining experiment duration. The initial decrease of BPA concentration was most likely associated with the transformation of the BPA molecules into bisphenolate ions due to the deprotonation of its hydroxyl group in a strong basic solution as illustrated in Eq. 4-1, which was reported to have a pK_a in the range of 9.6-10.2 [142, 143]. Therefore, the results shown in Figure 4-5 confirmed that BPA molecules did not suffer from self-degradation in either strong basic or its natural pH aqueous medium.

Figure 4-5 Variation of the normalized BPA concentrations in blank BPA aqueous solutions with initial pH values of 5.5 and 11.5 respectively as a function of time under dark ambient condition.

4.4 BPA Degradation over High-Energy Ball Milled SFO Metal Oxide

Figure 4-6 compares the normalized BPA concentrations in BPA aqueous solution under dark ambient condition over the milled SFO metal oxide particles to the unmilled SFO metal oxide particles with the same SFO metal oxide loading of 2.09 mM in the aqueous solutions. The BPA concentration in aqueous solution was observed to decrease under the action of the dispersed SFO metal oxide particles in the BPA aqueous solution. As shown in previous section, BPA molecules would not suffer from self-degradation even in strong basic aqueous medium, it could be concluded that the reduction of the BPA concentration in the presence of the dispersed SFO metal oxide particles was mainly attributed to adsorption and/or oxidative degradation of BPA by the dispersed SFO metal oxide particles.

Figure 4-6 Effect of high-energy ball milled SFO metal oxide on the normalized BPA concentrations under dark ambient condition. SFO loading: 2.09 mM.

It was apparent that high-energy ball milling of the as-formed SFO metal oxide particles for 3 hours significantly enhanced the BPA removal of the SFO metal oxide. After 8 hours of reaction duration, 95 % of BPA in the aqueous solution was removed by the milled SFO metal oxide, which was significantly higher than that of the unmilled counterpart (40 %). As shown in Section 3.4.2.3, the dispersion of milled SFO metal oxide particles in water were found to have positive zeta potential. In the presence of the milled SFO metal oxide particles, the BPA aqueous solution had a natural pH value of 11.5, a condition which favored the deprotonation of the hydroxyl groups of BPA molecules into forming negatively-charged bisphenolate ions (BPA^-). Consequently, the negatively-charged BPA^- ions were attracted toward the positively-charged surface of the milled SFO metal oxide particles, resulting in higher adsorption and interaction of the BPA molecules with the active sites on the SFO

metal oxide surfaces. On the other hand, the dispersion of the unmilled SFO metal oxide particles in water would have a negatively-charged surface potential which would tend to repel the BPA^- ions, causing lower adsorption of the BPA molecules and reduced the BPA removal efficiency.

Furthermore, as compared to the as-formed or unmilled counterpart, the milled SFO metal oxide had relatively larger surface area for increased adsorption of BPA^- ions and active sites that resulted in enhanced BPA removal efficiency. As reported in the literature, larger surface area is beneficial for improved BPA removal efficiency by providing more surface active sites [144, 145]. In addition, surface defects created during high-energy ball milling such as oxygen vacancies [146-148] could interact with adsorbed oxygen molecules to produce more active oxidizing species like $\text{O}^\cdot$, $\text{O}_2^\cdot$, and O_2^{2-} [15, 133]. Nemudry and coworkers had also acknowledged the important role of extended defects such as dislocations and stacking faults for the high reactivity of SFO at ambient temperature [149]. In summary, high-energy ball milling for a short duration was demonstrated to be promising in altering surface properties of the SFO metal oxide for potential use as material alternative for AOT application. The milled SFO metal oxide was subjected for further detailed investigations in the subsequent studies.

4.5 Loading Effect of Milled SFO Metal Oxide Particles on BPA Degradation

Figure 4-7 reveals the loading effect of the dispersion of milled SFO metal oxide particles on BPA removal under dark ambient condition, in which the BPA removal was improved with increasing milled SFO metal oxide particle loading.

Figure 4-7 Loading effect of the milled SFO metal oxide particles on the normalized BPA concentrations under dark ambient condition.

After treatment duration of 12 hours, the BPA removal efficiencies were found to be 39.5 %, 68.4 %, 89.2 %, 96.6 %, and 97.0 % in the presence of 0.52 mM, 1.04 mM, 1.57 mM, 2.09 mM, and 2.61 mM of the milled SFO metal oxide particles respectively. The increased adsorption and degradation of BPA could be attributed to

the increase in the available active surface area and more active surface sites being present when higher loadings of the milled SFO metal oxide particles was used.

The reduction of the BPA concentration in the aqueous solution might also be caused by the physical adsorption of the BPA molecules onto the milled SFO metal oxide surface. The adsorbed BPA molecules might be still partially intact without undergoing any oxidative degradation. To distinguish this possible physical adsorption process from the actual removal process of BPA under oxidative degradation action of the SFO metal oxide, the spent SFO metal oxide particles were recollected after the degradation experiments and examined by FTIR using the procedure described in Section 4.2. Figure 4-8 (b-f) shows the FTIR absorbance spectra of the spent SFO oxide particles used in the experiments to study the SFO particle loading effect at different loadings from 0.52 mM to 2.61 mM. Spectra of the pristine milled SFO metal oxide (a) and BPA (g) were included as reference.

For the pristine BPA molecules, two major overlapping adsorption bands between 1140 cm^{-1} and 1280 cm^{-1} could be observed in spectrum (g). The first band peaked at 1238 cm^{-1} was due to C–O stretching of the phenyl ring while the second band at 1178 cm^{-1} was attributed to in-plane bending of the *p*-substituted phenyl ring of the BPA molecules [150, 151]. These two bands were absent in the pristine milled SFO metal oxide, as shown in spectrum (a). For the spent SFO metal oxides after degradation experiment, two broad and weak FTIR absorption bands were observed at 1220 cm^{-1} and 1160 cm^{-1} for the SFO metal oxide loading at 0.52 mM, as shown in spectrum (b). These bands could be attributed to the C–O stretching of the phenyl ring and in-plane bending of the *p*-substituted phenyl ring of the BPA molecules respectively. The band shifting by 18 cm^{-1} toward lower wavenumber as compared to the pristine BPA

molecules could be due to the interactions of the phenyl ring of BPA molecules and/or intermediate byproducts with the SFO metal oxide surfaces.

Figure 4-8 FTIR spectra of (a) pristine milled SFO metal oxide and spent SFO metal oxide particles after BPA degradation for 12 hours of under dark ambient condition at different SFO metal oxide loadings of (b) 0.52 mM, (c) 1.04 mM, (d) 1.57 mM, (e) 2.09 mM, and (f) 2.61 mM. Spectrum (g) is for the pristine BPA molecules.

With increasing SFO metal oxide particles loading, both FTIR absorption bands became weaker and they were nearly negligible when the metal oxide loading was above 2.09 mM, as exhibited in spectra (e) and (f). Their disappearances reflected that BPA molecules and/or intermediate byproducts were absent on the surface of the SFO metal oxide, which in turn signified that the removal of BPA under dark ambient

condition was dominated in the oxidative degradation process. Milled SFO metal oxide loading of 2.09 mM and 2.61 mM gave comparable final degradation efficiency over extended experiment duration, the lower SFO particle loading of 2.09 mM was adopted in all subsequent experimental studies. To study the reproducibility of BPA degradation efficiency of the milled SFO metal oxide, four parallel experiments were conducted under dark ambient condition using the same SFO particle loading of 2.09 mM. As shown in Figure 4-9, BPA was almost completely removed by the milled SFO metal oxide within 12 hours for all four experiments with only slight difference in their initial degradation rates. This result indicated good reproducibility of the milled SFO metal oxide in degrading BPA under dark ambient condition.

Figure 4-9 Normalized BPA concentrations of the milled SFO metal oxide under dark ambient condition in four parallel experiments. SFO loading: 2.09 mM.

4.6 Complete Oxidation of BPA over Milled SFO Metal Oxide

Figure 4-10 illustrates the normalized BPA concentrations and TOC removal efficiencies in aqueous solution under the action of milled SFO metal oxide particles at the loading of 2.09 mM. After the first hour of reaction, the BPA concentration was found to decrease sharply by 69.4 % with a corresponding slightly lower TOC removal efficiency of 58.4 %. The difference between the BPA and TOC removal efficiencies was likely due to the remaining unreacted BPA molecules and intermediate byproducts.

Figure 4-10 Normalized BPA concentrations and TOC removal efficiencies of the milled SFO metal oxide under dark ambient condition. SFO loading: 2.09 mM.

In comparison, the UV-driven photocatalytic system developed by Kaneco and his group required a much higher concentration of TiO_2 photocatalyst (125 mM) to remove 63 % of BPA and 15 % of TOC in 1 hour [75]. Thus, the much better performance achieved in our current SFO-based treatment system further demonstrated its potential as a more economical candidate for advanced oxidation technology application.

It should be noted that both BPA and TOC removal rates dropped gradually with extended reaction duration. At the end of 12 hours reaction duration, near to complete removal of BPA was achieved while there was still 12 % of TOC remained in the solution. The residual TOC could be attributed to the formation of simple organic intermediate compounds upon the oxidative degradation of BPA, such as aliphatic acids and would require longer time to be further oxidized completely into CO_2 , water and inorganic ions [20].

4.7 Identification of Intermediate Byproducts during BPA Degradation over Milled SFO Metal Oxide

4.7.1 In Solution

Figure 4-11(a) presents the temporal HPLC profiles of the BPA solutions treated with the milled SFO metal oxide under dark ambient condition and sampled at different reaction durations. In the beginning (0 hour), only one HPLC peak (P1) of BPA was observed at the retention time of 5.3 minute. This profound BPA peak fell sharply after the first hour of treatment in the presence of milled SFO metal oxide and then

continued to decrease until totally diminished after treatment for 12 hours. The detection of reducing BPA concentration by HPLC method in the treated solution was in good agreement with the UV-Vis results shown in Figure 4-10. After 1 hour of reaction with the milled SFO metal oxide, two new HPLC peaks, denoted as P2 and P3, were detected as shown in Figure 4-11(a). The presence of both peaks indicated the formation of intermediate byproducts during BPA degradation, which further confirmed that higher TOC residual was present in the treated solution, as shown in Figure 4-10 and discussed in Section 4.6. Since these intermediate byproducts were eluted out from the HPLC column before BPA, they were more polar than BPA and they were likely to consist more hydroxylated structures than the parent BPA compound [74]. To identify these intermediate byproducts, seven standard chemical solutions of intermediate compounds commonly formed during BPA degradation by other AOPs were used as references. These chemicals included PP, *p*-IPP, AP, *p*-HAP, *p*-HBA, *p*-HBA acid and HQ.

Figure 4-11 (a) Temporal HPLC profiles of BPA solution treated with the milled SFO metal oxide at different reaction durations. HPLC profiles of reference standard solutions containing the chemicals of (b) *p*-HAP and (c) HQ. Inset: Enlargement of P2 peak in the HPLC profiles.

The enlarged inset in Figure 4-11(a) depicts the P2 peak located between 4.0 and 4.1 min in greater details. This peak could be matched with that of either *p*-HAP (in Figure 4-11(b)) or HQ (in Figure 4-11(c)), thus signifying the formation of either or both organic compounds as possible intermediate byproducts during the degradation of BPA over the milled SFO metal oxide. The disappearance of P2 peak after 30 hours of reaction reflected the complete degradation or oxidation of the intermediate byproduct in the solution. Further study was conducted with UV-Vis spectroscopy to verify the possible intermediate byproduct. As shown in Figure 4-12(a), a new absorption band was detected between 300 nm and 370 nm and it peaked at 326 nm

during the first hour of reaction. This new band was identical to the characteristic absorption band of *p*-HAP standard solution (in Figure 4-12(b)), therefore, this result confirmed that *p*-HAP was likely to be one of the intermediate byproducts. This band vanished after 30 hours of reaction, which indicated the successful oxidation of *p*-HAP. It should be noted that the absorption spectrum of HQ also appeared between 300 nm and 350 nm but its intensity was much smaller than that of *p*-HAP (in Figure 4-12(b)). As a result, the absorption band of HQ would overlap with that of *p*-HAP and could not be distinguished unambiguously in our experiments. Regardless, HQ was reported in the literatures to be a common intermediate byproduct formed alongside with *p*-HAP during the degradation of BPA [75, 77, 152], it was not without ground to assume that HQ would also be the intermediate byproduct as well in the BPA solution treated by the milled SFO metal oxide in our experiment. On the other hand, P3 peak in the HPLC profiles with the retention time between 3.0 and 3.5 minutes did not match with any of the other five reference standard chemical solutions. Despite the fact that the exact chemical nature of the intermediate byproduct corresponding to the P3 peak was not being able to be identified, this HPLC peak became weaker for a prolonged reaction duration and disappeared after reaction duration of 24 hours, as shown in Figure 4-11(a). This result signified the complete oxidation of this unknown intermediate compound in the solution.

Figure 4-12 (a) Evolution of a new UV band peaked at 326 nm during the oxidative degradation of BPA over the milled SFO metal oxide and (b) UV band of standard reference solutions containing the chemical of *p*-HAP and HQ.

4.7.2 On the Surface of Milled SFO Metal Oxide

To have a better understanding of the mechanism or pathway responsible for the degradation of BPA under the action of the milled SFO metal oxide, XPS technique

was used to study the adsorbed intermediate compounds on the surface of the milled SFO metal oxide. The surface carbon contents on the surface of the milled SFO metal oxide that had been subjected to different reaction durations, such as 0, 4, 12 and 30 hours were investigated and the results are shown in Figure 4-13. The binding energy of C 1s components and their corresponding surface carbon atomic concentration are summarized in Table 4-1. The C 1s core level of the pristine milled SFO metal oxide (0 h) comprised of three components. The components at 285 eV (label a) and 286 eV (label b) were contributed by C-H and C-O bonds respectively, and could be ascribed to hydrocarbon contamination [14, 126]. The higher energy component (label d) at 289.9 ± 0.1 eV could be associated with carbonate species [14].

The atomic concentrations of component a and b were found to grow considerably after 4 hours of reaction duration. This could be attributed to the adsorption of either BPA or intermediate byproducts on the surface of the milled SFO metal oxide. Furthermore, a new component (label c), which could be assigned to O-C=O bonding was detected at 288.7 ± 0.1 eV [126, 153]. Since the O-C=O bonding was absent in BPA molecule, its presence thus confirmed that BPA should have been broken down into intermediate byproducts consisting of acid-related compounds [154]. Nonetheless, the atomic concentrations of all three components gradually decreased with prolonged reaction duration, indicating that a further degradation of the corresponding adsorbed organic intermediate compounds on the milled SFO metal oxide had occurred.

Figure 4-13 XPS spectra of C 1s on the surface of the milled SFO metal oxide after different BPA degradation durations of 0, 4, 12 and 30 hours.

Table 4-1 Surface carbon atomic concentration over the milled SFO metal oxide after different BPA degradation durations.

Reaction Time	Peak Label, B. E (eV) and Peak Assignment		
	a	b	c
	285	286.1 ± 0.1	288.7 ± 0.1
	C-H	C-O	O-C=O
0 h	24.74	4.44	0
4 h	40.55	9.33	2.70
12 h	39.05	8.89	2.28
30 h	33.69	7.59	1.48

4.8 Proposed Mechanism or Pathway for BPA Degradation over Milled SFO Metal Oxide

In general, the degradation of BPA in other AOPs was reported to involve the generation and action of ROS such as $\text{OH}^\bullet$ [10, 77, 85], $\text{O}_2^{\bullet-}$ [20, 75] and $^1\text{O}_2$ [20, 155, 156]. In order to investigate the presence and role of ROS during the degradation of BPA by the milled SFO metal oxide under dark ambient condition, three different types of known ROS scavengers including DMSO, BQ and NaN_3 , were selected as scavenger for $\text{OH}^\bullet$ [157, 158], $\text{O}_2^{\bullet-}$ [60, 159, 160] and $^1\text{O}_2$ [60, 161, 162] respectively.

The action of the scavenger is to react with the ROS and the scavenger itself will be broken down or oxidized. Small quantity (0.4 mM) of the selected scavenger was added into the BPA solution for the degradation experiments over the milled SFO metal oxide for the indirect determination of the responsible ROS. The experimental degradation results are shown in Figure 4-14.

As illustrated in Figure 4-14, the BPA degradation efficiency is noticeably affected in the presence of 0.4 mM BQ. Since BQ is known to be an effective $\text{O}_2^{\bullet-}$ scavenger [60, 159, 160], the diminishing effect on the oxidation of BPA as compared with other types of scavengers strongly suggested that the ROS responsible for BPA degradation over the milled SFO metal oxide should be $\text{O}_2^{\bullet-}$.

Figure 4-14 Effect of 0.4 mM ROS scavengers on the BPA oxidative degradation over the milled SFO metal oxide under dark ambient condition. SFO loading: 2.09 mM.

To further verify the $O_2^{\bullet-}$ scavenging effect, 0.4 mM BQ in aqueous solution was treated with the milled SFO metal oxide under similar experimental condition as the BPA degradation experiment. The BQ solution was sampled and the absorption spectrum was measured using UV-Vis spectrophotometer at selected time intervals.

As shown in Figure 4-15, the absorption profile of BQ solution experienced a drastic change after the first hour of treatment with the milled SFO metal oxide. The BQ characteristic absorption peak between 200-300 nm was found to be greatly reduced and several new peaks appeared between 300-450 nm as the reaction continued. These results indicated the conversion of BQ by the milled SFO metal oxide and the formation of intermediate byproducts as the BQ molecules were being broken down

by the ROS originated from the milled SFO metal oxide surface. The disappearance of all newly formed peaks within 8 hours of reaction indicated that substantial $O_2^{\bullet-}$ had been produced by the milled SFO metal oxide to fully oxidize the BQ molecules.

Figure 4-15 Temporal absorbance spectra of 0.4 mM BQ solution after treated over the milled SFO metal oxide under dark ambient condition. SFO loading: 2.09 mM.

It had been reported that $O_2^{\bullet-}$ could be generated via the interaction between the oxygen vacancies on the metal oxide surfaces and their adsorbed oxygen molecules [136, 163]. As discussed in Section 3.4.2.1, the SFO metal oxide was inherently a non-stoichiometric metal oxide due to the presence of mixed iron ions of different states, Fe^{3+} and Fe^{4+} . As a result, the milled SFO metal oxide contained oxygen vacancies to maintain its electroneutrality. Furthermore, adsorbed oxygen species such as O^- and O^{2-} were detected on the surface of the milled SFO metal oxide (Table

3-1), therefore, it was safe to assume that $O_2^{\bullet-}$ was formed through the interaction between the adsorbed oxygen molecules and the oxygen vacancies on the surface of the milled SFO metal oxide. The atomic concentration of surface-adsorbed oxygen species on the milled SFO metal oxide after different BPA degradation durations was measured through XPS, as shown in Table 4-2. The atomic concentration of surface-adsorbed oxygen species decreased with prolonged reaction durations, as the results of the consumption of these species for $O_2^{\bullet-}$ formation.

Table 4-2 Atomic concentration of surface-adsorbed oxygen species on the milled SFO metal oxide after different BPA degradation durations.

Reaction Time	Atomic concentration (%)
0 h	2.75
4 h	2.63
12 h	1.74
30 h	1.48

As shown in Figure 4-14, the BPA degradation efficiency over the milled SFO metal oxide was only affected slightly with the addition of NaN_3 , which had been widely used to quench ROS 1O_2 [60, 161, 162]. This result showed that a marginal 1O_2 was produced by the milled SFO metal oxide and this ROS played an insignificant role in the breakdown and oxidation of BPA.

The BPA degradation also remained unaffected in the presence of DMSO, which was employed as an effective $OH^{\bullet}$ scavenger due to its high reactivity with $OH^{\bullet}$ [157, 158]. Since $OH^{\bullet}$ had been demonstrated to be a predominant ROS in other AOPs, thus,

DMSO at higher concentrations was employed to study its effect on the BPA degradation efficiency with the milled SFO metal oxide. As shown in Figure 4-16, no obvious change in the BPA degradation efficiency was observed even when 200 mM of DMSO was used. This observation indicated that no $\text{OH}^\bullet$ was generated by the milled SFO metal oxide for the BPA degradation reaction.

Figure 4-16 Effect of DMSO ($\text{OH}^\bullet$ scavenger) on the BPA oxidative degradation over the milled SFO metal oxide under dark ambient condition.

In brief, $\text{O}_2^{\bullet-}$ was determined to be the predominant ROS responsible for the dark oxidative degradation of BPA over the milled SFO metal oxide. As shown in Figure 4-8, both FTIR absorption bands at 1178 cm^{-1} and 1238 cm^{-1} , which reflect C–O stretching of the phenyl ring and in-plane bending of the *p*-substituted phenyl ring of the BPA molecules respectively, became weaker with increasing SFO metal oxide loading. After 12 hours of reaction time, both absorption bands still can be observed

on the FTIR spectra of the spent SFO metal oxide particles at a loading of 1.57 mM while almost complete oxidation of BPA was achieved (in Figure 4-7). This result indicated that the oxidative degradation of BPA involving $O_2^{\bullet-}$ mainly occurred on the surface of the milled SFO metal oxide particle after the BPA adsorption [164].

Based on the above results, a plausible BPA degradation pathway over the milled SFO metal oxide under dark ambient condition is proposed (see Figure 4-17).

Figure 4-17 Proposed pathways for the oxidative degradation of BPA over the milled SFO metal oxide under dark ambient condition.

As depicted in Figure 4-17, when the milled SFO metal oxide was added into an aqueous BPA solution, the organic BPA molecules were deprotonated and converted into bisphenolate ions (BPA⁻) – Step (I). The initial attack on the electron-rich O⁻ of

BPA⁻ ions by the highly reactive O₂^{•-} could lead to the formation of phenoxy radicals (denoted as BPA[•]) [77, 152], which were further transformed into quinone-like compound [77], as shown in Step (II) and (III) respectively.

Subsequent attack on the quinone-like compound by O₂^{•-} would break the organic molecule apart and yielded single-ring aromatic compounds such as *p*-HAP and HQ (Step (IV)). Those single-ring aromatic compounds were further oxidized via ring rupture reaction (Step (V)) and finally oxidized into carbon dioxide and water (Step (VI)), as supported by the substantial TOC removal.

4.9 Effect of Visible Light Illumination on Oxidative Degradation of BPA over Milled SFO Metal Oxide

Thus far, the study of BPA degradation had been carried out under dark ambient condition. However, due to availability of abundant sunlight shinning on the Earth, it was essential to investigate the effect of sunlight illumination on the BPA degradation over the milled SFO metal oxide for practical use in an open area. In this study, a direct sunlight simulator (intensity of ~ 100 kLux) was used to generate irradiation consisting only of the visible light spectrum.

Figure 4-18 compares the BPA degradation efficiency over the milled SFO metal oxide for both dark and visible light-illuminated conditions. The milled SFO metal oxide was found to exhibit higher BPA degradation efficiency under visible light illumination. Since the bandgap energy of the SFO metal oxide was 1.8 eV, the corresponding irradiated light energy ($\lambda = 689$ nm) could be absorbed by the SFO metal oxide to generate electron-hole pairs, which would subsequently initiate a series

of photocatalytic redox reactions to produce reactive species responsible for the degradation of BPA. On the other hand, negligible self-degradation of BPA was observed for both control samples at an initial pH value of 5.5 and 11.5 respectively under lighting condition, which further confirmed the photocatalytic degradation of BPA by the SFO metal oxide.

Figure 4-18 Normalized BPA concentrations of the milled SFO metal oxide under dark condition and visible light illumination. SFO loading: 2.09 mM.

It was noted that despite more BPA degradation occurred over the milled SFO metal oxide under irradiation, the overall efficiency enhancement was moderate. This was because the black colored SFO metal oxide increased the opacity of BPA solution and as a result, only limited visible light could penetrate through the solution for photo-induced activation of the milled SFO metal oxide. Regardless, the promoting effect which visible light illumination had on BPA degradation efficiency over the milled

SFO metal oxide suggested that in order to maximize the potential of the milled SFO metal oxide in treating organic pollutants, the treatment reactor should be built within a well-lit environment so that it could harvest the solar energy for photocatalytic action to degrade BPA during day time and then switch to dark oxidation process when night falls.

4.10 Summary

In this chapter, the oxidative degradation of BPA over the SFO metal oxide under dark ambient was discussed. The SFO metal oxide was shown to achieve good oxidation efficiency of highly concentrated BPA in a simple reactor, without the need of external stimulant or pre-conditioning. The high-energy ball milling treatment of the SFO metal oxide significantly improved its BPA degradation efficiency under dark ambient condition by more than two fold. Further investigations revealed that the improvement in the BPA degradation performance of the metal oxide was promoted by the milling treatment which reduced the particle size, increased the specific surface area and created a positively-charged surface, that in all favored higher adsorption of the target anionic BPA organic pollutant and increased their reactions with the surface active sites of the milled SFO metal oxide.

The milled SFO metal oxide also demonstrated good reproducibility of BPA degradation efficiency. By using proper ROS scavengers, $O_2^{\bullet-}$ was identified to be the predominant ROS during the oxidative degradation of BPA over the milled SFO metal oxide. $O_2^{\bullet-}$ was likely formed through the interaction between oxygen vacancies and adsorbed oxygen molecules. Based on the identified intermediate products and the responsible ROS, a possible BPA degradation pathway was proposed, whereby

BPA was first degraded into intermediate byproducts such as *p*-HAP and HQ, followed by further oxidation that resulted in ring opening reaction and complete oxidation of these products into carbon dioxide and water. The high efficiency for oxidation of endocrine disruptor in aqueous environment by the milled SFO metal oxide thus demonstrated its potential as a promising AOP.

Chapter 5 Advanced Oxidative Degradation of Acid Orange 8 (AO8) over SFO Metal Oxide

5.1 Introduction

The excessive release of azo dyes into aqueous environment through wastewater discharge is highly problematic to aquatic life and human health. AO8 is a synthetic azo dye, which has been widely used in textile dyeing operations for its bright color and good fastness (i.e. color of azo dyes does not easily fade away) [100]. But it is toxic and carcinogenic in nature [65]. However, there are limited reports on research works for the treatment of the azo dyes in wastewater. In this project, Acid Orange (AO8) was chosen as the target model pollutant to further extend the AOT application of the milled SFO metal oxide for the degradation of azo dye.

This chapter begins with the study of the self-degradation of AO8 chemical, followed by the discussion on the effects of high-energy ball milling and the particle loading of the milled SFO metal oxide on the degradation performance of AO8. This is followed by the systematic studies using XPS, UV-Vis spectroscopy and ion chromatography to identify the intermediate byproducts and final products, as well as the reactive

oxidative species (ROS) responsible for the AOP degradation of AO8 over the milled SFO metal oxide.

5.2 Experimental Condition and Characterizations

The experimental setup and procedure for the study of AOP degradation of AO8 was similar to that used for the study of BPA as discussed in Section 4.2. Unless specified, the oxidative degradation of AO8 was carried out in a batch reactor under dark ambient (room temperature) condition. The starting concentration AO8 aqueous solution was initially fixed at 150 μM for all studies and the degradation test was monitored with UV-Vis absorption spectroscopy for a scan range from 200 nm to 700 nm. A typical UV-Vis absorbance spectrum of AO8 aqueous solution is depicted in Figure 5-1. The most dominant adsorption band of AO8 is in the visible light region with peak at a wavelength of 487 nm. As shown in Figure 5-2, the absorbance at this wavelength is proportional to the concentration of AO8 aqueous solution. For the study of degradation of AO8 over the milled SFO metal oxide, the normalized absorbance for treated AO8 solutions sampled at different times with respect to the initial value of absorbance (at $t = 0$ hour) at this wavelength was used to report as temporal normalized concentration of AO8 dye (denoted as C/C_0) in the treated solution for the evaluation of dye degradation efficiency. Ion chromatography (IC) was used to identify the presence of any intermediate byproducts, mainly the aliphatic acids such as acetic, formic, and oxalic acids, which were formed during the degradation process of AO8 over the SFO metal oxide. The IC analysis was conducted using a Dionex ICS-1000 ion chromatography system, consisting of a 4 x 250 mm IonPac AS15 anion-exchange column and a conductivity detector. 36 mM of

KOH was employed as the eluent at a flow rate of 1.2 mL/min. The identification of the intermediate byproducts can be achieved by matching the retention times of these intermediates in the samples with the standard calibration solutions containing those carboxylic acids.

Figure 5-1 UV-Vis absorption spectrum of AO8 aqueous solution.

Figure 5-2 Absorbance at 487 nm vs. concentration of AO8 aqueous solution.

5.3 Self-degradation of AO8

A blank AO8 aqueous solution has a natural pH value of 5.5. When the SFO metal oxide was mixed with the AO8 aqueous solution, the pH value of the aqueous mixture would increase to 11.5 spontaneously. Thus, two blank AO8 aqueous solutions with initial pH values of 5.5 and 11.5 (adjusted by 1M NaOH solution) respectively were prepared as control samples to study the self-degradation of AO8.

Figure 5-3 shows the normalized AO8 concentrations of the aqueous solution as a function of time for both control samples under dark condition over a period of 8 hours. Negligible decrease of AO8 concentration was observed for the aqueous solution at its natural pH value of 5.5. On the other hand, the AO8 concentration in the basic control solution was found to vary slightly with time. The slight increase in C/C_0 after 1 hour was believed to be due to equilibrium formation between deprotonation and protonation for hydroxyl group of AO8.

Figure 5-3 Variation of the normalized AO8 concentrations in blank AO8 aqueous solutions with initial pH values of 5.5 and 11.5 respectively as a function of time under dark ambient condition.

The corresponding temporal UV-Vis absorption spectra of the AO8 control solution at the pH value of 11.5 are depicted in Figure 5-4. All the absorption peaks were observed to decrease by about 15 % after 1 hour, followed by gradual restoration with several isosbestic points (wavelengths at which all spectra intersect) being formed. Both peak falling and formation of isosbestic points had been reported by Oakes and Gratton when they modulated the pH values of the similar azo dye Acid Orange 7 (AO7) solution from pH 7.2 to pH 13.4 [91]. Such spectra change was attributed to the formation of anions upon deprotonation of the hydroxyl group (attached to the ortho position of the naphthalene ring) of AO7 molecules because the dye had a pK_a value of 10.8 in a basic environment. Since AO8 had a larger pK_a value of 11.4 than that of AO7 [91], similar explanation could be used to explain the spectral change in the basic AO8 solution. The absence of bathchromic and hypsochromic shifts toward

higher and lower wavelengths respectively confirmed that AO8 molecules and anions were stable under such basic condition. Thus, this result suggested no self-degradation of AO8 would occur in the control sample solutions in either its natural pH or basic environment under dark ambient condition.

Figure 5-4 Temporal absorption spectra measured at different times of a blank AO8 aqueous solution with its pH value of 11.5 under dark ambient condition.

5.4 AO8 Degradation over High-Energy Ball-Milled SFO Metal Oxide

Figure 5-5 shows the normalized AO8 concentrations in AO8 aqueous solution under dark ambient condition over the milled SFO metal oxide particles as compared to the as-formed SFO metal oxide particles with the same metal oxide loading of 1.57 mM in the aqueous solutions. The AO8 concentration was observed to decrease under the

action of the SFO metal oxide in the aqueous solution. The AO8 degradation efficiency increased remarkably for the milled SFO metal oxide and complete degradation of AO8 was achieved in 60 minutes. However, only 19 % of AO8 was degraded by the as-formed SFO metal oxide.

Figure 5-5 Normalized concentrations of AO8 aqueous solution containing the as-formed and milled SFO metal oxides respectively under dark ambient condition. SFO particle loading: 1.57 mM.

As discussed in Chapter 4, the tremendous enhancement in degradation efficiency was attributed to the larger surface area and the formation of positively-charged surface on the milled SFO metal oxide for higher adsorption of the anionic AO8 target pollutant molecules on the SFO metal oxide particles after high-energy ball milling. Furthermore, the surface defects created during ball milling process on the milled SFO metal oxide particles also provided more oxidative active sites to degrade the AO8 dye molecules. With its superior performance over the as-formed SFO metal oxide, the milled SFO metal oxide was used for all subsequent studies.

5.5 Further Insight on AO8 Degradation over Milled SFO Metal Oxide

In this section, a detailed study of AO8 degradation over the milled SFO metal oxide under dark ambient condition is illustrated. Figure 5-6 shows the temporal absorbance spectra at different times of AO8 aqueous solution treated with the milled SFO metal oxide up to 1440 minutes.

Figure 5-6 Temporal absorption spectra of AO8 aqueous solution treated with milled SFO metal oxide particles under dark ambient condition. Inset: absorption spectrum of 2-naphthol with an initial pH value adjusted to 11.5. SFO particle loading: 1.57 mM.

Prior to the addition of the milled SFO metal oxide at 0 minute, three distinctive absorption bands of the AO8 solution were detected at 487 nm (label i), 310 nm (label

ii), and 229 nm (label iii), which could be correlated with the hydrazone tautomer, naphthalene ring, and benzene ring respectively of the AO8 molecule [165, 166]. Under the oxidative degradation action of the milled SFO metal oxide particles, the absorption peak at 487 nm decreased drastically and vanished in 30 minutes, while the shoulder band between 400-440 nm (azo tautomer) also disappeared after 60 minutes. This result showed that hydrazone tautomer was more susceptible to attack from the milled SFO metal oxide than the azo one. The orange coloration of AO8 was attributed to its light-absorbing chromophore (i.e. azo-linkage), the reduced visible light absorption thus signified the successful degradation of AO8 dye molecules after the azo-linkages were cleaved.

The collapse of the azo-linkage broke the AO8 molecule into two primary intermediate compounds, which constituted either a naphthalene ring or a benzene ring. Formation of primary intermediate compounds was evidenced by the red-shift of peaks at 310 nm (label ii) to 346 nm (label iv) and 229 nm (label iii) to 255 nm (label v) respectively after 5 minutes of reaction. It had been reported that benzenesulfonate, 4-hydroxybenzenesulfonic acid, 4-diaminobenzenesulfonic acid, 2-naphthol and 1, 2-naphthoquinone were formed as primary intermediate byproducts during the oxidative degradation of acid orange dyes [92, 167, 168]. Standard solution of 2-naphthol with its pH adjusted to 11.5 also showed a distinctive absorption band at 346 nm (inset of Figure 5-6), the red-shifted absorption band at 346 nm (label iv) could be assigned to 2-naphthol or its derivatives. Furthermore, it had been known that the addition of auxochrome functional group such as -NH_2 and -OH to a compound would cause a bathchromic shift. Thus, the other red-shifted peak at 255 nm (label v) was most likely due to the formation of aromatic compounds containing -NH_2 or -OH auxochrome substituent such as 4-hydroxybenzenesulfonic acid and 4-

diaminobenzenesulfonic acid. Nonetheless, both absorption bands were gradually suppressed when the reaction time was extended. After 240 minutes of reaction, both bands disappeared and thus suggested further degradation of those primary intermediate compounds under the action of the milled SFO metal oxide.

After completion of the experiment at 1440 minutes, the milled SFO metal oxide particles were recollected and dried at 60 °C for 12 hours to remove any adsorbed water molecules. As each AO8 molecule contained two nitrogen atoms, one sodium atom and one sulfur atom, these elements would be detected by XPS analysis if the AO8 molecules were just adsorbed onto the surface of the metal oxide particles without being destroyed. XPS analysis was performed to determine if any AO8 molecules were adsorbed on the milled SFO metal oxide surface by focusing on the N 1s, Na 1s and S 2p core level peaks in the XPS spectra.

Figure 5-7 XPS spectra focusing on the core level of (a) C1s, (b) N 1s, (c) Na 1s and (d) S 2p elemental peaks on the milled SFO metal oxide particles after 24 hours of AO8 degradation under dark ambient condition.

Figure 5-7(a) shows the C 1s core level spectra, which comprises of four components at 285 eV (label a), 286 eV (label b), 288.8 eV (label c) and 289.8 eV (label d) due to C-H, C-O, O-C=O and CO_3^{2-} [14, 126, 153]. The former two components could be due to hydrocarbon contamination and adsorption of AO8 intermediate byproducts on the surface of the milled SFO metal oxide. The O-C=O bonding was absent in AO8 molecule, its presence thus confirmed that AO8 should have been broken down into intermediate byproducts consisting of acid-related compounds [19, 169]. Furthermore, no distinctive elemental peaks were observed in N 1s, Na 1s and S 2p core level spectra. These results indicated that no appreciable dye molecules were left on the SFO metal oxide surface and thus ruled out the possibility that the fast AO8 removal in the aqueous solution was caused by surface adsorption process. Since the milled SFO metal oxide had been demonstrated to be efficient for degrading BPA, it was likely the removal of AO8 molecules had occurred through oxidative degradation over the milled SFO metal oxide.

Figure 5-8 shows the variation of the normalized concentrations of the treated AO8 solution as a function treatment time for different absorption maxima, namely 487 nm, 346 nm, and 255 nm, these maxima in turn were a measure of the concentration of the azo-linkage of the pristine AO8 molecule, intermediate byproduct 2-naphthol, and aromatic intermediate compounds containing $-\text{NH}_2$ or $-\text{OH}$ auxochrome substituent respectively. The rate of decay followed the order of 487 nm > 346 nm > 255 nm and implied that the milled SFO metal oxide had different reactivity towards those compounds, whereby the azo-linkage of AO8 molecules was most susceptible to oxidative attack by the milled SFO metal oxide while the oxidizing rate for aromatic intermediate byproducts were less effective.

Figure 5-8 Normalized concentrations of AO8 and intermediate byproducts at three absorption maxima, 487 nm, 346 nm, and 255 nm treated by the milled SFO metal oxide under dark ambient condition. SFO particle loading: 1.57 mM.

5.6 Loading Effect of Milled SFO Metal Oxide Particles

AO8 Degradation

In this study, the dispersed solid particle loading of milled SFO metal oxide in the AO8 aqueous solution was varied between 0.52 mM and 2.09 mM. The results are depicted in Figure 5-9. As shown in Figure 5-9(a), for the oxidative degradation of the 150 μ M AO8 aqueous solution, similar AO8 degradation efficiency could be observed with the milled SFO metal oxide loading at and above 1.04 mM, whereby the azo-linkage of AO8 molecules was completely destroyed within 1 hour. When the loading of the milled SFO metal oxide was reduced to 0.52 mM, complete

degradation of the AO8 azo-linkages in the aqueous solution was achieved only after 4 hours.

As exhibited in Figure 5-9(b), a spike in the normalized concentration of naphthalenic intermediate byproducts such as 2-naphthol or its derivatives occurred in the first hour of reaction due to the degradation of AO8 molecules by the milled SFO metal oxide particles at a loading of 0.57 mM. Significant improvement in degradation efficiency for the naphthalenic intermediate byproducts was found when the milled SFO metal oxide particle loading was increased from 0.52 mM to 1.57 mM, which could be ascribed to the existence of more active sites or ROS on the surfaces of milled SFO metal oxide particles. The degradation efficiency of aromatic intermediate byproducts was also found to increase with increasing milled SFO metal oxide particle loading, as shown in Figure 5-9(c). The initial increase of normalized concentration for the milled SFO metal oxide particle loading of 1.04 mM at 1 hour was likely due to the further degradation of naphthalene ring into benzene ring. However, further increase in the SFO particle loading to 2.09 mM only resulted in diminished increment in degradation efficiency of both naphthalenic and aromatic intermediate byproducts. These results demonstrated a strong dependency of the degradation of these intermediate byproducts on the milled SFO metal oxide particle loading, while signifying that an optimal dispersion loading of the milled SFO metal oxide particles, i.e. 1.57 mM, was required for the oxidative degradation of the specific concentration of AO8 pollutant in water.

Figure 5-9 Normalized concentrations of AO8 and primary intermediate byproducts at (a) 487 nm, (b) 346 nm, and (c) 255 nm of the AO8 aqueous solution treated with different loadings of milled SFO metal oxide particles under dark ambient condition. AO8 concentration : 150 μ M

5.7 Identification of Intermediate Byproducts during AO8 Degradation over Milled SFO Metal Oxide

Ion Chromatography (IC) was used to identify the intermediate byproducts after the oxidative degradation of AO8 aqueous solution for 24 hours with the milled SFO metal oxide particles at the dispersed solid loading of 1.57 mM under dark ambient condition. It was expected that the intermediate byproducts should mainly be the low molecular weight aliphatic or carboxylic acids.

Figure 5-10 depicts the IC responses of the supernatant collected after centrifugation of the treated AO8 solution as compared to the IC responses of standard reference solutions containing the low molecular weight carboxylic acids, including the acetic, formic and oxalic acids. All three acids were detected in the supernatant. The presence of carboxylic acids was further supported by the drop in the pH value from 11.5 to 8 at the end of the reaction for the treated AO8 solution, as exhibited in Figure 5-11. These findings confirmed the reported results by others that the intermediate byproducts were usually the lowest-molecular weight aliphatic acids after degradation of Acid Orange dyes [167, 169, 170].

Figure 5-10 Top curves - IC response of AO8 solution treated with milled SFO oxide at the solid loading of 1.57 mM for 24 hours under dark ambient condition. Bottom curves – IC responses of standard reference solutions containing carboxylic acids: (a) acetic, (b) formic, and (c) oxalic acids. Inset: chemical structure of the corresponding aliphatic acids.

Figure 5-11 Change in pH value of AO8 solution treated with milled SFO oxide under dark ambient condition. SFO particle loading: 1.57 mM.

Based on the above results, the degradation and breakdown of AO8 azo dye over the milled SFO metal oxide under dark ambient condition would likely involve the cleavage of the azo-linkage of the AO8 molecules to form primary naphthalenic and aromatic intermediate compounds. Progressive degradation of these primary intermediate compounds under the action of the milled SFO metal oxide would lead to further ring rupture of the naphthalene rings and benzene rings, and resulted in the formation of simple carboxylic acids upon hydroxylation [167].

5.8 Identification of Responsible ROS for AO8 Degradation over Milled SFO Metal Oxide

The existence and type of ROS on the surfaces of the milled SFO metal oxide particles and their role on the degradation of AO8 under dark ambient condition can be identified indirectly by using appropriate ROS scavengers during the degradation experiments. The degradation experiments were performed for up to 60 minutes on the AO8 aqueous solution over the milled SFO metal oxide with the solid loading of 1.57 mM and the addition of 0.4 mM of different types of ROS scavenger. The normalized concentration of the remaining AO8 dye in the aqueous solution was monitored at different time intervals by measuring the optical absorbance of the solution at the wavelength of 487 nm, which was ascribed to the azo-linkage of the AO8 dye molecule.

Figure 5-12 exhibits the degradation results under the effects of different types of ROS scavenger. It was observed that the AO8 degradation by the milled SFO metal oxide was significantly suppressed in the presence of BQ ($O_2^{\cdot-}$ quencher). This result

reflected that $O_2^{\bullet-}$ should be generated on the surface of the milled SFO metal oxide particles and responsible as active oxidizing agent to degrade the AO8 molecules. On the other hand, negligible inhibitory effect of DMSO ($OH^{\bullet}$ scavenger) and NaN_3 (1O_2 scavenger) on the AO8 degradation indicated both $OH^{\bullet}$ and 1O_2 reactive oxidative species played an insignificant role in degrading the Acid Orange dye over the milled SFO metal oxide. In brief, degradation of AO8 over the milled SFO metal oxide under dark ambient condition could be initiated by the attack of $O_2^{\bullet-}$ on the electron-rich azo group, causing cleavage of the azo-linkage. This result was also in good agreement with that of the BPA degradation discussed in Section 4-8, hence confirming the role of $O_2^{\bullet-}$ in the degradation and breakdown of AO8 organic pollutants by the milled SFO metal oxide.

Figure 5-12 Effect of ROS scavengers on the oxidative degradation of AO8 over the milled SFO oxide under dark ambient condition. SFO particle loading: 1.57 mM; ROS scavenger concentration: 0.4 mM.

5.9 Effect of Visible Light Illumination on Oxidative Degradation of AO8 over Milled SFO Metal Oxide

As described in Section 4.9, it was demonstrated that visible light irradiation was beneficial for the milled SFO metal oxide to act as a photocatalyst to enhance the BPA degradation efficiency. Hence, the effect of simulated visible light illumination (400-700 nm) on the degradation of AO8 solution over the milled SFO metal oxide was also investigated. As depicted in Figure 5-13, the degradation performance of the AO8 solution over the milled SFO metal oxide did not show any discernable improvement under illumination condition as compared with the purely oxidative degradation effect under dark ambient condition for the cleavage of the azo-linkage of the AO8 molecules. This result indicated that the dark oxidation activity of the milled SFO metal oxide toward the initial breakdown of the AO8 molecules was very effective and more dominant than any photocatalytic reaction if existed. On the other hand, the degradation of naphthalenic and aromatic intermediate byproducts formed after the cleavage of the azo-linkage of the AO8 molecules exhibited some obvious photocatalytic activity under the simulated visible light illumination. It should be noted that these intermediate byproducts could only absorb light with wavelengths near the UV light region. Since no UV light source was present in the simulated visible light illumination, the improved degradation efficiency of these intermediate byproducts could only be contributed by the photocatalytic excitation of the milled SFO metal oxide rather than the self-induced photolysis of these byproducts. The enhanced effect with visible light illumination on the AO8 degradation further suggested that our SFO-based AOP system could be used at a well-lit location to fully realize the dual-functionality of the milled SFO metal oxide as a visible-light-

activated photocatalyst during day time and as a dark oxidant at nightfall. The rise in concentration of the aromatic intermediate byproduct during the initial 60 minutes of AO8 degradation could be due to the increased formation of monoaromatic compound from the degradation of naphthalenic intermediate byproduct along with the formation of aromatic intermediate byproducts from the cleavage of azo linkage of the AO8 molecules. Rivera-Utrilla and his co-workers had demonstrated that oxidative degradation of naphthalenic compounds via ozonation resulted in the formation of monoaromatic compounds before further broken down into the lowest-molecular weight aliphatic acids [171].

Figure 5-13 Comparison of normalized concentrations of AO8, naphthalenic and aromatic intermediate byproducts over the milled SFO oxide under dark and visible-light-illuminating conditions. SFO particle loading: 1.57 mM. The UV-Vis absorption peaks of AO8, naphthalenic and aromatic intermediate byproducts were at 487 nm, 346 nm and 255 nm respectively.

5.10 Reusability of Milled SFO Metal Oxide for AO8 Degradation

In comparison to other non-reusable dark AOPs such as ozonation and Fenton process, heterogeneous oxidant with good reusability is essential for economical industrial applications. Thus the reusability of the milled SFO metal oxide was examined over five cycles of AO8 degradation experiment under dark ambient condition. Each cycle lasted for 4 hours so that the azo-linkage was completely degraded within each such reaction cycle while high percentage of naphthalenic and aromatic intermediate byproducts were destroyed, as reflected by the disappearance of their corresponding absorption bands in Figure 5-6. After every cycle, the milled SFO metal oxide particles were retrieved by centrifugation and dispersed in de-ionized water for washing purpose to remove weakly adsorbed compounds on the particle surface. The collection and washing processes were repeated for two times. Without addition of any fresh SFO metal oxide particles, the recollected SFO metal oxide was reused in the subsequent cycle.

Figure 5-14 AO8 degradation efficiency of the milled SFO oxide reused for five cycles under dark ambient condition. SFO concentration: 1.57 mM.

As shown in Figure 5-14, the AO8 degradation efficiency over the milled SFO metal oxide was 99.1 %, 98.5 %, 97.3 %, 96.4 %, and 71.6 % for the five consecutive cycles respectively. It had been illustrated that longer reaction duration (> 4 hours) was required for total degradation of primary intermediate compounds (in Figure 5-6 and 5-8). Therefore, the slow decrease in degradation efficiency over the first four cycles could be due to the competition for adsorption for active surface sites on the SFO metal oxide between the remaining intermediate compounds generated in the previous cycle and the fresh AO8 molecules introduced in the subsequent cycle. The further reduction in degradation efficiency in the fifth cycle was likely compounded by the decomposition of the SFO metal oxide in aqueous solution.

Figure 5-15 XRD pattern of (a) the pristine milled SFO oxide and (b) the reused metal oxide for five cycles of AO8 degradation under dark ambient condition.

From Figure 5-15(b), the XRD pattern of the SFO metal oxide, after reused for five cycles of AO8 degradation experiment, was found to contain substantial phase of strontium carbonate. It had been reported that alkaline-earth-based metal oxides were vulnerable to carbon dioxide poisoning, resulting in the formation of carbonate species [14, 127]. Therefore, the observed strontium carbonate was likely formed through the interaction of surface strontium cations of the SFO metal oxide with dissolved carbon dioxide. Extensive formation of strontium carbonate was detrimental to the perovskite structure and the oxidative activity of the milled SFO metal oxide. Despite suffering from decomposition, the milled SFO metal oxide demonstrated good reusability for complete degradation of AO8 molecules under dark ambient condition in four cycles.

5.11 Summary

In brief, this chapter had covered and discussed the application of the milled SFO metal oxide for the degradation of an anionic azo dye, namely AO8 without any external stimulants. Through XPS analysis, the removal of AO8 by the SFO metal oxide under dark ambient condition was verified to be a non-adsorption process. The milled SFO metal oxide was found to outperform the as-formed sample for the degradation of AO8, in which the breaking of the azo-linkage resulted in the formation of primary naphthalenic and aromatic intermediate byproducts. Simple aliphatic acids such as acetic, formic and oxalic acids were subsequently formed through further degradation of those primary intermediate byproducts. $\text{O}_2^{\cdot-}$ was also found to be the primary ROS responsible for the oxidative degradation of AO8 under dark ambient condition. Lastly, the milled SFO metal oxide was demonstrated to have good reusability in degrading AO8 under dark ambient condition for up to four cycles, hence showing its potential to be a more economical oxidative process as compared to other reported non-reusable dark AOPs.

Chapter 6 : Strontium Titanate Ferrite (STF)

Metal Oxides for Advanced Oxidative Degradation of BPA and AO8

6.1 Introduction

As reported in previous chapter, the milled SFO metal oxide particles dispersed in aqueous solution was found to degrade into strontium carbonate due to carbon dioxide poisoning and hence affected its durability for advanced oxidative activity in the treatment of organic pollutants. It had been reported that the substitution of iron with titanium to form solid solution strontium titanate ferrite (hereafter referred as STF) metal oxides exhibited improved stability in reducing environments [116, 172]. Furthermore, solid solution STF metal oxides had been explored as visible-light-activated photocatalyst for water treatment application [173-176].

In this project, efforts were devoted to study the substitution of Fe content in the SFO with Ti to form the STF metal oxides for the oxidative degradation of BPA and AO8 in aqueous solutions. The resulting effects of Ti substitution for Fe on the physicochemical properties, oxidative activities and structural stability of milled STF

metal oxides with various Ti and Fe compositions (hereafter denoted as STF_x, where x is the molar ratio of Fe in the combined (Fe + Ti) composition, $0 \leq x \leq 1$), were investigated. STF_x metal oxide particles were synthesized by high temperature solid state reaction from the stoichiometric mix of starting materials containing Sr, Fe and Ti and then followed by the high-energy ball milling process similar to the synthesis of milled SFO metal oxide particles as described in Chapter 3. The effects of titanium substituent in the milled STF_x metal oxides on their performance in the oxidative degradation of AO8 and BPA under dark ambient condition are discussed in this chapter.

It is to be noted that from henceforth, the common notation of “ x ” for STF_x metal oxide, represents the molar % content of Fe in the total (Ti + Fe) composition of the STF_x material. Therefore, the sample names STF100 (or SFO), STF80, STF60, STF40, STF20, and STF0 (or STO) correspond to titanium composition of 0, 20, 40, 60, 80, and 100 molar % in the STF metal oxides respectively, as shown in Table 6-1.

Table 6-1 Sample notation of milled solid solution STF_x metal oxides with the corresponding Ti and Fe compositions.

Sample Notation x	Ti composition	Fe composition	Remark
STF100	0 %	100 %	SFO
STF80	20 %	80 %	
STF60	40 %	60 %	
STF40	60 %	40 %	
STF20	80 %	20 %	
STF0	100 %	0 %	STO

6.2 Strontium Titanate Ferrite (STFx) Metal Oxides

Strontium titanate ferrite, $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ is a continuous solid solution system between two end materials, strontium titanate, SrTiO_3 (STO) and strontium ferrite, $\text{SrFeO}_{3-\delta}$ (SFO) [102], and is denoted as STFx, where “x” represents the iron molar ratio in the total (Fe + Ti) composition. Both STO and SFO have cubic perovskite crystalline structure and studies have confirmed that the intermediate STFx metal oxides also have similar structure in the composition range of $0 < x < 1$ [102, 103, 177]. However, intermediate STFx metal oxides have properties steadily evolving from the characteristic properties of the two end materials [178, 179].

Figure 6-1 STFx bandgap energy as a function of iron composition (x) [18].

In the STFx metal oxides, the iron cations play a crucial role in shaping their energy band structures [18]. STO is a wide bandgap semiconductor with a bandgap energy of 3.2 eV [180], while the SFO is a narrow bandgap semiconductor with a bandgap

energy of 1.8 eV [16]. The bandgap energy of the intermediate STFx metal oxides was found to vary with increasing iron composition (“x” in between 0 and 1) according to the empirical relationship of $E_g(x) = 3.26 - 1.93x + 0.54x^2$ eV, as shown in Figure 6-1 [18]. Figure 6-2 shows the schematic band diagrams of STFx with low ($x = 0.10$), intermediate ($x = 0.35$) and high ($x = 0.50$) iron contents [18]. With increasing iron concentration, iron orbitals of $\text{Fe}^{3+}/\text{Fe}^{4+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ overlap to form impurity bands within the O 2p valence and Ti 2p conduction bands of SrTiO_3 . As a result, the effective bandgap energy of STFx decreases.

Figure 6-2 Schematic band diagrams for STFx solid solutions with low ($x = 0.10$), intermediate ($x = 0.35$) and high ($x = 0.50$) iron contents. [18].

For a stoichiometric STFx, the tetravalent iron (Fe^{4+}) should be substituted by tetravalent titanium (Ti^{4+}) at the B-site of the perovskite crystalline structure. Pertaining to the tendency of iron ion favoring the 3+ over the 4+ oxidation state, after substitution of some of the iron ions by Ti^{4+} in the STFx metal oxides, the remaining

iron ions in the structure have the tendency to exist with mixed oxidation states. To restore the electroneutrality of the STFx system without modifying the divalent strontium at the A-site, formation of oxygen vacancies is unavoidable [102, 178]. Both iron ions with mixed oxidation states and oxygen vacancies are responsible for the electronic and ionic conductivities of STFx. As SFO is a mixed conductor with the high level of electronic and ionic conductivities while STO has low values of electronic and ionic conductivities, the conductivities of intermediate STFx metal oxides are reduced with increasing titanium concentration [178, 179]. Figure 6-3 shows the mixed ionic-electronic conductivity of STFx as a function of oxygen partial pressure and temperature. For instance, at 850 °C and $10^{-15} < p(\text{O}_2) < 10^5$, the electronic and ionic conductivities is on the order of ~ 0.2 and $\sim 60 \text{ Scm}^{-1}$ for SFO while $\sim 9 \times 10^{-4}$ and $\sim 0.01 \text{ Scm}^{-1}$ for STO [178]. Nonetheless, the STFx system gained improved structural stability with higher titanium composition [116, 172].

Figure 6-3 Conductivities isotherms as a function of oxygen partial pressure ($p(\text{O}_2)$) for STFx with iron concentrations (a) at $T = 850 \text{ °C}$ and (b) temperatures vary from 750 °C to 1000 °C [178].

6.2.1 STFx Applications

Due to its good electronic and ionic conductivities, STFx is highly suitable for applications in gas sensors [18, 181-184], oxygen permeation membrane [172, 185], solid oxide fuel cell [186] and heterogeneous catalysis [115, 116]. The reported works of STFx-based AOP mainly involved photocatalytic reaction. A pioneer study was conducted by Wrighton and coworkers in 1976, whereby they found that STO can photocatalytically dissociate water molecules into H₂ and O₂ gases at zero applied potential in an aqueous alkaline solution under UV irradiation while remained non-destructed [187]. Ahuja and Kutty [176] found that high temperature-annealed STO metal oxide particles could completely oxidize phenol in the presence of electron scavengers such as H₂O₂ or NaClO₃ under UV irradiation. Maximum photoactivity was observed for the STO annealed at 1300 °C and further increment in annealing temperature was detrimental to the photocatalytic efficiency due to grain growth and recrystallization. Even though it was reported that STO metal oxide particles were inefficient in the photocatalytic degradation of phenol without the co-existence of oxidizing agent, a STO polycrystalline film could decompose MB more efficiently than TiO₂ under UV irradiation [174]. However, due to its wide bandgap energy with limited visible light photoactivity, the usefulness of STO photocatalyst still remains minimal. A patent had been filed on the use of nanoparticulate STFx ($0 \leq x \leq 1$) as visible-light-activated photocatalyst for anti-bacterial activity and degradation of Methylene Blue under both indoor and outdoor conditions, as illustrated in Figure 6-4 [175]. Under 40 W UV-filtered office fluorescent light irradiation, nanosized STFx particles were demonstrated to have superior photocatalytic activity than the well-known TiO₂-P25 photocatalyst. Recently, Chen and teammates reported the use of

STF90 as an active magnetic photocatalyst for the degradation of Methyl Orange under sunlight irradiation [173]. The STF90 could be easily recycled under an external magnetic field and re-dispersed in solution for reuse purpose, as shown in Figure 6-5.

Figure 6-4 (a) Photocatalytic degradation of Methylene Blue for STF90 and (b) anti-bacterial effects for STF40, P25 and control [175].

Figure 6-5 (a) Magnetic properties and reusability of STF90 for photocatalytic degradation of Methyl Orange [173].

6.3 In-house Synthesis of STFx Metal Oxides

Figure 6-6 Flow chart of the synthesis of STFx metal oxide particles.

The synthesis of STFx metal oxide particles was similar to SFO as described in Section 3.3. Together with strontium carbonate (SrCO_3 , 99.9+ % purity) and iron (III) oxide ($\alpha\text{-Fe}_2\text{O}_3$, hematite, 99.945 % purity), an additional starting material, titanium (IV) oxide (TiO_2 , rutile, 99+ % purity) purchased from Alfa Aesar was used to replace iron (III) oxide to prepare a series of STFx metal oxide particles. Stoichiometric

quantity of all starting materials were homogenized through wet milling prior to the high temperature solid state annealing and then followed by high-energy ball milling for 3 hours, as shown in Figure 6-6. The milled STFx metal oxide particles were used directly for characterization of their physicochemical properties.

6.4 Material Characterization

The same material characterization methodologies as described in Section 3.4 for the study of milled SFO metal oxide particles were used for the study of the milled STFx metal oxides. These included the determination of the physical properties, such as crystallography, crystallite size, and morphology, as well as the characterization of the surface properties of the milled STFx metal oxides including the surface elemental oxidation states, specific surface area, and surface charge through XPS, BET, and zeta potential measurements.

6.4.1 Physical Property of Milled STFx Metal Oxides

6.4.1.1 Crystallography and Crystallite Size

Figure 6-7 depicts the XRD patterns of the milled STFx metal oxides with various titanium to total (Ti + Fe) composition ratios between 0 and 100 %. The cubic perovskite crystalline phase in the STFx metal oxides was well formed after high temperature solid state reaction and well preserved after high-energy ball milling process regardless of the titanium content. Furthermore, no trace of titanium dioxide was found in all XRD patterns, which indicated that titanium had successfully

replaced iron and been incorporated into the perovskite structure to form the STFx solid solutions.

Figure 6-7 XRD patterns of STFx metal oxides, with Ti ratio to total (Ti + Fe) composition varying from (a) 0 to (b) 20, (c) 40, (d) 60, (e) 80, and (f) 100 %.

The diffraction peaks for all crystal planes shifted to lower diffraction angles with increasing titanium content. Figure 6-8 shows the enlarged XRD diffraction peaks for (110) plane. Such shift in diffraction peaks of the same crystallographic plane signified an expansion of the lattice constant in the STFx metal oxides, due to the substitution of the smaller iron cations (on size of 0.059 nm for Fe^{4+} and 0.067 nm for Fe^{3+}) by the relatively larger Ti^{4+} ions (0.069 nm) [110]. As presented in Figure 6-9, the extracted lattice constants in the STFx metal oxide increased from 0.385 nm to

0.390 nm for the titanium ratio from 0 % (SFO) to 100 % (STO). This result was consistent with the reported findings by other research groups [102, 103]. Figure 6-9 also shows the variation of the extracted crystallite sizes from the prominent XRD peaks of the synthesized STFx metal oxides as function of titanium content. The crystallite size of Ti-free metal oxide or SFO was 14.6 nm. The STFx crystallite size was relatively constant until the Ti content was above 60 %, then a gradual increase of crystallite size was observed. When Ti completely replaced iron in the STO metal oxide, the crystallite size reached the maximum value of 18.7 nm. The result was somewhat in line with the variation of the lattice constant for higher Ti content.

Figure 6-8 Enlarged XRD peaks of the reflection from (110) plane of the STFx metal oxides in Figure 6-7.

Figure 6-9 Crystallite size of the STFx oxides as a function of titanium content.

6.4.1.2 Particle Size Distribution and Morphology

Even though the STFx metal oxides had the crystallite sizes in the range of less than 20 nm as extracted from the XRD method above, the as-grown metal oxide would agglomerate to form larger size aggregated particles after the high temperature solid state reaction at 1200 °C. High-energy ball milling process was used to reduce the particle sizes as described in Chapter 3 in the synthesis of the milled SFO metal oxides. The particle size distribution of the milled STFx metal oxides dispersed in ethanol was analyzed by a dispersed particle size analyzer (Malvern Nano ZetaSizer, model ZEN3600 fitted with a 633 nm red laser, as shown in Figure 3-10). The particle size measurement was performed using a Dynamic Light Scattering (DLS) process, in which the particle was first illuminated with a laser and the intensity fluctuations in the resulted scattered light was then analyzed to calculate the size of the particles

through an in-built algorithm [188]. Measurement sample was prepared by dispersing the milled STFx metal oxide particles in ethanol with 30 minutes of ultrasonic agitation.

Figure 6-10 Particle size distribution of the milled STFx metal oxides with different Ti content dispersed in ethanol with ultrasonic agitation.

Figure 6-10 shows the particle size distribution for the various milled STFx metal oxides dispersed in ethanol. Without titanium substitution ($Ti = 0\%$) in the perovskite structure, the particle size of the milled SFO metal oxide ranged between 200 nm and 675 nm. With increasing titanium content, the mean particle size became smaller and also span of the particle size distribution first became narrower when the Ti content reached 40 % (for STF60). Further increase in Ti content resulted in almost no change in the mean particle size but increasing percentage of smaller particles with wider

particle size range from 100 nm to 800 nm for titanium content of 80 % or above (STF20 and STO). Nonetheless, the majority of the milled STF_x metal oxide particles was predominately < 500 nm (0.5 μm) in size, independent of the Ti content.

Figure 6-11 exhibits the SEM micrograph of the milled STF_x metal oxide particles under a magnification of 10,000 X. The metal oxide particles were first dispersed in ethanol before coating on solid surface for SEM inspection. Based on these micrographs, the particle size of all milled STF_x metal oxides was mainly < 500 nm, in a good agreement with the dispersed particle size measurement results in ethanol as shown in Figure 6-10. In addition, some mild aggregates were also observed and they were probably formed during the dispersing process in ethanol. Relatively smaller particle size was observed for the Ti-rich STF_x metal oxides, i.e. titanium content > 60 % (STF40, STF20, and STO). This reduction of particle size could be attributed to the hardness or compactness of the STF_x metal oxides. When the smaller iron cations (on size of 0.059 nm for Fe⁴⁺ and 0.067 nm for Fe³⁺) were substituted with the relatively larger Ti⁴⁺ cations (0.069 nm) [110], there is an increase of lattice constant. Therefore, there would be increase of lattice strain and weakening of the bond strength with increasing Ti composition [189]. As a result, the bond is more easily broken during the high-energy ball milling, leading to formation of smaller particles. Another possible explanation for the compactness of the agglomerates might be related to the magnitude of the surface charges of the STF_x metal oxides with different Ti content.

Figure 6-11 SEM micrograph of the milled STF_x metal oxides at the magnification of 10, 000X.

6.4.2 Surface Property of Milled STFx Metal Oxides

6.4.2.1 Surface Elemental Chemical State and Composition

Table 6-2 summarizes the surface elemental binding energy (B. E.) and atomic concentration of the milled STFx metal oxides. As shown in Figure 6-12, the C 1s core level spectra of the metal oxides can be de-convoluted into three components at 285 eV (label a), 286.0 ± 0.1 eV (label b) and 289.5 ± 0.2 eV (label c) respectively. The former two components (label a and label b) were attributed to C-H and C-O bonding of hydrocarbon contaminants while the latter was attributed to the presence of carbonate species (CO_3^{2-}) [14, 126, 127]. Since the XRD patterns (in Figure 6-7) were free of strontium carbonate, the observed surface carbonate was likely formed through reaction between the surface strontium of the STFx metal oxides with the ambient carbon dioxide [172, 185].

Table 6-2 Surface elemental binding energy and atomic concentration of the milled STF_x metal oxides.

Elemental Core Level	Label	Binding Energy, B. E. (eV)	Description	Atomic Concentration (%)					
				Ti (%) = 0	20	40	60	80	100
C 1s	a	285	C-H	24.74	25.37	25.41	26.70	31.48	27.65
	b	286.0 ± 0.1	C-O	4.44	3.82	5.23	3.50	4.04	4.18
	c	289.5 ± 0.2	CO ₃ ²⁻	8.00	7.21	6.85	5.33	4.29	3.46
O 1s	a	528.1 ± 0.1	O _{latt,I}	3.05	2.87	2.53	0.00	0.00	0.00
	b	529.2 ± 0.2	O _{latt,II}	11.73	13.28	15.72	21.08	22.25	27.56
	c	530.4 ± 0.1	Adsorbed oxygen species	2.75	2.52	2.35	2.10	2.01	1.76
	d	531.3 ± 0.2	CO ₃ ²⁻	24.03	23.59	20.52	18.1	13.43	11.31
	e	532.8 ± 0.1	Adsorbed H ₂ O	1.81	1.75	1.09	1.32	1.26	1.10
Ti 2p	3/2	457.9 ± 0.2	Ti ⁴⁺	0.00	1.21	2.41	3.81	4.81	6.83
	1/2	463.7 ± 0.2	Orbital splitting	0.00	0.60	1.20	1.90	2.39	3.41
Fe 2p	3/2 a	709.8 ± 0.2	Fe ³⁺	2.24	1.69	1.38	0.99	0.59	0.00
	3/2 b	711.4 ± 0.2	Fe ⁴⁺	1.85	1.47	1.28	1.07	0.68	0.00
	3/2 c	717.9 ± 0.2	Fe ³⁺ satellite	0.46	0.43	0.30	0.25	0.18	0.00
	1/2 a	723.5 ± 0.3	Orbital splitting Fe ³⁺	1.11	0.85	0.68	0.49	0.29	0.00
	1/2 b	725.0 ± 0.3	Orbital splitting Fe ⁴⁺	0.92	0.73	0.64	0.56	0.34	0.00
	1/2 c	731.6 ± 0.3	Orbital splitting Fe ³⁺ satellite	0.23	0.22	0.15	0.12	0.09	0.00
Sr 3d	5/2 a	132.2 ± 0.1	Sr-O _I	1.82	1.67	1.44	0.00	0.00	0.00
	3/2 a	134.1 ± 0.2	Orbital splitting	1.21	1.11	0.96	0.00	0.00	0.00
	5/2 b	133.0 ± 0.1	Sr-O _{II}	1.03	1.45	1.91	4.40	4.55	5.66
	3/2 b	134.8 ± 0.1	Orbital splitting	0.69	0.96	1.27	2.93	3.03	3.77
	5/2 c	133.8 ± 0.1	SrCO ₃	4.73	4.31	4.01	3.21	2.58	1.98
	3/2 c	135.5 ± 0.1	Orbital splitting	3.15	2.87	2.67	2.14	1.72	1.32

Figure 6-12 XPS spectra of C 1s core level of the milled STF_x metal oxides (from bottom to top: Ti = 0, 20, 40, 60, 80, and 100 %).

Figure 6-13 shows the XPS spectra of the (i) Ti 2p core level and (ii) Fe 2p core level in the milled STF_x metal oxides with different Ti contents. The Ti 2p spectra of the STF_x metal oxides could be defined by a symmetry spin-orbit Ti 2p_{3/2}-Ti 2p_{1/2} doublet, located at 457.9 ± 0.2 and 463.7 ± 0.2 eV respectively. The doublet is a signature characteristic of Ti⁴⁺ [190, 191]. With increased titanium content in the STF_x metal oxides, the doublet became more prominent and shifted gradually toward higher binding energy. This doublet shift could be correlated to the strong inductive effect of titanium species in “pulling” the electron cloud toward itself during the formation of Fe-O-Ti bonding [191, 192].

Figure 6-13 XPS spectra of (i) Ti 2p core level and (ii) Fe 2p core level of the milled STF_x metal oxides (from bottom to top: Ti = 0, 20, 40, 60, 80, and 100 %).

The Fe 2p spectra in Figure 6-13(ii) were found to contain three spin-orbit Fe 2p_{3/2}-Fe 2p_{1/2} doublet pairs except for that of iron-free STO metal oxide. The titanium in the STF_x metal oxides should only present as Ti⁴⁺ states, therefore, the iron ions present in the STF_x metal oxides should also be in a tetravalent state to maintain a stoichiometric STF_x solid solution system. However, the preferable oxidation state of iron ions is 3+, which in turn led to a co-existence of Fe⁴⁺ and Fe³⁺ in the milled STF_x metal oxides [110, 172, 193]. Thus, the first doublet pair at 709.8 ± 0.2 eV (label 3/2 a) and 723.5 ± 0.3 eV (label 1/2 a) was attributed to the presence of Fe³⁺ while the second pair at 711.4 ± 0.2 eV (label 3/2 b) and 725.0 ± 0.3 eV (label 1/2 b) was attributed to Fe⁴⁺. The third doublet pair at 717.9 ± 0.2 eV (label 3/2 c) and 731.6 ± 0.3 eV (label 1/2 c) belonged to the characteristic shake-up satellite of Fe³⁺ [127,

134]. The presence of the satellite peak further confirmed the presence of Fe^{3+} in the milled STFx metal oxides. Without modifying A-site cations (Sr^{2+}) in the perovskite structure, the presence of mixed iron oxidation states caused formation of oxygen vacancies in order to maintain charge neutrality of the STFx system. However, substitution of iron by titanium suppressed the ratio of $\text{Fe}^{3+}/\text{Fe}^{4+}$, as shown in Table 6-3. As a result, the reduced amount of Fe^{3+} caused less oxygen vacancies to be present in the titanium-rich STFx metal oxides.

As shown in Figure 6-14(i), the Sr 3d spectra composed of two common spin-orbit Sr $3d_{5/2}$ -Sr $3d_{3/2}$ doublet pairs. The doublet pair at 133.0 ± 0.1 eV (label 5/2 b) and 134.8 ± 0.1 eV (label 3/2 b) could be assigned to lattice Sr^{2+} [14, 135] while another pair at 133.8 ± 0.1 eV (label 5/2 c) and 135.5 ± 0.1 eV (label 3/2 c) was due to SrCO_3 [14, 127]. Atomic concentration of SrCO_3 -related strontium ions was nearly equivalent to that of the corresponding carbon species (label c), as shown in Table 6-2. When more iron was substituted with titanium, lesser surface carbonate species was detected and thus signifying that the presence of titanium ions in the perovskite structure could reduce the vulnerability of surface strontium from being poisoned by ambient carbon dioxide and increase the stability of STFx metal oxides. Prior to titanium substitution, a doublet pair was also detected at lower binding energy of 132.2 ± 0.1 eV (label 5/2 a) and 134.1 ± 0.1 eV (label 3/2 a) and it was related to the formation of another type of Sr-O bonding in the perovskite structure (in Section 3.4.2.1), denoted as Sr-O_I . When the titanium content was increased to 40 %, this doublet pair was gradually suppressed while the neighboring lattice Sr^{2+} doublet pair was in the opposing trend. The Sr-O_I doublet pair was found to disappear when the titanium content was increased to and beyond 60 %.

Figure 6-14(ii) depicts the XPS spectra of O 1s core level of the milled STFx metal oxides. As discussed in Section 3.4.2.1 and Figure 3-7, the XPS spectrum of the milled SFO metal oxide (before titanium substitution) could be de-convoluted into five components at 528.1 ± 0.1 eV (label a), 529.2 ± 0.2 (label b), 530.4 ± 0.1 (label c), 531.3 ± 0.2 (label d) and 532.8 ± 0.1 eV (label e). The former component was believed to be originated from another type of lattice oxygen, which was denoted as $O_{\text{latt,I}}$, while those four latter components were corresponding to lattice oxygen ($O_{\text{latt,II}}$), adsorbed oxygen species, surface carbonate and adsorbed water respectively [15, 128]. When iron was replaced by titanium, the $O_{\text{latt,II}}$ was growing at the expense of the $O_{\text{latt,I}}$ until the latter was completely diminished at and above 60 % of titanium content. This observation was similar to the evolution of Sr- O_{II} and devolution of Sr- O_{I} doublet pairs. Furthermore, the ratio of $O_{\text{latt,I}}/\text{Sr-}O_{\text{I}}$ was found to approach unity, as shown in Table 6-3. Therefore, two types of Sr-O bonding were present in the milled STFx metal oxide when ≤ 40 % of iron was replaced by titanium.

From Table 6-3, it could be seen that the ratio of $O_{\text{latt, II}}/(\text{Fe}+\text{Ti})$ was growing and getting closer to the stoichiometric value of 3 with an increase in titanium content. This result indicated that the introduction of titanium helped to minimize the formation of oxygen vacancies on the surface of the milled STFx metal oxides, i.e. by reducing the Fe^{3+} concentration. The decrease of oxygen vacancies was in good agreement with the reduced amount of adsorbed oxygen species detected (in Table 6-2) [15, 173].

Figure 6-14 XPS spectra of (i) Sr 3d core level and (ii) O 1s core level of the milled STF_x metal oxides (from bottom to top: Ti = 0, 20, 40, 60, 80, and 100 %).

Table 6-3 Ratio of $\text{Fe}^{3+}/\text{Fe}^{4+}$, $\text{O}_{\text{latt,II}}/(\text{Fe}+\text{Ti})$ and $\text{O}_{\text{latt,I}}/\text{Sr-O}_\text{I}$ for the milled STF_x metal oxides.

Ti (%)	0	20	40	60	80	100
$\text{Fe}^{3+}/\text{Fe}^{4+}$	1.21	1.15	1.08	0.93	0.87	0.00
$\text{O}_{\text{latt,I}}/\text{Sr-O}_\text{I}$	1.01	1.03	1.05	0.00	0.00	0.00
$\text{O}_{\text{latt,II}}/(\text{Fe}+\text{Ti})$	1.72	1.84	1.96	2.29	2.37	2.69

6.4.2.2 Specific Surface Area

Figure 6-15 Variation of BET specific surface area of the milled STFx metal oxides as a function of titanium content.

Figure 6-15 presents the measured BET specific surface area of the milled STFx metal oxides with varying titanium content. The experimental data could be well fitted with a straight line, indicating a linear relationship between the specific surface area and titanium content in the milled STFx metal oxides, which reached a maximum value of 10.4 m²/g in the STO metal oxide particles when iron was completely substituted by titanium. These results were in line with the measured particle size distribution and SEM surface morphology inspection of the milled STFx metal oxide particles as shown in Figure 6-10 and 6-11 respectively. Material with smaller particle size and/or higher porosity tends to have larger surface area. The reduced particle size

of the milled STFx metal oxides with increased titanium content was likely to be the main contributing factor toward an increase of specific surface area.

6.4.2.3 Surface Charge Analysis

Zeta potential analyses (with Malvern Nano ZetaSizer, model ZEN3600 fitted with a 633 nm red laser) of the aqueous dispersions of the milled STFx metal oxides were conducted and analyzed with the Malvern Dispersive Technology Software version 5.10 to obtain the zeta potentials of the milled STFx metal oxides in aqueous solution. A positive zeta potential signifies a positively-charged surface while a negative value for negatively-charged surface.

Figure 6-16 Variation of zeta potential of the milled STFx metal oxide particles dispersed in aqueous solution as a function of titanium content.

As displayed in Figure 6-16, the measured values of the zeta potential of the milled STFx metal oxides dispersed in water are plotted against the titanium content. In the absence of titanium, the milled SFO metal oxide had a positive zeta potential, representing a positively-charged surface. The surface of the milled STFx metal oxides remained positively-charged even when 60 % of iron ions were replaced by titanium (STF40). The positively-charged surface could be attributed to the presence of surface lattice cations and positively-charged surface defects, such as unfilled oxygen vacancies [136, 194]. However, negative zeta potential was observed when the titanium content was further increased to ≥ 80 % (in STF20 and STO). The negative value reflected that the corresponding metal oxides, i.e. STF20 and STO had negatively-charged surface in water, which in turn was most likely caused by the predominant presence of surface lattice O^{2-} ions (Table 6-2). Figure 6-17 shows the zeta potential distribution of the milled STFx metal oxide particles dispersed in water.

Figure 6-17 Zeta potential distribution of the milled STFx metal oxide particles dispersed in aqueous solution various titanium contents from (a) 0 % (SFO) to (b) 20 % (STF80), (c) 40 % (STF60), (d) 60 % (STF40), (e) 80 % (STF20), and (f) 100 % (STO).

Figure 6-17 (cont.).

6.5 Milled STFx Metal Oxides for Dark Oxidative Degradation of BPA and AO8

To study the effect of titanium content in the milled STFx metal oxides on their dark oxidative activity under ambient condition (at room temperature), AO8 and BPA were once again used as the target pollutants. The same solid contents and pollutant concentration as that in the study of oxidative activity of the milled SFO metal oxide particles were used. For the study of AO8 degradation, the solid content of the milled STFx and aqueous AO8 concentration were set at 1.57 mM and 150 μ M respectively; while higher solid content of STFx metal oxide particles of 2.09 mM was used to degrade the highly concentrated BPA aqueous solution at 440 μ M.

From Figure 6-18(a), it could be seen that the degradation efficiencies of AO8 aqueous solution under the oxidative activity of the milled STFx metal oxides with titanium content of 0 % (SFO), 20 % (STF80), 40 % (STF60), 60 % (STF40), 80 % (STF20), and 100 % (STO) were 99.6 %, 92.1 %, 60.8 %, 42.1 %, 20.6 %, and 9.4 % respectively after 8 hours of reaction duration. The reduced oxidative degradation performance of the milled STFx metal oxides with increasing titanium content signified that the presence of titanium in the perovskite structure was detrimental to its oxidative capability despite providing larger specific surface area. Due to the reduction in adsorbed oxygen species on the surfaces of the milled STFx metal oxide particles with increased titanium content (in Table 6-2), the generation of superoxide anion radicals was suppressed. As a result, lesser oxidizing ROS was formed to degrade the azo dye molecules. In addition, the much stronger suppression of degradation efficiencies for replacement of iron by titanium with Ti content $\geq$ 80 %

could be attributed to the effect of surface charge on the milled STFx metal oxide particles. The slightly negatively-charged surface of both milled STF20 and STO metal oxides tended to repel the negatively-charged anionic AO8 dye molecules and hence causing poorer adsorption of AO8 molecules on their surface for efficient oxidative degradation. Similar trend of reduction in efficiency was also observed for the oxidative degradation of BPA (in Figure 6-18(b)). The oxidative degradation efficiency of BPA aqueous solution was suppressed significantly from 96.1 % in SFO to 1.9 % in STO when titanium content was increased from 0 % to 100 % for the reaction duration of 24 hours.

Figure 6-18 Effect of titanium content of the milled STF metal oxides on the normalized concentrations of (a) AO8 and (b) BPA under dark ambient condition.

6.6 Effect of Visible Light Illumination on Oxidative Degradation of BPA and AO8 over Milled STFx Metal Oxides

Figure 6-19 shows the oxidative degradation efficiencies of BPA and AO8 aqueous solutions containing the milled STFx metal oxide particles under both dark and visible-light illumination (irradiation wavelength from 400 nm to 700 nm). With increasing titanium content in the milled STFx metal oxides, the difference between dark and photo-assisted oxidative degradation became less prominent. This was due to the increase in bandgap energy from 1.9 to 3.2 eV for the milled STFx metal oxides when the titanium content was increased from 0 % to 100 % [18]. The range of these bandgap energies corresponds to an optical absorption edge between 653 nm and 388 nm, thus indicating that the milled Ti-rich STFx metal oxides required UV irradiation for effective photocatalysis activation. Nonetheless, visible light illumination did not exert any negative impact on the oxidative activity of the milled STFx metal oxides.

Figure 6-19 Effect of visible light on the normalized concentrations of (a) BPA and (b) AO8 over the milled STF metal oxides with various titanium content from 0 % to 100 %.

6.7 Structural Stability of Milled STFx Metal Oxides after BPA Degradation

Figure 6-20 exhibits the XRD patterns of the milled STFx metal oxides after subjected to 24 hours of BPA degradation under dark ambient condition. Substantial amount of strontium carbonate was observed in the titanium-free metal oxide (SFO with Ti = 0 %), which suggested that severe decomposition of the perovskite structure had occurred on the SFO metal oxide surface during the oxidative degradation reaction due to carbon dioxide poisoning effect. However, the perovskite decomposition and formation of strontium carbonate became less obvious with increased substitution of iron by titanium in the milled STFx metal oxides. Furthermore, when the iron content was completely replaced by titanium (STO, Ti = 100 %), the perovskite structure was well-preserved with negligible presence of strontium carbonate. These observations further confirmed that titanium substitution for iron was beneficial for enhancing the structural stability of the milled STFx metal oxides, but at the expense of the oxidative reactivity of the milled STFx metal oxides.

Figure 6-20 XRD patterns of the milled STF metal oxides after BPA degradation under dark ambient condition for 24 hours. Note the presence of XRD diffraction peaks corresponding to SrCO_3 in the SFO (Ti = 0 %) and their nearly absence in STO (Ti = 100 %).

6.8 Summary

In brief, the milled STF metal oxides with different titanium contents were successfully synthesized through a combined high temperature solid state reaction and high-energy ball milling process. The single perovskite structure was well-preserved, with an increase in the lattice constants due to the larger ionic radius of titanium cations over that of iron. The particle size of the milled STF metal oxides was found to be reduced with an increase in titanium content, resulting in larger specific surface

area. Despite having larger specific area, both BPA and AO8 oxidative degradation efficiencies by the milled STFx metal oxides were suppressed when more iron was substituted with titanium. The two main reasons for the decreased oxidative degradation efficiency included: (a) lesser surface oxygen vacancies was available for both the adsorption of oxygen molecules and the generation of active oxygen species, responsible to degrade target pollutants; (b) reduction in adsorption of anionic target pollutants on the negatively-charged surface of Ti-rich STFx metal oxides ($\text{Ti} \geq 80\%$) due to electrostatic repulsion effect. On the other positive note, the structural stability of the milled STFx metal oxides was greatly enhanced with increased titanium content. Thus, it was revealed that a tradeoff between oxidative reactivity and structural stability of the milled STFx metal oxides tended to occur.

Chapter 7 : Conclusion and Recommendations

7.1 Conclusion

In this thesis, advanced oxidation processes currently used for water treatment as well as properties and applications of the SFO metal oxide were reviewed thoroughly. SFO was explored as potential material for the development of bi-functional advanced oxidation technology, with and without the use of external light stimulant. Single perovskite phase SFO metal oxide particles were successfully prepared by a combination of high temperature solid state reaction and high-energy ball milling process.

One of the achievements for this project was the study of milling effect on the surface properties of the SFO metal oxide. A short milling duration, i.e. 3 hours was found to be beneficial for the increment of the oxide surface area through particle size reduction and surface roughening. Through repeated fragmentations caused by mechanical impacts and bond breaking during ball milling, oxygen escaped from the perovskite structure of the SFO metal oxide, which in turn resulted in increased concentration of surface oxygen vacancies. Such available surface vacancies promoted more adsorption of oxygen molecules to form related active oxidizing

species such as O^- , O_2^- , and O_2^{2-} . Furthermore, the unfilled oxygen vacancies together with substantial surface cations rendered the milled SFO metal oxide surface to become positively-charged, leading to better adsorption of anionic materials for efficient oxidative activity.

With better knowledge of the surface properties of the in-house-synthesized SFO metal oxide, the metal oxide was applied for the degradation of two toxic and carcinogenic target pollutants, namely BPA and AO8. The milled SFO metal oxide demonstrated superior performance over the as-formed counterpart during the oxidative degradation of both target pollutants at high concentration without the use of any external stimulants. The removal of BPA and AO8 by the milled SFO metal oxide under dark ambient condition was confirmed to be a non-adsorption process via FTIR and XPS analyses. Both target pollutants were degraded into intermediate products and simple aliphatic acids. Through indirect probing technique with the use of appropriate ROS scavengers, superoxide anion radicals formed on the surface of the milled SFO metal oxide were identified to be the key ROS responsible for the oxidative degradation of both target pollutants. In addition, with regards to BPA, the milled SFO metal oxide demonstrated high and complete oxidation of the pollutant into carbon dioxide and water. Based on the identified intermediate products, a plausible BPA degradation pathway was proposed. On the other hand, the milled SFO metal oxide had also been reused for four cycles of AO8 degradation experiments with comparable good efficiency despite some decomposition of the SFO metal oxide into strontium carbonate due to carbon dioxide poisoning during the reusability tests. In addition, moderate improvement in the efficiency was observed during the degradation of both pollutants under visible light illumination. These results showed

the dual-functionality of the SFO metal oxide as both a dark oxidant and a photocatalyst.

To improve the structural stability of the SFO metal oxide, the iron in the perovskite crystalline structure was substituted by titanium for different molar percent, varying from 0 to 100 %. This resulted in the form of perovskite solid solutions STFx metal oxides. Increased titanium concentration was beneficial for the structural integrity of the milled STFx metal oxides with larger surface area due to smaller particle size. However, the replacement of iron by titanium also deterred the oxidative activity of the milled STFx metal oxides due to the reduction on the numbers of surface oxygen vacancies and lesser active oxidative species being generated. The surface charge of the milled STFx metal oxides was also inverted from positive to negative (when Ti content ≥ 80 %), leading to an inhibition of the adsorption of the anionic BPA and AO8 molecules, and a reduction in their oxidative degradation efficiencies. These results showed that there was a tradeoff between structural stability and oxidative activity when substituting iron with titanium.

In summary, this project had discovered for the first time the potential application of the perovskite SFO and STFx metal oxides, in particular for iron molar content, $x > 20$ % as alternative low-cost and energy-efficient material candidates for the development of novel bi-functional advanced oxidation technology for water treatment.

7.2 Recommendations for Future Research

Although we have demonstrated the capability of the milled SFO metal oxide particles for effective and efficient degradation of BPA and AO8, there are several potential works that can be performed in future to improve its practical use as an advanced oxidation technology for water treatment.

i. Widen the variety of target pollutants

In this project, only BPA and AO8 with anionic nature were selected as model pollutants. Since typical wastewater effluent contains various contaminants, therefore, it is worthy to broaden the list of probe pollutants, e.g. contaminants with cationic nature and microorganisms, for further investigation using our SFO-based system. Rhodamine B (RB), a cationic dye, is one of the commonly chosen organic compounds as model pollutant for the study of advanced oxidation processes [195-197]. Our preliminary result showed that the milled SFO metal oxide was capable of degrading RB under dark ambient condition. As depicted in Figure 7-1, 1.04 mM solid content of the milled SFO metal oxide could completely degrade 15 μ M of RB aqueous solution in 24 hours, despite the possible repelling of the cationic RB dye by the positively-charged surface of the milled SFO metal oxide. Therefore, it is interesting to further investigate the possible mechanism of the RB degradation over the milled SFO and STFx metal oxides. Besides that, real wastewater should also be adopted as test sample to validate the practical application of our SFO-based system.

Figure 7-1 Normalized RB concentrations of the milled SFO metal oxide under dark ambient condition. RB concentration: 15 μM ; SFO concentration: 1.04 mM.

ii. Hybridize SFO-based system with biological post-treatment

In general, water treatment system comprises multiple processing units based on different technologies for efficient performance at reasonable operating and maintenance costs. Our SFO-based dark oxidation process has demonstrated its merits in the elimination of toxic and carcinogenic compounds. However, complete oxidation of these compounds through such an approach requires long treatment duration. On the other hand, conventional biological treatment is known to be a cheap alternative for water treatment, but it does not always provide satisfactory results in treating industrial wastewater which contains highly concentrated and bio-recalcitrant compounds. Since it has been reported that the combination of AOPs with biological treatment creates a synergistic effect that improve both cost effectiveness and

degradation efficiency [198-200], it is thereby worth to couple our SFO-based system with biological treatment too.

iii. Alternative stability enhancement of SFO metal oxide

Chemical stability is a crucial parameter for determining the reusability of a material. Although enhanced chemical stability of the SFO metal oxide was achieved through the substitution of iron by titanium, the stability was gained at the expense of the oxidative activity. Alternative methods should be explored to achieve better stability without suppressing the oxidation performance substantially. Substitution of strontium cation with lanthanum and/or cerium ions has been explored by other research groups for the stability enhancement of Sr-based perovskite metal oxides [201, 202]. However, the resulted metal oxides have yet to be explored for water treatment application. Therefore, it is interesting to study the potential of these metal oxides for practical use in environmental-related applications. But optimization of the substituent concentration should be carried out because over-substitution is detrimental to the reactivity of the metal oxide [202, 203].

iv. Design and development of scale-up suspension reactor

A scale-up reactor is necessary for trial implementation of our SFO-based system in water treatment application. The design and development of a scale-up reactor should take into consideration the optimal operating condition for high quality treated effluent in economical means. Kinetic modeling of the oxidative degradation reaction would be useful for the optimization process. To fully utilize the dual-functionality of our SFO-based system, it is suggested that the reactor should be constructed at an area, which can harvest the most intense sunlight illumination to activate the photocatalytic

reaction during day time while not exerting any negative impact on its dark oxidation process.

v. Fabrication of supported SFO-based oxide

The suspension system used in the current research work requires post-separation process to prevent loss of the fine SFO particles. However, the post-separation process is known to be tedious and expensive. Therefore, it is worth to immobilize the SFO or STFx particles on a supporting substrate to avoid such problems. However, it is also likely that such supported SFO or STFx metal oxide particles will suffer mass transfer limitations and reduction of active surface sites if conventional non-porous substrate is used. To address these challenges, porous substrate with large surface area such as mesoporous clays, activated carbon, glass beads, and membrane could be a more ideal substrate choice [4, 204].

Author's Publications

Journal Papers:

1. **M. Y. Leiw**, G. H. Guai, X. Wang, M. S. Tse, C. M. Ng, O. K. Tan, Dark Ambient Degradation of Bisphenol A and Acid Orange 8 as Organic Pollutants by Perovskite $\text{SrFeO}_{3-\delta}$ Metal Oxide, J. Hazard. Mater., 260 (2013) 1-8.
2. **M. Y. Leiw**, M. S. Tse, G. H. Guai, C. M. Ng, O. K. Tan, Surface Properties of Nanostructured $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ Perovskite Oxides for Advanced Oxidation of Bisphenol A: Effect of Iron Concentration and High-Energy Ball Milling. 2013, submitted.
3. X. Wang, Y. Tang, **M. Y. Leiw**, T. -T. Lim, Solvothermal synthesis of Fe-C codoped TiO_2 nanoparticles for visible-light photocatalytic removal of emerging organic contaminants in water. Appl. Catal. A, 2011. 409(41): p. 257-266.

International Conference Presentations:

1. **M. Y. Leiw**, G. H. Guai, O. K. Tan, M. S. Tse and C. M. Ng, "Preparation and Characterization of Nano-structured $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ Particles for Removal of Endocrine Disruptor in Water: Case Study on Bisphenol A", International

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- Conference of Young Researchers on Advanced Materials 2012 (ICYRAM 2012), Singapore, 1-6 Jul 2012.
2. **M. Y. Leiw**, X. Wang, O. K. Tan, M. S. Tse, and C. M. Ng, "Self-induced $\text{SrFeO}_{3-\delta}$ Catalyst for Degradation of Bisphenol A", E-MRS 2012 Spring Meeting, Strasbourg, France, 14-18 May 2012.
 3. **M. Y. Leiw**, O. K. Tan, M. S. Tse, and C. M. Ng, "Synthesis of $\text{SrTi}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ @ TiO_2 Core-Shell Particles for Visible Light Photocatalytic Degradation of Bisphenol A", 5th MRS-S Conference on Advanced Materials, Singapore, 20-22 Mar 2012.
 4. **M. Y. Leiw**, O. K. Tan, M. S. Tse, and C. M. Ng, "Nano-structured $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x \geq 0.5$) Particles for Acid Orange 8 Degradation" 17th International Conference on Advanced Oxidation Technologies for Treatment of Water, Air and Soil (AOTs-17), San Diego, USA, 7-10 Nov 2011.

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