Structure – Magnetic Property Correlations in TiO$_2$ Nanotube Arrays

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ABSTRACT

TiO₂ nanotube arrays are promising candidates for applications such as photocatalysis and for potential employment in spin-electronic (spintronic) devices. The functionality of TiO₂-based nanotubes is highly dependent on their structure (microstructure and crystallographic symmetry) and magnetic properties. Unified understanding of the influence of these factors on the electronic structure of TiO₂ is of paramount importance towards engineering these materials.

This Dissertation aims at investigating the correlations of the morphology, crystallinity, crystal structure, electronic structure and magnetic properties of TiO₂ nanotubes, with potential relevance to their functionality. Self-ordered arrays of amorphous TiO₂ nanotubes (pure and Fe-doped with cationic concentration of ~2.1 at%) were synthesized by the electrochemical anodization technique, followed by subjecting them to thermal treatments up to 450 °C to crystallize these nanostructures. A variety of probes – morphological, structural, magnetic and spectroscopic – were used to characterize the properties of these nanostructures as functions of their processing conditions and the dopant content. Structure-functionality relationships in these nanostructures were verified by examining the photodegradation rate of methyl orange (a model water pollutant) in presence of TiO₂ nanotubes under UV-Visible light irradiation.

Results from this Dissertation research demonstrated that post-synthesis processing conditions – specifically, the nature of the annealing environment, as well as the presence of an external dopant, can alter the crystal structure and local electronic environment in TiO₂ nanotubes, with subsequent effects on the magnetic properties of
these nanostructures. The fundamental knowledge obtained in this research, on the interrelations of structural-magnetic properties and their potential influence on the functionality of TiO$_2$-based nanotubes, can be extended to the metal oxide semiconducting systems in general and is anticipated to provide avenues toward novel materials with enhanced functionality that originates from such tailored structural and magnetic characteristics.

Despite the success achieved in this Dissertation, there are still open questions to be addressed in order to further enhance the fundamental knowledge of structure–magnetic property correlations in TiO$_2$ nanotubes. In this regard, the concluding section of this Dissertation provides recommendations for additional experiments. Accomplishment of these recommendations is anticipated to provide enhanced insight into the various aspects of property-functionality relationships in TiO$_2$-based nanomaterials, and provides paths to engineer novel multifunctional oxide-based materials for energy-related applications.
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1.0 INTRODUCTION

Wide-band-gap titanium dioxide (TiO₂) nanostructures are promising candidates for photocatalytic applications including water splitting to produce hydrogen, employment in energy-storage devices such as Li-ion batteries, and for self-cleaning windows and sensors. [1] Recently, it has been demonstrated that crystalline TiO₂ nanotube arrays exhibit superior properties as compared to other morphologies, largely due to their larger effective surface area, vertical pathways for electron transport and suppressed electron-hole recombination. [2, 3] The functional properties of TiO₂-based nanotubes are highly dependent on their morphology and structure; thus, unified understanding of the influence of the structural attributes on the electronic structure of TiO₂ is of paramount importance toward engineering these materials.

Furthermore, introducing magnetic transition metal impurities (such as Fe) into the nanotubes’ structure is anticipated to further enhance the photoactivity of the nanotubes, for instance, by generating mid-gap energy levels that would modify the band structure and photocatalytic response of the nanotubes. In addition, positive correlations are reported among ferromagnetism, optical properties and catalysis, with unclear but intriguing conclusions. [4-7]

Fe-doped TiO₂ nanotube arrays have a high surface area and defect-rich structures, which are anticipated to enhance inherent functional responses. Examination of such systems can provide the knowledge to develop novel multifunctional nanostructures for combined spintronic, optical and photocatalytic properties, at room temperature and in one material. To this end, it is critical to understand the formation of magnetic impurities and their interaction in semiconducting TiO₂-based systems. In this
manner there is a potential to create a novel multifunctional nanostructured material with simultaneous magnetic and semiconducting properties (i.e. dilute magnetic semiconductor) for spintronic applications, in which both spin and charge degrees of freedom are employed to enable advances in enhanced data processing technologies such as instant boot-up computers. [8, 9]

The aim of this Dissertation is to obtain fundamental understanding of the interrelations of microstructure (morphology and crystallinity), crystal structure, electronic structure and magnetism in TiO$_2$ nanotubes that may influence their functionality. These properties are evaluated and correlations are investigated as functions of the following conditions:

(a) Post-synthesis processing conditions – specifically the annealing temperature/duration and the nature of annealing environment, and

(b) Introducing an external dopant (Fe).

As a relevant functionality of TiO$_2$ materials, the photocatalytic activity of nanotubes in degrading an organic dye is also examined to further clarify and evaluate the effects of structural attributes and magnetic character on the nanotube functionality.

In this Dissertation research, nominally-pure and Fe-doped TiO$_2$ nanotubes are fabricated and processed to understand their electronic structure, magnetic spin and optical response. Fe additions not only perturb band structure of TiO$_2$ but also serve as sensitive probe of lattice modification due to its large magnetic moment. Examination of Fe-doped TiO$_2$ nanotube arrays as a system with potential combined semiconducting and magnetic properties provides the opportunity to study connections between the structural
attributes and magnetic response.

In this Dissertation fundamental knowledge is achieved on the following aspects of TiO$_2$ nanotube arrays:


2. The influence of post-fabrication processing conditions on the properties and functionality of the dopant-free TiO$_2$ nanotubes, such as developing unique morphological features and tailored electronic structure.

3. The bonding state and the local electronic environment of incorporated iron in Fe-doped TiO$_2$ nanotubes, and their influence on the microstructure, crystal structure and magnetic response of TiO$_2$ nanotubes relevant to their electronic structure and functionality.

Understanding of such interrelations among band structure, magnetic character, and dopant concentration with potential relevance to the functionality of TiO$_2$-based nanotube arrays can be extended to metal-oxide semiconducting systems in general. In this Dissertation, ordered arrays of amorphous (pure and Fe-doped) TiO$_2$ nanotubes are synthesized by the electrochemical anodization technique, followed by subsequent thermal treatments in various conditions (temperatures up to 450 °C and atmospheres with oxidizing, inert or reducing nature) to crystallize these structures. A variety of probes – morphological, structural, magnetic and spectroscopic – are used to obtain a fundamental understanding of the correlations of their structural and magnetic properties.
relevant to their functionality as functions of the processing conditions and composition (Fe content).

This Dissertation contains seven main Chapters: (1) Introduction (current chapter); (2) Critical Literature Review; (3) Experimental Techniques and Methodologies; (4) Results; (5) Discussion; (6) Conclusions, and (7) Recommendations for Future Work. In the critical literature review (Chapter 2), background information concerning titanium dioxide polymorphs and structures and their semiconducting, transport and magnetic properties is presented, as well as the historic and modern applications of TiO₂ materials. An overview of synthesis methods to fabricate bulk and nanoscaled TiO₂ (pure and doped) is also provided in the same Chapter, with a focus on anodization technique for TiO₂ nanotube synthesis. Literature reports on the influence of synthesis and processing conditions on the properties (morphology, optical, structural) of anodized nanotubes and their functionality are also briefly surveyed.

In Chapter 3, Experimental Techniques and Methodologies, the procedures that are followed in this Dissertation research for fabrication, post-fabrication processing and characterization of pure and Fe-doped TiO₂ nanotube arrays are thoroughly explained. This Section includes descriptions of nanotube (pure and Fe-doped) fabrication and processing methods, characterization techniques and methods, as well as the data analysis approaches. In addition, principles of operation for fabrication and characterization equipment employed in this work are presented. Chapter 4 is dedicated to the results obtained in this Dissertation from synthesis, processing and characterization of the pure and Fe-doped TiO₂ nanotubes. Results on the morphological features, crystallinity and crystal structure, crystallization behavior, structural defects and local electronic
environment, magnetic behavior as well as the photocatalytic activity of nanotubes are presented in this Chapter.

Results from Chapter 4 provide insight for understanding and discussing the relationships between the morphology, crystal structure, local structure and magnetic behavior of the TiO$_2$ nanotubes. This Discussion forms Chapter 5.

A synopsis of the Results and Discussion (Chapters 4 and 5) are presented in Chapter 6 that forms the Conclusion Chapter. Recommendations for future work are provided in Chapter 7. Finally, the Appendix section includes the characterization studies of the nanotubes’ precursors, i.e. titanium foil and arc-melted Ti(Fe) sheet.

The knowledge obtained from this work on the properties of pure and Fe-doped TiO$_2$ nanotube arrays as functions of the synthesis and processing conditions and degree of iron incorporation into the lattice may be generalized to tailor and optimize the functional properties of other transition metal oxide nanostructures, and lead to new applications such as new catalytic or spintronic devices for a greener environment.
2.0 CRITICAL LITERATURE REVIEW

The aim of this Chapter is to review literature reports on the following aspects of titanium dioxide:

(i) Common polymorphs of titanium dioxide and their structure, along with the semiconducting and magnetic properties of bulk and nanoscaled titanium dioxide;

(ii) Various synthesis methods to fabricate bulk and nanostructured titanium dioxide, with a focus on the anodization method for synthesis of titanium dioxide nanotube arrays;

(iii) The effects of synthesis and post-synthesis processing conditions on typical properties of titanium dioxide nanostructures;

(iv) Aspects of the functional properties of titanium dioxide, in particular the photoelectric, photocatalytic and spintronic character, as influenced by the synthesis and annealing conditions and the presence of dopant.

The assessment of the literature is presented in this Chapter within three primary sections. Section 2.1 provides an introduction to TiO₂ polymorphs, structures and properties, with a focus on the semiconducting, transport and magnetic character of titanium dioxide. Various applications of titanium dioxide are reviewed in the same section. Section 2.2 presents an overview on the synthesis approaches to fabricate titanium dioxide nanostructures such as the thin films, nanoparticles and nanotubes, with a focus on the direct anodization of titanium foil for nanotube synthesis. Reports on the effects of
synthesis and processing conditions are also reviewed in this section. Finally, an overview of multiple aspects of titanium dioxide functionality is provided in Section 2.3.

2.1 **Introduction to Titanium Dioxide (TiO$_2$, Titania)**

In this section common polymorphs of titanium dioxide and their structures are introduced, followed by an overview on the electronic and magnetic properties of bulk and nanoscaled titanium dioxide. In the end, historic and modern applications of titanium dioxide are reported.

2.1.1 **Polymorphs and Crystal Structures**

Titanium dioxide (titanium (IV) oxide or titania) is a transition metal oxide that may exist in crystalline polymorphs as well as in the amorphous state. The most common polymorphs of TiO$_2$ in nature are brookite, rutile and anatase. [10, 11] Brookite is typically not found in pure phase form and it usually contains some rutile or anatase and is often not considered for experimental investigations. [10, 12, 13] Rutile is the most stable form of titanium dioxide (up to 60 kbar) and forms under high-temperature and high-pressure conditions. [14] Figure 1 provides schematic representations of the crystal structure of TiO$_2$ in these two polymorphs, anatase and rutile, along with a schematic representation of TiO$_2$ in an amorphous state. Both rutile and anatase have a tetragonal crystal structure, with unit cells containing six and twelve atoms, respectively. Titanium atoms are coordinated to six oxygen atoms to form distorted TiO$_6$ octahedra. In rutile, the octahedra share two edges whilst in anatase the octahedra share four edges; the distortion of TiO$_6$ octahedra is more significant in anatase than in the rutile structure. [15, 16] The lattice parameters and structural information of anatase and rutile are summarized in Table 1. It is reported that after reaching a specific particle size of > 14 nm, the anatase
structure transforms into the more stable rutile phase reflecting the lower surface energy of rutile for larger particle sizes. [17, 18]

Figure 1: TiO$_2$ in the amorphous state and in the form of crystalline structures of anatase and rutile.

Table 1: Lattice and structural information of anatase and rutile, two common polymorphs of TiO$_2$. [10, 19]

<table>
<thead>
<tr>
<th></th>
<th>Anatase</th>
<th>Rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Lattice parameters [Å]</td>
<td>$a = 3.78$</td>
<td>$a = 4.59$</td>
</tr>
<tr>
<td></td>
<td>$c = 9.52$</td>
<td>$c = 2.96$</td>
</tr>
<tr>
<td>Volume/molecule [Å$^3$]</td>
<td>34.06</td>
<td>31.22</td>
</tr>
<tr>
<td>Molecules/unit cell</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Density [g/cm$^3$]</td>
<td>3.79</td>
<td>4.13</td>
</tr>
</tbody>
</table>

Many metal-oxides are non-stoichiometric (defective) when synthesized under typical processing conditions. [20] Crystal structures of TiO$_2$ may contain bulk and surface structural defects such as oxygen vacancies and interstitial titanium. [21, 22] Oxygen vacancies are the most common defect in TiO$_2$ [23], and are slightly more
energetically favorable in anatase than in rutile, while Ti interstitials form more easily in rutile than in the anatase structure. TiO\textsubscript{2} can lose oxygen and become oxygen-deficient via the following reaction [20],

\[ \text{TiO}_2 \leftrightarrow \text{TiO}_{2-\delta} + \frac{1}{2} (\delta)\text{O}_2 \]

in which \( \delta \) is the deviation from stoichiometry. Structural defects can influence the electronic structure, charge transport and surface properties of TiO\textsubscript{2}-based materials, as will be explained in Section 2.3.2.

2.1.2 Electronic Properties

The electronic properties of TiO\textsubscript{2} are important in the determination of its functionality. In the following sections, semiconducting, transport and magnetic characteristics of titanium dioxide are reviewed.

2.1.2.1 Semiconducting and Transport Properties

TiO\textsubscript{2} is a wide-band-gap semiconductor and is a promising candidate for photocatalysis due to its low cost, chemical inertness and non-toxicity. [10] The anatase band-gap energy is \( E_g = 3.2 - 3.3 \) eV, corresponding to absorption wavelengths of 380 – 376 nm, and that of rutile is \( E_g = 3.0 - 3.1 \) eV, which corresponds to absorption wavelengths of 410 – 400 nm. These wavelengths are within the ultraviolet (UV) range of sunlight, \textit{i.e.} wavelengths of 400 – 10 nm.

When TiO\textsubscript{2} receives the appropriate energy radiation corresponding to its band-gap energy, an electron is excited from the valence band to the conduction band; in this way electron-hole pairs are generated, as shown in Figure 2. The generation of charge carriers, \textit{i.e.} electrons and holes, is important for the operation of many semiconductor
devices and photocatalysts, as they will be involved in the catalytic reactions; for
instance, photogenerated holes that are produced on TiO$_2$ surfaces have strong oxidizing
power to oxidize carbon monoxide. However, these photogenerated pairs may be
destroyed by recombination, Figure 2(b), and no longer react with nearby molecules to
initiate photocatalytic reactions.

Figure 2: (a) Generation of electron-hole pair in TiO$_2$
upon receiving the appropriate energy
equivalent to or larger than their band-gap
energy, (b) recombination of the electron-
hole pair, and (c) photocatalytic degradation
of an organic compound to its components in
the presence of photoactivated TiO$_2$. [24]

The catalytic functionality of TiO$_2$ is activated when some of these electron-hole
pairs persist with appreciable lifetime to achieve charge separation and then diffuse to the
surface of TiO$_2$ to initiate redox reactions such as decomposing an organic compound to its constituents, Figure 2(c). The electrons and holes that reach the surface of TiO$_2$ without recombination can reduce and oxidize the adsorbed reactants. [25]

The semiconducting properties of TiO$_2$ nanostructures can facilitate photocatalyzed reactions, for instance to produce hydrogen fuel from water. During hydrogen production from water, the energy level of the semiconductor’s conduction band should be more negative than the energy level of hydrogen production (i.e. $E_{H_2}/E_{H_2O}$, as shown in Figure 3) and the energy level of the semiconductor valence band should be more positive than the energy level for water oxidation (i.e. $E_{O_2}/E_{H_2O}$, as shown in the same Figure). The energy levels of TiO$_2$ satisfy these criteria for hydrogen production, Figure 3. [25, 26]

![Figure 3: Mechanism of photocatalytic water splitting to generate hydrogen using TiO$_2$. [25]](image)

The following reactions are involved in hydrogen production in presence of TiO$_2$: [25]

$$2 \text{ (TiO}_2 \xrightarrow{hv} e^-_{\text{TiO}_2} + h^+_{\text{TiO}_2})$$
\[2h^+ + H_2O \rightarrow \frac{1}{2}O_2 + 2H^+\]
\[2e^- + 2H^+ \rightarrow H_2\]

And the overall reaction is: \(H_2O + 2hv \xrightarrow{TiO_2} \frac{1}{2}O_2 + H_2,\)

where \(h\) is the Plank’s constant and \(v\) is the wavelength of irradiated light. However, the photocatalytic efficiency of TiO\(_2\) (defined as the ratio of change of reactant in concentration per unit time divided by the total incident light flux from the source [27]) is low, predominantly due to the following factors: [25]

1. The high recombination rate of the photogenerated charge carriers (electron-hole pairs): Electrons in the conduction band can very quickly recombine with holes in valence band and release energy in form of heat or photons before they can diffuse and reach the surface of TiO\(_2\). In pure TiO\(_2\) the lifetime of an electron-hole pair is \(\sim 30\) ns, which is quite short, Table 2.

2. Inability to utilize visible light to generate the electron-hole pairs: visible light comprises \(\sim 50\%\) of the solar spectrum, Figure 4; however, the band-gap of anatase TiO\(_2\) (\(E_g = 3.2\) eV) corresponds to the energy of UV light which only accounts for \(\sim 6\%\) of the solar spectrum. [29] Therefore only a small portion

<table>
<thead>
<tr>
<th>Primary Process</th>
<th>Characteristic Time Domains</th>
</tr>
</thead>
<tbody>
<tr>
<td>electron-hole generation</td>
<td>fs (very fast)</td>
</tr>
<tr>
<td>electron-hole trapping</td>
<td>0.1 ns – 10 ns (fast)</td>
</tr>
<tr>
<td>electron-hole recombination</td>
<td>10 ns (fast) – 100 ns (slow)</td>
</tr>
<tr>
<td>interfacial charge transfer</td>
<td>100 ns (slow) – ms (very slow)</td>
</tr>
</tbody>
</table>
of the solar energy can be used to activate TiO$_2$ for initiating the catalytic reactions.

Figure 4: Solar radiation spectrum, showing that the ultraviolet, visible and infrared light comprise 6, 50 and 44% of the solar spectrum, respectively. [30]

The electronic structure of TiO$_2$, such as the band-gap, can be engineered by controlled doping of this material. Figure 5 shows a schematic representation of the band-gap of pure and Fe-doped anatase. Depending on the type of dopant, i.e. metal or non-metal, intermediate energy levels may form above the valence band or below the conduction band of TiO$_2$, and thus narrow the band-gap.
In general, the main purpose of doping TiO$_2$ with other elements, including transition metals such as iron, is to modify the catalytic properties of titania-based structures, *e.g.* by engineering the band-gap or by modifying the electron-hole recombination rate. [31-33] For instance, in Fe-doped TiO$_2$, Fe$^{3+}$ ions may act as both electron and hole traps and transform to Fe$^{2+}$ or Fe$^{4+}$, [31] both of which are less stable than the Fe$^{3+}$ ions and thus can easily release the trapped charges and transform back to Fe$^{3+}$. In this manner, the electron-hole pairs may reach the surface of TiO$_2$ without recombining with each other.

Another purpose of doping TiO$_2$ (or other metal oxide semiconductors) with transition metals is to introduce magnetic moments into its structure. Literature reports on introducing magnetic moments into the TiO$_2$ structure are reviewed in Sections 2.1.2.2 and 2.3.3.
2.1.2.2 Magnetic Properties

TiO₂ has the electronic configuration of a noble gas and thus is expected to exhibit diamagnetic behavior, i.e. negative magnetic susceptibility (descriptions of the magnetic susceptibility and the relevant concepts can be found in Chapter 3, Section 3.3.6). [34] However, a range of positive and negative values of magnetic susceptibilities are reported for rutile-type TiO₂ ranging from $\chi = -0.3$ to $+0.37 \, \mu\text{emu/g.Oe}$, as summarized in Table 3. The difference in the values of magnetic susceptibility reported for rutile is attributed to the presence of adsorbed oxygen and iron impurities, which can act as paramagnetic species. [34] Further, although stoichiometric TiO₂ contains only Ti⁴⁺ ions and considered to be non-magnetic, positive temperature-dependent value of magnetic susceptibility is reported for the anatase-type TiO₂ when it has an oxygen-deficient structure. [34, 35]

<table>
<thead>
<tr>
<th>Source</th>
<th>Temperature</th>
<th>Magnetic susceptibility $(10^{-4} , \text{emu per gram})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meyer¹</td>
<td>298 K</td>
<td>0.37</td>
</tr>
<tr>
<td>Wedekind and Hausknecht¹</td>
<td>room</td>
<td>0.066</td>
</tr>
<tr>
<td>Berkman and Zocher²</td>
<td>room</td>
<td>-0.20</td>
</tr>
<tr>
<td>Hüttig⁴</td>
<td>room</td>
<td>-0.30</td>
</tr>
<tr>
<td>Raychaudhuri and Sengupta³</td>
<td>90° and 293°K</td>
<td>0.08</td>
</tr>
<tr>
<td>Ehrlich⁶</td>
<td>293°K</td>
<td>0.134</td>
</tr>
<tr>
<td>Zimmes and Hedvall⁸</td>
<td>301°K</td>
<td>0.061¹</td>
</tr>
<tr>
<td>Hill and Selwood⁹</td>
<td>room</td>
<td>0.075</td>
</tr>
<tr>
<td>Reyerson and Honig½</td>
<td>301°K</td>
<td>0.061¹</td>
</tr>
<tr>
<td>Gray, McCain, and Masse³</td>
<td>301°K</td>
<td>0.061¹</td>
</tr>
</tbody>
</table>

The presence of ferromagnetism in nominally-pure titanium dioxide nanostructures and other metal oxides, such as pure wurtzite zinc oxide [36] and vacuum-annealed pure hafnium oxide [37], is reported by various researchers. The source of this
type of magnetism is still under debate and is mostly attributed to the creation of structural defects such as oxygen vacancies, which can be a reversible process. [37]

In 1972, Danley and Mulay [38] studied the magnetic behavior of non-stoichiometric titanium dioxide (Ti$_n$O$_{2n-1}$) and reported a field-independent, Figure 6(a, b), but temperature-dependent, Figure 6(c), magnetic susceptibility in these structures. The $M(T)$ curves of the oxygen-deficient samples was statistically a combination of a Curie-Weiss behavior and a temperature-independent contribution. They attributed the Curie-Weiss behavior to a small number of the unpaired electrons that exist in these structures, while the majority of these unpaired electrons act as delocalized electrons and contribute to the temperature-independent component of the susceptibility. [38-40]

![Figure 6](image)

**Figure 6:** (a) Magnetic susceptibility of Ti$_4$O$_7$ as a function of the magnetic field; (b) Magnetization (emu/g) for the same sample as a function of field, showing no ferromagnetic contribution; (c) temperature-dependence of the magnetic susceptibility for Ti$_n$O$_{2n-1}$ (n = 3 to 10). [38]

Yoon *et al.* [35, 41] fabricated dopant-free thin film of magnetic TiO$_2$ with a reproducible saturation moment, Figure 7. TiO$_2$ film was fabricated in an oxygen-deficient environment and anionic defects were introduced into the film structure by controlling the titanium-to-oxygen atomic ratio.
Recently Alivov et al. [42] studied the magnetic properties of nominally-pure anatase, rutile and amorphous TiO$_2$ nanotube arrays with different pore size diameters of 40 – 160 nm. They observed similar paramagnetic behavior for all the nanotubes within the temperature range of 1.8 – 300 K, regardless of their pore size diameter. The low temperature $M(H)$ curves of these anatase nanotubes were non-linear, similar to a typical ferromagnetic behavior, Figure 8. However, the complementary electron spin resonance spectroscopy measurements showed that the $g$-factor (a dimensionless quantity which characterizes the magnetic moment and gyromagnetic ratio of a particle) is temperature-independent, which can imply the absence of long-distance magnetic ordering despite the presence of Ti$^{3+}$ species.
Figure 8: Low temperature $M(H)$ curves of anatase (a), rutile (b), and amorphous (c) TiO$_2$ NTs measured at three different temperatures. Inset in (a) shows the magnified region near zero field to show the hysteresis.

Apart from pure TiO$_2$, magnetic properties of transition metal-doped TiO$_2$ nanostructures have also been studied, including Mn-, V-, Co- and La-doped TiO$_2$ powder [43], Cu-doped rutile thin film [44], and Co- and Cr-doped TiO$_2$ nanorods [45]. Effects of the annealing temperature, annealing atmosphere and structural defects are evaluated on these doped materials. In addition, several groups have studied the magnetism in Fe-doped TiO$_2$ in form of thin films [46], nanoparticles [47-49], nanorods [50] and nanotube arrays [51]. These reports are reviewed in more details in Section 2.3.3.

2.1.3 Historic and Modern Applications of TiO$_2$

The commercial availability of titanium dioxide dates back to the early twentieth century [52]. Traditionally, the main use of titanium dioxide was as pigmentation for paints and plastics. In 1972 the photocatalytic activity of TiO$_2$ for water splitting was reported, known as the Honda-Fujishima Effect [53], that involves photocatalyzed electrolysis of
water to generate hydrogen. This material then became a focus of attention for many researchers and various promising applications were proposed, promoting TiO\textsubscript{2} to the front stage in selected energy-related technologies including photocatalysis, water splitting for production of hydrogen, sensing, photoelectrolysis, polymer-based bulk heterojunction photovoltaics, dye-sensitized solar cells (DSSC) and energy-storage devices such as Li-ion batteries. [54, 55]

In dye-sensitized solar cells, which convert the solar energy into electrical energy, TiO\textsubscript{2} nanomaterials are coated with a dye that can absorb light in the visible range and rapidly inject the photoexcited electrons into the conduction band of TiO\textsubscript{2}. [56] These electrons then travel through the TiO\textsubscript{2} layer to reach the back contact in the solar cell. Dye-sensitized solar-cells have high efficiency values (up to 11%) in conversion of solar energy to electrical energy. [56, 57]

Surface-modified TiO\textsubscript{2} nanomaterials with superhydrophilic or superhydrophobic nature are currently used for antifogging mirrors, glasses and eyeglasses, as well as for self-cleaning or stain-proof surfaces such as self-cleaning paints. In addition, TiO\textsubscript{2} nanostructures are considered promising for environmentally-benign photocatalytic applications against pollutants such as methyl mercaptane. [52]

TiO\textsubscript{2} nanotube arrays can be employed in the same applications as the other TiO\textsubscript{2} nanostructures. In addition, the nanotubular assembly provides a preferred dimensionality to the devices, for instance when their vertically aligned arrays provide a direction for the charge transfer toward the electrode [58]. Further, the controllable uniform top openings of these nanotubes make them appropriate for the size-selective applications such as filters or as templates for fabrication of other materials. Additionally, the well-defined
and regular inner volume of the nanotubes is beneficial as nano-test-tubes, for instance in fluorescence immunoassay which is a sensitive technique to measure the concentration of many compounds including drugs, hormones and proteins. [59]

2.2 Synthesis of Titanium Dioxide

This section is dedicated to a review of the synthesis approaches for production of bulk and nanostructured TiO\textsubscript{2} (i.e. thin films, nanoparticles, nanotubes and composites), with a focus on literature reports on synthesis of TiO\textsubscript{2} nanotubes by direct anodization of titanium foil, mechanism of nanotube formation, and the synthesis/processing parameters that influence the nanotube properties.

2.2.1 Synthesis of Bulk Titanium Dioxide

Bulk titanium dioxide is mostly used in as pigment in coatings such as paints or as filler in plastic industry, and is commercial manufactured by the Sulfate Process or the Chloride Process. [60] In both Sulfate and Chloride Processes, titanium is first separated from its ores, such as ilmenite (FeTiO\textsubscript{3}), followed by participating in specific chemical reactions to synthesize TiO\textsubscript{2}. Details of these two processes are provided in Winkler’s book on Titanium Dioxide. [60]

2.2.2 Overview: Synthesis of Nanoscaled Titanium Dioxide

TiO\textsubscript{2} has been synthesized and studied in different physical forms, from micron-size powder to nanoparticles, thin films, nanorods, nanofibers, nanoporous membranes and nanotubes. The functionality of TiO\textsubscript{2} nanostructures is influenced by their morphology and crystal structure, which are in turn functions of the fabrication and post-fabrication processing methods. In the following sections, common synthesis methods for fabrication
of pure and doped TiO₂ nanostructures (nanoparticles, thin films, nanotubes and composites) are briefly reviewed, with a focus on the synthesis of TiO₂ nanotubes.

2.2.2.1 Nanoparticles

TiO₂ nanoparticles can be fabricated through various methods, including the sol-gel method [61, 62], the micelle and inverse micelle methods [63] and the hydro/solvothermal method. [64] The advantage of micelle and inverse micelle methods compared to the sol-gel methods for the synthesis of titania nanostructures is the higher control of size and shape distribution. [65] The hydro/solvothermal method may be used to synthesize ultra-small powders and well-dispersed anatase structures. [64, 66]

Several routes for incorporation of Fe in TiO₂ nanoparticles are reported that produce Fe-doped nanoparticles. These methods include ball-milling TiO₂ nanoparticles with iron [47-49, 67, 68], mechanically mixing TiO₂ powder and Fe powder followed by pressing and annealing [69], introducing Fe ions during the formation of TiO₂ nanoparticles in a microemulsion [70] or in the sol-gel synthesis methods [71], and IR laser pyrolysis of TiCl₄ and Fe(CO)₅. [72] The iron electronic state (i.e. metallic or ionic) and its distribution within the TiO₂ nanoparticles depend on the synthesis and iron incorporation method.

2.2.2.2 Thin Films

Thin films of titanium dioxide can be fabricated on different substrates using the chemical vapor deposition (CVD) method [73] that involves condensation of a vapor phase on a substrate to form a solid-phase material. TiCl₄ [73] and titanium (IV) tetraisopropoxide [74] are typical precursors that form the vapor phase for TiO₂ film fabrication. The dip-coating process [75], and the atomic layer deposition technique [76]
are two other approaches to fabricate thin films of TiO$_2$ thin films. Pulsed laser deposition method can be employed to fabricate Fe-doped TiO$_2$ thin films, using iron and TiO$_2$ targets [46] or a Fe$_{(1-x)}$Ti$_x$O$_2$ target [48].

2.2.2.3 Nanotubes (NTs)

Nanotubular TiO$_2$ is considered superior to the other morphologies of TiO$_2$ due to its larger effective surface area (Figure 9(a)) vertical pathways for electron transport (Figure 9(b)) and suppressed electron-hole recombination. [2, 3, 54, 58, 77, 78] In addition, a tubular morphology can enhance the absorption of irradiated light in comparison with a planar morphology, Figure 9 (c). [58]

![Figure 9](image.png)

Figure 9: (a) 3D chart of the dependence of the NT’s effective surface area on its length and pore size radius. [79] (b) Schematic representation of the electron path through a percolated and an oriented nanostructure. [55] (c) Illustration of the superiority of tubular geometry in capturing the reflected light. [58]

Formation of nanotubular TiO$_2$ was first reported by Hoyer in 1996. [80] They used an anodically-grown alumina template coated with a thin layer of gold, which was subsequently coated with a layer of polymer. The alumina template was removed to
create a template of polymer rod arrays with gold layer that served as an electrode for electrochemical deposition of TiO$_2$. Figure 10 illustrates the schematic representation of the procedure that Hoyer et al. employed to fabricate TiO$_2$ nanotube arrays.

![Figure 10](image)

**Figure 10**: (a) Schematic representation of the replication process employed by Hoyer et al. to fabricate TiO$_2$ nanotube arrays, and (b) SEM image of the nanotube arrays created by this method. [80]

Randomly oriented TiO$_2$ nanotubes can be fabricated by the sol-gel template method [81] and by the hydrothermal method. [82] The sol-gel fabrication method involves the following steps to form the nanotubular morphology: [82]: (1) synthesis of an external template such as an alumina template; (2) nanotube formation inside the template pores typically from mixed solution of titanium tetraisopropoxide, 2-propanol and 2,4-pentanedione, and (3) removal of the alumina template to release the TiO$_2$ nanotubes, Figure 11.
In the hydrothermal synthesis method [83, 84], TiO₂ powder is transformed into a lamellar structure as shown in Figure 12(a) and then is chemically bent and rolled up into nanotubular morphology, Figure 12(b), to reduce the total surface energy. If an iron salt such as FeCl₃ is introduced to the solution during the hydrothermal synthesis of TiO₂ nanotubes, randomly oriented Fe-doped nanotubes are synthesized. [50, 85]

The first report on the synthesis of template-free TiO₂-based nanotube arrays was in 1999 by Zweiling et al. who employed the electrochemical anodization technique and an electrolyte consisting of chromium acid/hydrofluoric acid. [86, 87], Figure 13.
The simplicity of synthesizing self-ordered arrays of TiO$_2$ nanotubes using the one-step anodization of titanium foil, and the controllable morphological features (e.g. tube length, wall thickness and pore diameter) has made this method as a preferred fabrication technique to produce ordered TiO$_2$ nanotubes. A summary of the advantages/disadvantages of different fabrication methods of TiO$_2$ nanotubes is presented in Table 4.

Table 4: Summary of advantages/disadvantages of TiO$_2$ NT synthesis methods. [88]

<table>
<thead>
<tr>
<th>Fabrication method</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>TNT features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Template-assisted method</td>
<td>(1) The scale of nanotube can be moderately controlled by applied template</td>
<td>(1) Complicated fabrication process</td>
<td>Ordered arrays (powder form)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2) Tube morphology may be destroyed during fabrication process</td>
<td></td>
</tr>
<tr>
<td>Electochemical anodic oxidation method</td>
<td>(1) More desirable for practical applications</td>
<td>(1) Mass production is limited</td>
<td>Oriented arrays (thin film)</td>
</tr>
<tr>
<td></td>
<td>(2) Ordered alignment with high aspect ratio</td>
<td>(2) Rapid formation kinetics is subjected to the utilization of HF</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3) Feasible for extensive applications</td>
<td>(3) Highly expense of fabrication apparatus</td>
<td></td>
</tr>
<tr>
<td>Hydrothermal treatment</td>
<td>(1) Easy route to obtain nanotube morphology</td>
<td>(1) Long reaction duration is needed</td>
<td>Random alignment (powder form)</td>
</tr>
<tr>
<td></td>
<td>(2) A number of modifications can be used to enhance the attributes of titanium nanotubes</td>
<td>(2) Highly concentrated NaOH must be added</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3) Feasible for extensive applications</td>
<td>(3) Difficult in achieving uniform size</td>
<td></td>
</tr>
</tbody>
</table>

2.2.2.4 **Composites**

Fabrication of composite structures of titania nanotubes with other metal oxides are reported, primarily with the purpose of modifying the functionality of nanotubes for
energy-harvesting applications. Using TiO$_2$ as a template for electrodeposition of other metals is a versatile route to fill or decorate these nanotubes and create hybrid structures. However, there are challenges in electrodeposition of material into the nanotubes that should be considered. TiO$_2$ is an n-type semiconductor and during electrodeposition a cathodic potential is needed to establish a forward bias. As a result, the tube wall adopts a high conductivity leading to preferential deposition of metal on top of the layers rather than inside the tubes. A strategy has been developed to overcome this issue, by carrying out reductive self-doping of only the nanotube bottoms by selective Ti$^{3+}$ formation. In this manner, electrodeposition starts at the tube bottom and facilitates the bottom-to-top filling of the tubes.

Mohapatra et al. [89] fabricated a nanorod-nanotube hybrid structure of titanium oxide/iron oxide composites by filling TiO$_2$ nanotube arrays with iron using pulsed electrodeposition, followed by thermal treatment to oxidize the iron, Figure 14.

![Figure 14: A schematic showing the process to synthesize Fe$_2$O$_3$ nanorods inside TiO$_2$ nanotube arrays. [89]](image)

Liang et al. [90] loaded iron/iron oxide nanoparticles on to already-synthesized...
TiO$_2$ nanotube arrays using the electrochemical deposition technique, Figure 15. The fabricated composite structure had ferromagnetic behavior and its saturation magnetization decreased upon annealing up to 450 °C in air. Filling TiO$_2$ nanotube arrays with other metal oxides such as NiO or copper oxide has been also reported. [91]

![Figure 15: (SEM) Top view of samples electrodeposited in water/glycerol/0.02M FeCl$_3$.6H$_2$O for 30 min at (a) −1V, (b) −3V. The inset in (b) indicates the sphere-like structures formed in certain area on TiO$_2$ NT surface. [90]](image)

As another approach in decorating nanotubes with metal nanoparticles, Kontos et al. [92] dipped TiO$_2$ nanotube arrays in a solution containing iron oxide nanoparticles. The iron oxide nanoparticles attached to the TiO$_2$ nanotubes’ surface, yielding higher photocatalytic performance, as well as appreciable magnetization anisotropy parallel and perpendicular to the tube axis.

Abd Elmoula et al. reported the controlled attachment of gold nanoparticles on the TiO$_2$ nanotube arrays, using a deposition-precipitation method. [93] These structures were suggested to be suitable for photocatalytic applications, such as oxidation of carbon monoxide.

Another approach is anodization of titanium/other metal alloy (alloyed metal substrate) to fabricate a composite metal oxide nanotube structure with tuned ionic,
electronic, magnetic or optical properties. [56] In this kind of approach, dealloying (selective etching) should be prevented through optimization of the anodization condition and use of a single-phase alloy as the precursor. To date, anodization of several binary alloys has been reported, including TiNb, TiZr and TiW. [94-96] Fabrication of the Fe-doped TiO$_2$ nanotube arrays is recently reported using the anodization technique, starting from a co-sputtered Ti(Fe) thin films on a substrate [97], and arc-melted Ti(Fe) foils. [98, 99] In these studies, the exact concentration of Fe within the anodized nanotubes is not reported and only the nominal concentration of the initial Fe in the starting alloy film/foil is mentioned. The limited number of approaches for doping the nanotube arrays with iron can be related to the synthesis method of these nanotubes and their ordered structure which makes it impractical to use the common doping techniques such as ball-milling or laser deposition to dope the nanotube arrays.

2.2.3 Detail: TiO$_2$ Nanotubes Produced by Direct Anodization

Ordered arrays of TiO$_2$ nanotubes can be synthesized by anodization (anodic oxidation) of titanium metal foil. In this method, a titanium foil is anodized in an aqueous hydrogen fluoride electrolyte solution for 10 – 30 min at an applied voltage of 10 – 20 V$_{DC}$. A platinum mesh is typically used as the cathode in an arrangement that is illustrated schematically in Figure 16. The as-anodized TiO$_2$ nanotubes are amorphous and crystallization occurs after thermal treatment for 2 – 6 hours at 350 – 500 °C in oxygen purging gas.
In the process of electrochemical anodization of titanium foil, oxide ions are produced via dissociation of water molecules and the following reactions are hypothesized to occur at the electrolyte/oxide interface:

\[ \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+ \]

\[ \text{OH}^- \rightarrow \text{O}^{2-} + \text{H}^+ \]

\[ \text{TiO}_2 \rightarrow \text{Ti}^{4+} + 2\text{O}^{2-} \]

The cations travel to the cathode (typically platinum mesh) and the anions migrate through the oxide layer and are consumed to form titanium dioxide and hydroxide at the oxide/Ti interface:

\[ \text{Ti} + 2\text{O}^{2-} \rightarrow \text{TiO}_2 + 4\text{e}^- \]

\[ \text{Ti} + x\text{OH}^- \rightarrow \text{Ti(OH)}_x + xe^-, \quad x = 1 \text{ to } 4 \]

The already formed oxide is dissolved in the electrolyte in the presence of the fluoride ions:

\[ \text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O} \]
A portion of the oxide ions also reacts to form oxygen at the anode (titanium) which results in bubble formation:

\[ 2O^{2-} \rightarrow O_2 + 4e^- \]

Oxygen formation is negligible if the anodization process reaches steady state [77]. The overall reaction at the electrolyte/oxide interface is:

\[ TiO_2 + nH_2O + 6F^- \rightarrow [TiF_6]^{2-} + (n + 2 - x)O^{2-} + xOH^- + (2n - x)H^+ \]

In the above reaction, \( n \) indicates the dissociation ratio of water to the dissolution of titanium dioxide and affects the porosity of the final oxide film.

Nanotubes can be grown in two types of electrolyte media, aqueous and organic. The choice of these media can significantly influence the morphology of the fabricated nanotubes. Figure 17 shows typical morphologies of two types of the nanotube arrays synthesized in aqueous and organic media.

![Figure 17: (SEM) Typical morphologies of two types of NT arrays synthesized in the aqueous and organic media. [100]](image)

Based on the type of the electrolyte three main generations of anodized TiO\(_2\) nanotubes can be formed [100]:
- 1\textsuperscript{st} generation: synthesized in hydrofluoric acid to produce short NTs up to \( \sim 500 \) nm long.

- 2\textsuperscript{nd} generation: synthesized in water-based electrolytes containing fluoride salts to produce NTs up to 5 \( \mu \)m long.

- 3\textsuperscript{rd} generation: synthesized in organic electrolytes containing fluoride ions to produce smooth NTs with no ribs on the tube sides and up to 100 – 1000 \( \mu \)m long.

Typical scanning electron micrograph images of these three generations of anodized TiO\(_2\) nanotubes are presented in Figure 18, highlighting their significantly different morphologies.

In this Dissertation most of the studies are carried out on the long nanotubes (3\textsuperscript{rd} generation, fabricated in the organic electrolyte solution) and a part of studies are done on the short nanotubes (1\textsuperscript{st} generation).

![Figure 18: (SEM) Morphologies of three generations of anodized TiO\(_2\) NTs fabricated by different electrolyte types. [100]](image)
2.2.3.1 Mechanism of NT Formation

Figure 19 presents a schematic representation of the evolution of TiO$_2$ nanotube arrays during the potentiostat (constant voltage) electrochemical anodization process. Upon application of a given voltage, an oxide layer is formed on the surface of titanium foil, as noted in Figure 19(a), followed by localized dissolution of this oxide layer due to the presence of fluorine ions to form pit holes, Figure 19(b). Formation of these pit holes causes the barrier (oxide) layer at the bottom of the pits to become thinner, leading to an increase in the intensity of the local electric field and continuous pore growth, Figure 19(c). The electric-field-assisted oxide dissolution does not affect the entrance of the pore, but the bottom of the pore becomes deeper and widens due to the local electric field distribution, resulting in a scallop-shaped pore. Due to the relatively low ion mobility and relatively high chemical solubility of the oxide in the electrolyte solution, only pores with thin walls can be formed. Thus, un-anodized metallic portions can initially exist between the pores, Figure 19(c), and can start to grow in the same manner as the already-grown adjacent pores as soon as the electric field intensity in the local region increases, Figure 19(d). This phenomenon results in the simultaneous formation of well-defined inter-pore voids; the growth of both voids and pores (tubes) come to equilibrium, Figure 19(e). The length of the nanotubes increases until the corrosion (dissolution) rate at the bottom of the nanotubes equals the chemical dissolution rate of their top surface. At this point the nanotubes’ length no longer increases upon consumption of the titanium metallic foil.
Figure 19: Schematic representation of the self-organized TiO$_2$ NT evolution during an electrochemical anodization: (a) formation of the oxide layer, (b) pit formation on the oxide layer, (c) growth of the pits and pore formation, (d) the metallic region between the pores undergoing oxidation and field assisted dissolution, (e) fully developed nanotubes and their top view. [63]

2.2.3.2 Effects of the Synthesis Variables

Various factors can affect the growth of TiO$_2$ nanotubes during the anodization process. As described in Section 2.2.1, nanotube formation is the result of a balance between two reactions: (1) oxide formation and (2) chemical dissolution of the oxide; thus, alteration of either of these two reactions affects the nanotube formation and growth. The most critical parameters that may affect these chemical reactions are the follow: the type of the electrolyte (aqueous or non-aqueous), the pH of the electrolyte, fluoride concentration, temperature, anodization voltage and anodization duration. A brief overview of the literature that addresses effects of some of these parameters (type of electrolyte,
Anodization voltage and duration) on TiO$_2$ nanotube formation and growth is presented in this section.

**Anodization Electrolyte:** Organic electrolytes produce nanotubes that are smoother with a more regular morphology as compared to those fabricated in an aqueous media. A small amount of water is typically added to the non-aqueous media to provide the oxide ions, which are required for the anodization process. However, there are reports of nanotube fabrication in non-aqueous solutions in the absence of water molecules, in which the organic electrolyte dissociates itself in order to provide the oxide ions [101]. The water content in the electrolyte solution affects the final achievable length of the nanotubes, with long nanotubes arrays achieved in an electrolyte with a water content of < 5%. Thus, substitution of aqueous by non-aqueous anodization electrolyte allows creation of nanotubes that are several microns long (see Figure 18). Organic electrolytes have a lower tendency to donate oxygen as compared to the water molecules; this tendency slows down the oxidation process and formation of the nanotubes. Concurrently, the low water content in the non-aqueous electrolyte restricts the oxide dissolution which results in the formation of longer nanotubes for a given time duration [102].

**Anodization Voltage:** The voltage applied during the anodization determines the strength of the electric field across the titanium dioxide and consequently affects the ion migration, thus impacting nanotube pore diameter. The applied anodization voltage that is used is typically $5 – 30 \text{ V}_{\text{DC}}$ in aqueous and $10 – 60 \text{ V}_{\text{DC}}$ in non-aqueous electrolytes. [100] In long nanotubes a linear relationship is reported between the diameter of the nanotubes and the applied voltages up to $60 \text{ V}$. [100]
**Anodization Duration:** The duration of anodization affects the nanotube’s length and for short durations it can affect the ordering of the arrays, too. In aqueous electrolytes and anodization duration of 0.5 – 2 hours is usually required to allow for nanotube formation and rearrangement into a self-ordered structure. [103-105] The growth rate in organic electrolytes is much slower, so longer anodization duration is required to form nanotubes of several microns long. [106] In these organic electrolytes a porous oxide layer usually forms on top of the nanotubes and remains there during the anodization, which can affect the dissolution paths for the electrolyte. The porous oxide layer can be removed after anodization when the supported nanotubes (i.e. nanotube arrays attached to the titanium substrate) are usually ultrasonicated in alcohol.

### 2.2.3.3 Effects of Post-Synthesis Processing

As-anodized TiO\textsubscript{2} nanotube arrays are amorphous, unlike the hydrothermally-synthesized nanotubes (the other most common method for nanotube fabrication) which are partially crystalline with anatase structure. In their as-anodized state, TiO\textsubscript{2} nanotubes do not exhibit an efficient photoactivity and should be crystallized by a thermal treatment (annealing) process. Annealing the TiO\textsubscript{2} nanotubes causes changes in both the crystal structure and the crystalline character. According to Zhu *et al.* [107], the average crystallite size of devitrified TiO\textsubscript{2} affects the electron dynamics which is a critical factor in determination of photocatalytic behavior. Thus, understanding the effects of thermal treatment on the crystallinity of the amorphous as-anodized TiO\textsubscript{2} nanotube arrays is critical. In this section literature reports on the effects of annealing on various properties of nanotubes are presented.
The anatase structure is produced from amorphous nanotubes after annealing for 2–6 hours at 350–500 °C in oxygen purging gas. In oxygen-rich annealing environments, the anatase structure starts to form at ~ 285 °C [108]. The amount of amorphous-to-anatase transformation depends on the annealing temperature; at low annealing temperatures (e.g. 300 °C) the nanotubes may not be fully crystalline. [78] On the other hand, annealing at high temperatures, i.e. \( T > 450 \) °C, causes the anatase-to-rutile phase transformation.

Zhang et al. [109] proposed a model for the crystallization kinetics of TiO\(_2\) which also describes the percentage of transformation from amorphous to anatase structure and the final particle size. This model explains that when the thermal fluctuations at the interface of two contacting amorphous particles is insufficient, e.g. at \( T = 300 \) °C, more than two amorphous TiO\(_2\) particles may coarsen and form a larger amorphous particle. These larger particles are metastable with respect to the same size anatase particle and thus upon further annealing they can transform into the anatase structure.

Su et al. [110] reported on the formation of a single crystal nanotube with anatase structure obtained by annealing. Upon annealing the nanotubes at 285 °C for 24 hours, the hydroxide layer and the O-ring shape connections (ribs) which link the tubes together become fully crystallized into a single crystal shell on the nanotubes. Then, after 5 hours of annealing at 600 °C, nanocrystallites form in the inner oxide layer and continue to grow in size, while the tubular morphology of the nanotubes remains intact. In this manner, the shell of single crystal formed on the outer surface of the nanotube walls may allow the extension of crystallization from the outer surface into the inner surface via the
Ostwald Ripening process. This leads to formation of a single crystal nanotubular array as the larger particles grow by consuming the smaller neighbors.

Thermal stability of TiO$_2$ nanotubes during the annealing process is an important factor that should be considered if it is desired to maintain the tubular morphology. The nanotubes are usually annealed as supported on the titanium foil substrate. At high annealing temperatures, typically $T > 580 \, ^\circ\mathrm{C}$, oxidation and crystal grain growth in the titanium support may interfere with the stability of TiO$_2$ nanotubes and deteriorate the nanotubular morphology. Meanwhile, as will be studied in Chapter 4.0, unsupported arrays of TiO$_2$ nanotubes (free-standing flakes) may exhibit different thermal stability as compared to the supported nanotubes, although to the best of the author’s knowledge this is not reported in the literature. In addition, annealing environment (i.e. oxygen-rich versus oxygen-deficient or reducing atmosphere) may affect the tubular morphology and induce the development of morphological features, which will be studied in Chapter 4.0.

2.3 Functional Properties of Titanium Dioxide

In this section, functional properties of TiO$_2$ are reviewed. Considering the insignificant functional properties of bulk titania, the focus of this section will be on the functional properties of nanostructured TiO$_2$ materials.

2.3.1 Aspects of Photoelectric Character

The photoelectrical properties of anodized nanotubes are influenced by the annealing conditions of various annealing conditions, such as the type of the annealing gas (reducing versus oxidizing), temperature and duration of annealing.

Zhu et al. studied the influence of annealing temperature on the charge transport and recombination properties of the dye-sensitized nanotube arrays. [111] They reported
that the nanotube’s microstructure has an observable dependence on the annealing temperature that was correlated to the annealing-induced changes in nanotube’s electron transport and recombination kinetics. For nanotubes annealed at different temperatures from \( T = 200 \) °C to 600 °C, the highest electron diffusion coefficient belonged to the nanotubes annealed at 400 °C, the temperature at which the nanotubes are fully crystalline. At annealing temperatures below \( T < 400 \) °C, the TiO\(_2\) nanocrystallites are presumed to be isolated from each other and this can slow down the electron diffusion.

Nishanthi et al. reported the influence of annealing duration on the photoelectrochemical response of the nanotubes when they were annealed in air at 480 °C for 1 – 9 hours. [112] Their results indicate that the nanotube crystallinity increases by increasing the annealing duration. Concurrently, the optical band-gap decreases from 3.04 to 2.81 eV for these annealing durations and a maximum photoconversion efficiency of 25.5% was achieved after 9 hours of annealing. They stated that the nanotube morphology remained stable up to 5 hours of annealing at 480 °C, but the structure was slightly oxygen deficient which was assumed to be a possible reason for reduction of the band-gap via introducing impurity-type energy levels above the valence band.

Improvement in the photoelectrochemical properties of TiO\(_2\) nanotube arrays in presence of Fe is reported recently (Mor et al. [97], Wang et al. [98], Guangzhong et al. [99]) but very little is known about the underlying reason of such improvement. Mor et al. [97] co-sputtered Fe and Ti on a substrate to form Ti-xFe films (\( x = 3.5, 6.6, 20, 26, 37, 44 \) and 69 at%) up to ~ 1.5 micron thick for subsequent anodization and nanotube formation. They claimed that annealing the initially amorphous nanotubes resulted in the substitution of a portion of the Fe for Ti ions in the crystal structure, and the remaining Fe
either formed α-Fe$_2$O$_3$ crystallites or remained in an amorphous state. They reported that when the Fe content is too low, *i.e.* 3.5 at% Fe in the initial metallic film, the Fe$^{3+}$ ions act as trapping sites, and if the content is too high, *i.e.* >20 at% Fe in the initial metallic film, the Fe$^{3+}$ ions increase the recombination rate of the photogenerated electron-hole pairs. They found the highest photocurrent density versus potential for the nanotubes with 6.6 at% Fe in the starting metallic film.

Wang *et al.* [98] anodized Ti-xFe ($x = 0.05, 0.5$ and $1$ wt%) alloy to fabricate Fe-doped TiO$_2$ nanotubes followed by a four-hour annealing in air at 460 °C. The Fe-doped nanotubes showed an improved photocurrent response for the Fe content of 0.05 wt% (in the starting metallic film), as compared to that of the undoped annealed nanotubes or of the doped nanotubes with higher Fe content. The photocurrent enhancement in presence of iron was attributed to the redshift in the UV-VIS absorption spectra of the Fe-doped nanotubes and reached an optimum concentration of the carrier recombination centers when the Fe content was as low as 0.05 wt% in the starting metallic film. [98] It was claimed that higher concentrations of Fe created more defects or carrier traps that decreased the photocurrent density despite the presence of the redshift in their UV-VIS absorption spectrum.

### 2.3.2 Aspects of Photocatalytic Character

The photocatalytic activity of TiO$_2$ nanostructures is influenced by the crystallographic structure, surface area, particle size distribution and porosity. [113] These properties can affect the production of electron-hole pairs and the surface adsorption/desorption process. For instance, the catalytic activities of anatase and rutile are different as they have different values of band-gap energy as well as different titanium-oxygen bond lengths.
that can affect the charge carrier diffusion and electron-hole recombination rates. [109] The anatase structure has higher electron mobility, a lower dielectric constant and lower density as compared to those of the rutile structure, and thus is considered as a better candidate for solar cell applications. [14]

Apart from the type of the crystal structure, the functionality of TiO₂ is closely related to the presence of bulk and surface defects in the structure, such as oxygen vacancies and interstitial titanium. [21, 22] Oxygen vacancy is the most common defect in TiO₂ structures, as well as the other types of metal oxides [23] and can serve as active sites for catalytic reactions. [114] In addition, presence of oxygen vacancies can influence the electronic structure, charge transport and surface properties of TiO₂-based materials. Creation of oxygen vacancies is typically associated with formation of two free electrons in the defective crystal through the following reaction,

\[ O^{2−}_{\text{TiO}_2} \rightarrow \text{V}_O + \frac{1}{2} \text{O}_2(g) + 2e^- \]

where \( \text{V}_O \) is the oxygen vacancy in Kröger-Vink notation. [115]

Formation of these electrons affects the electronic structure of TiO₂ as they can form a donor level below the conduction band, as illustrated in Figure 20.
Doping TiO₂ with other elements can also influence its photocatalytic activity. The main purpose of doping is to decrease the band gap or introduce intra-band gap states to absorb more visible light (induce a bathochromic shift). [10]

Zhu et al. [85] employed the hydrothermal approach to prepare Fe-doped anatase powder (0.03 to 0.15 wt%) followed by thermal treatment to induce crystallization. A red shift in UV-VIS diffuse reflectance spectroscopy was observed indicating the capability of the doped nanotubes in absorbing light at longer wavelengths (visible range) compared to the un-doped TiO₂. Choosing the proper dopant precursors was proved to be critical in tailoring the catalytic activities, as FeCl₃ precursor performed better than FeCl₂ in enhancing the catalytic functionality of doped TiO₂ powder.

Guangzhong et al. [99] reported that Fe-doped TiO₂ nanotube arrays fabricated by anodization of Ti-xFe (x = 6, 9, 12 and 15 wt%) alloy, exhibit a redshift in their UV-VIS absorption spectra, which was also reported by Wang et al.. [98]

Deposition of noble metals, such as Ag and Au, on TiO₂ nanostructures is another approach in influencing the photocatalytic behavior of TiO₂. [117, 118] The Fermi levels
of noble metals are lower than that of the titanium oxide, thus the photogenerated electrons are transferred from the conduction band of TiO$_2$ to the deposited metal nanoparticles and the photogenerated holes remain in the valence band of TiO$_2$. In this manner, the charge separation is more efficient and the recombination rate decreases.

### 2.3.3 Aspects of Spintronic Character

Several efforts are reported on introducing magnetic moments (e.g. magnetic transition metals) into the crystal structure of TiO$_2$ to integrate magnetic and semiconducting properties and create dilute magnetic semiconductors (DMS) [119], in which the spin degree of freedom is used along with the electron charge in a single device to develop, for instance, instant-on-computers. [9] The concept of ferromagnetic semiconductors is not new and was first reported by Mauger et al. in 1986, when they observed magnetism in europium chalcogenides. [120] Following their report and in the same year, Story et al. reported carrier-mediated ferromagnetism. [121] The reason these systems did not get significant attention at that time was that the ferromagnetism was only observable at liquid helium temperatures. A Curie temperature of $T_C > 500$ K is usually required to qualify a ferromagnetic material for employment in room-temperature devices (Curie temperature is defined as a temperature above which a ferromagnetic material becomes paramagnetic). [122]  When the first report on relatively high Curie temperature, $T_C > 100$ K, magnetic semiconductor was published on III-V compounds of InAs and GaAs [123, 124], these systems became a center of attention for many researchers and scientists. The high-temperature ferromagnetism noted in the oxide nanostructures doped with magnetic dopants is still controversial [125]; some scientists consider these systems
as DMS, and some others claim that the observed magnetism is due to the secondary ferromagnetic impurity phases in the semiconducting host.

Various groups have studied the magnetic characteristics of transition-metal-doped TiO$_2$ materials. [43-45, 47-51, 67-72, 85, 126, 127] The observed magnetism in these systems was reported to depend on various parameters such as the dopant (e.g. Mn, Fe, Co, Ni, Cu) [126], dopant concentration, presence of oxygen vacancies, annealing temperature [43] and annealing atmosphere (e.g. vacuum versus air). [44]

Room-temperature ferromagnetism with a Curie temperature of approximately 77 °C was reported in Cu-doped rutile thin films (5 – 20 at%) [44] despite the non-magnetic nature of copper.

Cluster formation of the dopant is an important factor in determination of the magnetic behavior. Curie temperature of $T_C = 377$ °C is reported for ball-milled Fe-doped TiO$_2$ powder (2.7 wt% Fe) without any detectable bulk metallic iron or iron oxide species. [67] However, another report assigned the observed room temperature ferromagnetism in the ball-milled Fe-doped TiO$_2$ (5 at% Fe) to the unreacted metallic iron. [68]

Torres et al. [127] prepared the Fe-doped anatase nanoparticles (2.8 and 5.4 at% Fe) by microemulsion method and during the synthesis process Fe$^{3+}$ replaced Ti$^{4+}$ in the structure. At room temperature a paramagnetic behavior was observed and at $T = 5$ K isolated paramagnetic Fe$^{3+}$ ions and antiferromagnetically coupled Fe$^{3+}$ ions were detected.
Ding et al. [50] studied the Fe-doped TiO$_2$ nanorods (0.5 at% Fe) synthesized by the hydrothermal method and quantified a high temperature ferromagnetism and temperature-independent paramagnetism in the doped nanorod samples.

Study of the magnetic properties of Fe-doped TiO$_2$ nanotube arrays is reported recently [51], for nanotubes fabricated by anodization of arc melted Ti(Fe) pieces. The Fe : Ti molar ratio in the starting metallic alloy was 1 : 1, equivalent to wt ratio of 1.17: 1. The $M(H)$ behavior of these nanotubes was studied as a function of the annealing temperature (from 400 °C to 600 °C). The change in magnetism with annealing temperature was attributed to the change in the crystalline structure of the nanotubes.

There is still a long road ahead to reach the required characteristics of a dilute magnetic semiconductor for titania-based nanostructures. These characteristics include reproducible ferromagnetism in these structures with high Curie temperature ($T_c > 500$ K), and stability of this magnetic character for specific applications. On this road, however, understanding the underlying correlations of structural attributes and magnetic character of TiO$_2$ nanostructures is critical in providing insight to create novel multifunctional nanomaterials with simultaneous practical semiconducting and magnetic properties.
3.0 EXPERIMENTAL TECHNIQUES AND METHODOLOGIES

This Section provides the details of experimental techniques related to the objective of this Dissertation that is to obtain fundamental understanding of the interrelations of the morphology, crystal structure, electronic structure and magnetism in TiO₂ nanotubes (NTs), with potential relevance to their functionality. This objective is pursued by synthesis and systematic processing of pure and Fe-doped TiO₂ nanotubes, followed by characterizing them to understand their morphology, crystal structure, electronic structure and magnetic behavior as well as evaluating their photocatalytic functionality to elucidate such correlations.

The experimental part of this research consists of four main steps:

1. Synthesis of the pure and Fe-doped TiO₂ nanotube (NT) arrays,

2. Post-fabrication processing of NTs, i.e. annealing to induce crystallization,

3. Characterization of the NTs using variety of probes (including morphological, structural, spectroscopic and magnetic),

4. Evaluation of the NTs’ functionality (catalytic activity).

The functionality of the TiO₂ NTs is affected by their morphology, crystal structure, electronic structure and magnetic behavior. Thus it is critical to understand the morphology (such as the tube length), structural attributes (crystal structure, degree of crystallinity, crystallite size), electronic structure (oxidation state of titanium and atomic local environment, bonding state of the external dopant) and magnetic response of these nanotubes in the pure state as well as in presence of an external dopant (Fe). In this manner, realization of the relationships between the synthesis and processing conditions,
chemical composition, properties and their functionality will be facilitated. The information obtained from characterization of the nanotubes provides the opportunity to better understand and tailor the electronic, magnetic and optical properties and thereby the functionality of TiO₂-based nanostructures for potential energy-related applications.

In this Chapter, the techniques of synthesis and processing of TiO₂ nanotube (NT) arrays are presented in Sections 3.1 and 3.2. Section 3.3 describes the methodology and equipment employed to characterize the nanotubes. Finally, the approach to evaluate the catalytic functionality of the nanotubes is described in Section 3.4. Meanwhile, an overview on the principles of operation for each synthesis and characterization equipment that is used in the experimental part of this research is presented in the related section.

Fe-incorporated titanium metallic sheet, used as the starting material of the Fe-doped nanotubes, is fabricated by arc-melting alloying technique. The electrochemical anodization of this metallic precursor is then carried out in presence of corrosive fluorine ions in order to create the pure (from commercially available titanium foil) and Fe-doped TiO₂ NT arrays.

Imaging of the specimens is done using scanning electron microscopy, and an estimation of the elemental composition is obtained by the energy-dispersive x-ray spectroscopy. Crystallographic investigations are carried out using x-ray diffraction and quantitative information such as the lattice parameters and crystallite size are obtained through examination of the XRD patterns and proper mathematical equations. In addition, transmission electron microscopy provided qualitative information on the local crystalline states. Information on the local electronic structure of titanium, iron and oxygen near the surface region of the nanotubes is attained using synchrotron-based near-
edge x-ray absorption spectroscopy. Superconducting quantum interference device (SQUID) magnetometry is employed to characterize the magnetic properties of the samples within the field ($H$) range of $-20 \text{kOe} < H < 50 \text{kOe}$ and the temperature ($T$) range of $2 \text{K} < T < 400 \text{K}$. Evaluation of the catalytic activity of the nanotubes is carried out by monitoring the degradation rate of an organic dye in presence of the supported nanotubes when they are exposed to the UV-VIS light irradiation.

The fabrication and characterization equipment used in the course of this Dissertation research are available at Northeastern University laboratories and at the George J. Kostas Nanoscale Technology and Manufacturing Research Center located at Northeastern University. The synchrotron-based spectroscopy and the measurements of the catalytic performance are carried out at the National Synchrotron Light Source (NSLS) and the Center for Nanomaterial and Nanotechnology (CNF), respectively, both of which are located at the Brookhaven National Laboratory (BNL), Upton, NY.

3.1 **Synthesis of Pure and Fe-doped TiO$_2$ Nanotube (NT) Arrays and their Metallic Precursors**

The nanotubes were synthesized using the electrochemical anodization technique. For the pure nanotubes, commercially available titanium foil was used in the anodization set up, and experimental modifications were carried on the precursors and/or synthesis conditions when the synthesis of Fe-doped nanotubes were desired, as described in the following sections.
3.1.1 Fabrication of Pure TiO$_2$ NT Arrays

Different morphologies of the pure nanotubes were obtained by changing the anodization conditions such as the duration (affecting the length of nanotubes) or the applied voltage (which affects the nanotube’s pore diameter) and the electrolyte composition (aqueous versus non-aqueous). In the two following sub-sections, the fabrication conditions that were employed to synthesize long ($3^{rd}$ generation) and short ($1^{st}$ generation) pure nanotubes are explained based on the type of the electrolyte.

**Long TiO$_2$ NT Arrays:** Room temperature potentiostat electrochemical anodization was used to synthesize nominally-pure TiO$_2$ nanotubes, starting from a 127 µm thick titanium foil (99.97%, Sigma Aldrich). A piece of 1 in. by 1.5 in. of titanium foil served as the anode after being ultrasonicated for 10 minutes in isopropyl alcohol (99.9%, Sigma Aldrich, USA), spaced 1.6 in. apart from the cathode (a $1 \times 1$ in.$^2$ piece of platinum mesh). The non-aqueous anodization electrolyte consisted of ethylene glycol (98%, Sigma-Aldrich, USA), potassium fluoride (KF) (0.05 M) and 1-5 vol% deionized (DI) water properly mixed in a polypropylene container (Figure 21). Fresh solutions were used for each set of anodization. The voltage of 45 – 60 V$_{DC}$ was applied using a computer-assisted Agilent 6811B power supply (Agilent Technologies, USA). Monitoring of current versus time was carried out using a LabVIEW program on a PC (Figure 21). Anodization duration was 45 minutes to 24 hours and after anodization, the nanotube arrays were rinsed with 99.9% pure isopropyl alcohol followed by ten-minute sonication in isopropyl alcohol to remove residual and precipitated oxides from the surface of nanotubes. The anodized piece was then dried under gentle airflow.
Unsupported nanotube arrays (free-standing flakes) were created when the as-anodized supported TiO$_2$ nanotubes were rinsed with deionized (DI) water immediately after anodization (instead of isopropyl alcohol), followed by drying in air and slightly bending the titanium substrate to release the flakes.

**Short TiO$_2$ NT Arrays:** To synthesize the short nanotubes, same anodization set up and method is used as employed for synthesis of the long nanotubes. The electrolyte, however, was an aqueous solution consisting of 0.25 M hydrogen fluoride (HF) in DI-water and the anodization duration was 45 minutes under an applied voltage of 15 V$_{DC}$. The titanium-supported short nanotube arrays were then ultrasonicated for 30 minutes in isopropanol and dried under a gentle air flow and characterized as-supported on the Ti foil.

### 3.1.2 Fabrication of Fe-Doped TiO$_2$ NTs

Developing a proper technique to incorporate Fe in the TiO$_2$ lattice is challenging. There is the possibility of formation of an iron secondary phase due to aspects such as the grade (purity, density) and amount of the starting iron. Based on the solubility limit of Fe in
anatase, no more than 1 wt% of iron should be incorporated in TiO₂ crystal lattice structure, otherwise iron clusters might be formed. [80] On the other hand, incorporation of too little Fe would show no significant or observable change in structural or magnetic properties. The synthesis approach utilized in this work was to fabricate Ti(Fe) arc-melted alloy sheet, followed by anodization for nanotube formation. In this method, Ti(Fe) sheets (5 wt% equivalent to 4.4 at% Fe) was purchased from ACI Alloy, USA. According to the manufacturer, these pieces (2.54 cm × 2.54 cm and 1 mm thick) were made by vacuum arc melting of 5 wt% iron in Ti(Fe) followed by cold rolling to obtain sheets with the desired thickness (more detail on the Ti(Fe) alloy sheet can be found in Part (B) of the Appendix). These sheets were subsequently anodized for 6 hours to form Fe-doped nanotubes. The anodized nanotubes were then removed from the sheet by scraping with a glass slide to prepare the Ti(Fe) sheet for further anodization. The nanotubes that are characterized and studied in this Dissertation are from the 4th anodization set of this alloy sheet.

Arc melting is an alloying method that provides an elevated mechanical homogeneity. In this alloying method, the metallic shots in proper weight ratio (herein, 5 wt% Fe wrt Ti) are brought to a vacuum environment in a water-cooled crucible plate (typically made from copper). An electrode (typically from tungsten) is brought to the vicinity of the shots to start the melting process. Several kiloamperes of DC current is then applied through the electrode to form an arc between the electrode and the metallic shots to initiate the melting.
3.2 **Post-Fabrication Processing of the NTs**

A quartz tube furnace was used for annealing the as-anodized nanotubes placed in ceramic boats as supported or free-standing flakes, in order to induce crystallization. The crystallinity of the nanotubes was varied by varying the final annealing temperature from 250 °C to 450 °C and by duration of annealing from 1 to 2 hours.

Annealing of the nanotubes was performed under a constant gas flow rate (30 cm³/min) of either O₂, Ar and H₂ with a heating/cooling rate of 1 °C /min. By changing the annealing atmosphere it was possible to study the effect of annealing atmosphere (oxygen-rich, inert or reducing gas) on the crystallinity and thermal stability of the nanotubes.

3.3 **Characterization Techniques, Principles and Methodologies**

The pure and Fe-doped TiO₂ nanotubes and TiO₂-based reference compounds were characterized by several techniques, which are described in the following sections.

3.3.1 **Morphology Observation**

The morphology of the nanotubes was observed using scanning electron microscopy (FE-SEM, Hitachi S4800). In this manner, information regarding the surface smoothness of the precursors, optimization of the fabrication process to yield nanotubes instead of a porous structure as well as the tube length, pore diameter and uniformity of the synthesized samples was obtained. To achieve enhanced conductivity during morphology observation and avoid surface charging phenomenon, all the samples were mounted on double-side carbon tape placed on top of the aluminum SEM stub.
Electron microscopes use a beam of electrons to image surfaces; [128] their development was motivated by the limitations of optical microscopes which per se were limited by the physics of visible light. A schematic of the main features of a scanning electron microscope is illustrated in Figure 22 in comparison with those of an optical microscope.

In SEM, energetic electrons (1 – 30 keV) are focused by magnetic lenses and form a beam of 2 – 10 nm in diameter. This electron beam reaches the specimen surface and ionizes the nearby atoms, creating secondary electrons. Some of the generated secondary electrons leave the surface and are collected and counted by a positively charged detector. The specimen should be conductive enough to dissipate the charge of electrically charged electrons. The large depth of focus in SEM allows a wide range of height to be in focus at the same time.

Figure 22: Comparison of the principal features in optical and scanning electron microscopy.

3.3.2 Compositional Analysis

A rough approximation of the elements present in each nanotube sample or in the Fe-doped nanotubes’ precursors was obtained using energy dispersive x-ray spectroscopy
X-rays are photons within the energy range of $10 - 10^5$ eV, which is between the energy limits of UV light and gamma rays. [129] Controlled generation of the x-rays is through bombardment of a target with medium-energy electrons. When these primary electrons reach the target, the atomic electrons of the target get excited into the higher energy levels and then they relax back to their ground state (lowest energy state) by releasing their excess energy in form of x-rays. The largest energy that is released in form of x-ray depends on the primary beam, as each element (target) can generate specific energies of x-rays corresponding to the energy difference between its excited energy level and its ground state, so the x-rays are called as characteristic x-rays, Figure 23.

![Figure 23: Schematic of electron transitions in an atom which produce the characteristic x-ray emissions: $K_{\alpha}, K_{\beta}, L_{\alpha}$ (based on the Bohr atomic model).](image)
Energy dispersive x-ray spectroscopy in conjunction with scanning electron microscopy detects the x-rays emitted from the sample, when the SEM primary electron beam bombards it. The electron bombardment on to the sample surface results in emission of different particles or waves such as secondary electrons, back-scattered electrons, x-ray photons, Auger electrons, Figure 24. The secondary and backscattered electrons are used for imaging (i.e. in SEM), and the x-rays are used in EDS measurements. [130] The relative abundance of the emitted x-rays is measured by the EDS detector as a function of their energy. [131] In this manner, information on the elemental composition of the sample is attained through analysis of the spectrum of x-rays energies versus their intensity when the spectrum is compared with that of the known characteristic x-ray energy values. The minimum limit for detecting an element varies from 0.1 to a few at%, depending on the element and the sample. The probing depth in EDS analysis is typically 1 – 3 µm.

Figure 24: Schematic of the electrons and x-rays emitted when a primary electron beam is focused on the sample surface in EDS in conjunction with SEM. [130]
3.3.3 Determination of the Crystal Structure

Identification of the bulk crystal structure, crystallite size and phase composition of the metallic precursors and nanotubes was done using x-ray diffraction (XRD) technique. In addition, transmission electron microscopy (TEM) was employed to extract short-range and nano-scale crystallographic information in the nanotubes. The selected area electron diffraction (SAED) technique in TEM was employed to attain some qualitative confirmation on the crystalline phase of specific locations in the sample.

In the following sub-sections first an overview of the crystallographic information is provided (Section 3.3.3.1) and then the three crystallography techniques, i.e. XRD, TEM and SAED and the analytical expressions employed for data analysis are explained in Sections 3.3.3.2 and 3.3.3.3. [132]

(A) Overview of Fundamental Concepts of Crystallography:

A fundamental concept in description of crystalline solids is Bravais lattice, which specifies the periodic arrays in which the repeated units of the crystal are arranged. [133] These units maybe single atoms, groups of atoms, molecules, ions, etc., but the Bravais lattice only summarizes the geometry of the underlying periodic structure, regardless of what the actual units are. The smallest repeating unit of the crystal lattice is called unit cell and is defined by lattice parameters $a$, $b$, $c$ along the crystallographic axes $x$, $y$, $z$, and angles between these axes: $\alpha = b^\gamma c; \beta = a^\gamma c; \gamma = a^\gamma b$, Figure 25.
A unit cell has a lattice point (for instance, an atom) on each corner and sometimes more lattice points elsewhere (e.g. within the center of the body). There are seven crystal systems, depending on the relationships between the lattice parameters and their angles, namely: Triclinic, Monoclinic, Orthorhombic, Tetragonal, Rhombohedral, Hexagonal and Cubic. [133] In this Dissertation research, Cubic, Hexagonal and Tetragonal crystal systems are involved, thus general schematic of these three crystal structures are presented in Figure 26.
(B) Evaluation of the Crystal Structure, Crystalline Phase Composition and Crystallite Size:

The bulk crystal structure of the precursors and the as-anodized and annealed nanotubes was analyzed using x-ray diffraction (XRD) techniques (Philips X-ray Diffratometer X’Pert Pro, PANalytical, USA) with Cu Kα as the radiation source.

XRD is a non-destructive method that can be used for a specimen to determine its crystalline phase composition, unit cell lattice parameters and Bravais lattice symmetry, crystal structure, crystallite size, residual strain and texture. In laboratory-scale x-ray diffraction, the electrons are boiled off of a cathode and accelerated through a strong electric potential (~ 50 kV). After reaching a high speed, they collide with a metal plate (commonly, copper due to its high thermal conductivity), Figure 27(a). As a result of this colliding, the x-rays corresponding to the excitation of inner-shell electrons of that metal are generated, Figure 27(b).

![Figure 27: X-ray generation due to the colliding of electrons with a metal plate. [134]](image)

The generated parallel beam of x-rays passes through a monochromator and radiates on the specimen, Figure 28. Based on the crystal structure of the sample, the x-ray beam is diffracted at specific angles and produces a diffraction pattern that can be interpreted to
provide crystallography information, for instance, when the pattern is compared with standard patterns (Powder Diffraction Files (PDF)) of crystalline compounds/elements found in databases such as Joint Committee of Powder Diffraction Society (JCPDS).

![Figure 28: Principles of x-ray diffraction. [135]](image)

Based on Bragg’s relationship, it is possible to determine the \( d \)-spacing (spacing between the lattice planes) of the crystal structure when the conditions for constructive interference of the diffracted x-rays (at specific angles) are met:

\[
 n \lambda = 2d \sin \theta \quad \text{(Bragg’s Law)} \quad (1)
\]

where: 
- \( n \) = Order of reflection (taken as \( n = 1 \))
- \( \lambda \) = Wavelength of the incident radiation (nm)
- \( d \) = Interatomic spacing (nm)
- \( \theta \) = Angle of incident x-ray beam (degrees)

By obtaining the value of \( d \)-spacing for various incident angles it is possible to calculate the lattice constants of the crystal unit cell. [136]
In this research, nanotubes were handled on the Ti substrate or as free-standing pulverized flakes on a glass sample holder and a goniometer $\theta - 2\theta$ XRD scan was performed on them. Once the XRD pattern was obtained for each sample, it was compared to PDF cards of the standard compounds/elements from M. D. Jade Software v. 5.0.37, Materials Data Inc. in order to extract the crystallographic information.

The average crystallite size was calculated according to the Scherrer formula,

$$D(2\theta) = \frac{k\lambda}{L \cos \theta}$$  \hspace{1cm} (1)

where: $D(2\theta)$ = Average grain/particle size (Å)

$k$ = Scherrer constant (taken as 0.9, [137])

$\lambda$ = Wavelength of Cu K$_\alpha$ radiation (1.5418 Å)

$L$ = Full width at half maximum, FWHM, intensity (R)

The Scherrer formula calculates the volume-weighted average of the coherently diffracting crystalline domain. [111] Information regarding the lattice parameters of the crystal structures was obtained using a least squares method for cell parameter refinement based on the Bragg equation, as explained by Novak and Colville. [136]

(C) Local Structure and Short-Range Order:

The short-range order and lattice planes of isolated nanotubes were observed with transmission electron microscopy (TEM, JEOL 2010F). The nanotubes were isolated by ultrasonication of the free-standing flakes of nanotube arrays in isopropanol and pouring a few drops on a TEM grid and allowing the alcohol to evaporate.
TEM is the first type of electron microscopes and was developed before SEM. In TEM, the beam of electrons passes through the specimen and the transmitted part is projected onto a phosphorescent screen. The darker area on the image represents thicker or denser points. TEM can provide information regarding morphology and crystallographic arrangements. Figure 29 demonstrates the basic features of TEM.

![Transmission Electron Microscopy](image)

**Figure 29:** Principal features in transmission electron microscopy.

When qualitative confirmation on the presence of a crystalline phase versus that of an amorphous phase in the nanotubes was required, the selected area electron diffraction (SAED) technique in TEM was used. SAED takes advantage of the small wavelength of fast moving electrons ($\lambda_e = 0.025$ Å versus that of Cu Kα x-rays with $\lambda_{Cu} = 1.5418$ Å) which is much smaller than the spacing of the atomic planes. SAED is a fast technique and can take patterns in seconds on specially-localized spots on the sample (< 200 nm). Figure 30 shows the TEM images and corresponding SAED patterns of an oxide in its amorphous and crystalline states.
3.3.4 Determination of Phase Transition and Crystallization Behavior

The phase transition and devitrification processes of the as-anodized TiO$_2$ nanotubes were studied using simultaneous differential scanning calorimetry/ thermogravimetric studies (DSC/TG, NETZSCH-STA-449-F3).

Differential scanning calorimetry is a thermal analysis technique that works based on the differences in energy required to maintain the sample and reference (an empty pan, typically from Al$_2$O$_3$) at an identical temperature, Figure 31. Considering that crystallization is a phase transformation and involves the latent heat of formation, DSC can be used to monitor the crystallization process to obtain information on the onset temperature of crystallization, enthalpy and activation energy of crystallization.
Figure 31: Schematic of the DSC setup used in this work. The sample is mounted in an Al₂O₃ pan and the reference pan is an empty Al₂O₃ pan.

Thermogravimetric analysis (TGA) detects changes in the sample’s mass on heating and can record data on the mass change as function of temperature (or time) simultaneously with DSC measurements. Comparison of the TGA and DSC curves at the given time or temperature can provide complementary information on the phase transition behavior of the sample.

Pulverized nanotube flakes (approximately 10 mg) were placed in alumina crucibles (pans) for assessment in an inert environment (high purity argon, >99.995%) and in a reducing environment (high purity argon with 2% hydrogen), in the temperature range of 50 °C to 450 °C and at heating rates of 5, 10 and 15 °C/min. The DSC peaks were fitted to Gaussian curves to determine the crystallization peak temperature, \( T_p \). The activation energy for crystallization, \( E_a \), was calculated from the non-isothermal Kissinger equation [139-141] as,

\[
\frac{d \ln\left(T_p^2/\beta\right)}{d(1/T_p)} = \frac{E_a}{R}
\]  

(2)

where: \( T_p = \) Crystallization peak temperature (K)

\( \beta = \) Heating rate (degrees/min)
\[ E_a = \text{Activation energy for crystallization (kJ/mol)} \]

\[ R = \text{Universal gas constant (8.314 J/mol.K)} \]

The overall enthalpy of crystallization, \( \Delta H \) in terms of kJ/mol, was determined as the area of the DSC crystallization peak.

### 3.3.5 Determination of the Local Electronic Structure

Element-specific information regarding the surface electronic structure of unoccupied states above the Fermi level in pure and Fe-doped nanotubes was attained using near edge x-ray absorption fine structure spectroscopy (NEXAFS) at the U7A beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. Strong dependence of both O \( K \)-edge and Ti \( L \)-edge features on the local bonding environment in TiO\(_2\) makes NEXAFS a proper method to study the crystal structure, oxidation state of titanium and oxygen vacancies on the surface of TiO\(_2\) nanostructures. [142] The NEXAFS spectra were collected in terms of partial electron yield (PEY) intensities at room temperature and in a vacuum better than \( 10^{-8} \) Torr, with the photon beam normal to the sample surface. A schematic of the electron yield collection in NEXAFS is shown in Figure 32.

**Figure 32:** Schematic of electron yield data collection in x-ray absorption spectroscopy. [143]
Data were acquired for the titanium L-edge (440 – 480 eV), oxygen K-edge (515 – 585 eV) and Fe L-edge (670 – 740 eV) normalized to the incident photon flux, using a monochromator grating with an energy resolution of the 0.2 eV in the energy range studied. The x-ray absorption spectra of commercial reference metallic and oxide compounds (titanium foil (99.7%), iron foil (99.5%), anatase (99.9%), rutile (99.99%), TiO (99.5%), Ti₂O₃ (99.8%), Fe₃O₄ (99.997%), Fe₂O₃ (99.99%), FeTiO₃ (99.8%) and Fe₂TiO₅ (99.9%) powder) were also examined. The samples (reference compounds in form of foil or powder, and nanotube samples in form of finely pulverized free-standing flakes) were manually pressed into copper tape sample holders (1 mm deep and ¼ inch diameter and were charge-neutralized using a low energy electron gun. Any possible shift in the spectra was compensated for, by examining a reference mesh main peak position in the U7A beamline. Deconvolution of the spectra to individual peaks was attained by fitting the Ti L-edge spectra into six [seven] Voigt peaks in the as-anodized [annealed] state. All the fittings were carried out after subtracting two step functions as the background. The centroid of each Voigt peak was designated as the peak position and the peak intensity (I) was defined as the area underneath the Voigt function peak. The split peaks ascribed to e₉ symmetry were denoted as e₉(a) (with lower energy) and e₉(b) (with higher energy). The position of the L₃-e₉ peak was determined as the average value between the e₉(a) and e₉(b) positions. The spectra were normalized to the intensity tail at energies larger than 550, 485 and 735 eV for O K-edge, Ti L-edge and Fe L-edge, respectively.

Part of the NEXAFS experiments was also carried out at the U4B beamline at the National Synchrotron Light Source, Brookhaven National Laboratory (NSLS/BNL). The
Ti $L$-edge and O $K$-edge x-ray absorption spectra for the supported short and long TiO$_2$ nanotubes were collected with the incident beam parallel to the surface normal of the Ti substrate in total electron yield (TEY) mode by measuring the sample drain current. The absorption data were normalized to the incident beam intensity with an energy resolution of $\sim 0.3$ eV. The collected spectra were compared with those of the reference titanium oxide-based powders, 99.6% pure anatase, 99.8% pure rutile, and 99.8% pure Ti$_2$O$_3$, all purchased from Alfa Aesar and examined in the same conditions as explained above.

The probing depth of the electron-yield NEXAFS on Ti $L$-edge is 2 – 4 nm since it is limited by the escape depth of Auger electrons. The mean free path of oxygen Auger electrons is smaller (approximately 1 nm). [144] Such probing depth makes NEXAFS a surface sensitive technique. The element specificity of the NEXAFS comes from the fact that different elements have x-ray absorption edges of different energies. [145] The main difference between this technique and the other related x-ray photoemission spectroscopy (XPS) technique is that in NEXAFS the x-ray intensity is measured when the x-ray energy is scanned, and in XPS the photon energy is fixed and the electron intensity is measured as a function of electron kinetic energy. [145] In electron yield detection of NEXAFS, the photoelectrons that were created by the absorbed x-rays are measured, rather than the absorbed x-ray intensity. The x-rays are absorbed when the core electrons are excited to the empty states at or above the Fermi level, leaving holes behind, Figure 33. In addition, NEXAFS is superior to the XPS in the sense of providing information on the local structure (bonding environment) by exhibiting considerable fine structure above each elemental absorption edge (see Figure 34 (a) and (b)). These fine structures are often used as fingerprints to determine the local bonding environments. [145]
Figure 33: Schematic illustration of the x-ray absorption and excitation of (a) a core electron to the empty valence state [146] (b) an electron from the 2p level of a 3d transition metal atom.

Figure 34: (a) NEXAFS spectra of the Ti $L_{2,3}$-edge and the O K-edge. [147] (b) XPS spectrum of anatase; the insets are high resolution XPS spectra of Ti 2p and O 1s levels. [148]

3.3.6 Magnetic Characterization Techniques and Analysis Methodologies

Magnetic measurement can be used as a sensitive probe to determine the presence of Fe, its dispersion homogeneity and how it is interacting with other elements in TiO$_2$ as well
as its effect on the electronic structure of titanium. In case of pure nanotubes, the magnetic measurements are useful to detect/explain possible changes in the atomic electronic structure as function of the processing conditions. In this Dissertation research, bulk magnetic measurements were carried out using superconducting quantum interference device (SQUID) magnetometry.

In this section, first an overview of some definitions and different magnetic behaviors that are encountered in this Dissertation research is presented. Then the SQUID magnetometry technique and methods and its principles of operation are explained.

(A) Overview of Fundamental Concepts of Magnetism and Terminology:

There are two possible atomic origins of magnetism that can lead to the magnetization of magnetic materials: orbital motion and spin of the electron. [149] The magnetic moments of technological important magnetic atoms such as iron are mostly caused by electron spin, because the orbital magnetic moment is almost quenched by the crystalline field which is produced by the surrounding atoms, and thus the atomic magnetic moment is usually called spin. In general, i.e. when the orbital momentum is not quenched such as in rare-earth metals, the total magnetic moment of an atom would be composed of spin and orbital magnetic moments.

Based on the Vector Model of magnetic atoms, the state of an atom can be defined by four quantum numbers: [149]

(i) The total quantum number, \( n = 1, 2, 3, \ldots \) (or \( K, L, M, \ldots \) shells), which determines the size and energy of the orbit.
(ii) The orbital angular momentum quantum number, \( l = n-l \) (or 0, 1, 2,…), which is a measure of the angular momentum of the orbital motion of the electron. The electrons with \( l = 0, 1, 2, 3,… \) are referred to as \( s, p, d, f,… \) electrons, respectively. For instance, the \( L \) shell \( (n = 2) \) has \( s \) and \( p \) electrons.

(iii) The spin momentum quantum number, \( s \), which is always \( \frac{1}{2} \).

(iv) The total angular momentum number, \( j \), which is the vector sum of \( l \) and \( s \), as illustrated in Figure 35.

![Figure 35: Total angular momentum as the vector sum of the spin momentum and orbital momentum [150], where \( S = \sum_{i=1}^{n} s_i \) and \( L = \sum_{i=1}^{n} l_i \) for the \( i \)th electron in a shell, and \( J = L + S \). [149]](image)

As illustrated in Figure 35, in an atom composed of many electrons the angular momenta of the variously oriented orbits combine vectorially to give the orbital angular momentum of the atom (quantum number \( L \)). Also, the individual electron spin momenta
combine vectorially to give the spin momentum of the atom (quantum number $S$). Finally, these orbital and spin momenta of the atom combine to give the total angular momentum of the atom (quantum number $J$). The value of the total angular momentum, $J$, may be an integer or half-integer, ranging from $J = \frac{1}{2}$ for a pure spin with no orbital contribution ($L = 0, J = S = \frac{1}{2}$) to $J = \infty$ which means an infinite number of $J$ values corresponding to an infinite number of moment orientations. [151]

The net magnetic moment of the atom, $\mu_{\text{eff}}$, is given in terms of $g$-factor and $J$: \[ \mu_{\text{eff}} = g \sqrt{J(J+1)} \mu_B \] (3)
in which $g$ is the $g$-factor or Landé $g$-factor, a dimensionless quantity which characterizes the magnetic moment and gyromagnetic ratio of a particle, and is defined by the Landé equation as: [151]\[ g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \] (4)

If there is no net orbital contribution to the moment, $L = 0$ and $J = S$, then $g = 2$.

The magnetic properties of materials can be characterized by evaluation of the magnitude of their moment, $M$, and the way it changes with variations of external magnetic field, $H$, or temperature, $T$. [152]

Typical curves of $M$ versus $H$ are called magnetization curves, the shape of which depends on magnetic nature of the material. The $M/H$ ratio is called the susceptibility, $\chi$: \[ \chi = \frac{M}{H} \left( \frac{\text{emu}}{\text{Oe.mole}} \right) \] (5)
The magnitude of magnetic susceptibility, $\chi$, can range from $10^{-6}$ (for very weak magnetism) to $10^6$ (for very strong magnetism). [149] There are various types of magnetism, namely, diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism, among which only the paramagnetism and ferromagnetism are observed and studied in this research work. Table 5 summarizes the magnitude of the corresponding susceptibility for para- and ferromagnetism.

**Table 5: Para- and ferromagnetism and the corresponding values of their magnetic susceptibility.**

<table>
<thead>
<tr>
<th>Type</th>
<th>Sign</th>
<th>Magnitude</th>
<th>Field Dependence of $\chi$</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paramagnetism</td>
<td>+</td>
<td>$0$ to $10^{-4}$ emu units</td>
<td>Independent</td>
<td>Angular momentum of the electron</td>
</tr>
<tr>
<td>Ferromagnetism</td>
<td>+</td>
<td>$10^{-4}$ to $10^{-2}$ emu units</td>
<td>Dependent</td>
<td>Spin alignment from dipole-dipole interaction of moments on adjacent atoms, $\downarrow$</td>
</tr>
</tbody>
</table>

In paramagnetic materials there is no net magnetic moment in the absence of an external magnetic field, as the atoms with non-zero (weak) magnetic moment are randomly oriented. Under an applied field, however, these moments can align and result in a net magnetic moment:

In ferromagnetic materials such as iron, nickel and cobalt, each atom has strong magnetic moment arising from the uncompensated electron spins. Many of atomic
moments interact with each other and align in regions, forming a magnetic domain. In the absence of a magnetic field, these domains are randomly oriented. In presence of an external field, these domains align themselves and if the applied magnetic field is strong enough, eventually all the domains can align themselves. The magnetization curve of a ferromagnetic material is not linear and passes through a maximum value. At large enough fields that all the domains are aligned, the magnetization reaches a constant value, called saturation moment, $M_s$. Figure 37 shows the typical behavior of a ferromagnetic material.

![Magnetization Curve and Spin Orientation](image)

Figure 37: (a) Typical magnetization curve of a ferromagnet; (b) schematic representation of the spin orientation in the ferromagnetic during its initial magnetization. [153]

Ferromagnetic materials have a critical temperature referred to as the Curie temperature, $T_C$, above which the material becomes paramagnetic. The typical temperature dependence of para- and ferromagnetic materials is shown in Figure 38.
It should be noted that there are different types of paramagnetic materials; the paramagnetism that is shown in Figure 38(a) is from a Curie paramagnet, in which the susceptibility, $\chi_C$, is inversely proportional to the absolute temperature through Curie law as in equation (6):

$$\chi_C = \frac{C}{T},$$

and:

$$C = \frac{N\mu^2}{3k_B}$$

where:

$C =$ Curie constant ($\text{emu mole.Oe.K}^{-1}$)

$T =$ Temperature (K)

$N =$ number of the magnetic atoms per unit volume with the magnetic moment, $\mu$

$\mu =$ Magnetic moment ($\mu_B$)

$k_B =$ Boltzmann constant ($1.38 \times 10^{-16} \text{ m}^2\text{kg} \text{s}^{-2}\text{K}$)

The derivation details of equation (7) are provided in Kittel’s book. [154]
The Curie law describes the behavior of a ferromagnet in the paramagnetic region, *i.e.* for temperatures above its Curie temperature, and is a special case of a more general law known as the Curie-Weiss law, as illustrated in Figure 39.

![Figure 39: Variation of susceptibility, $\chi$, with temperature, $T$, for Curie and Curie-Weiss paramagnets. [151]](image)

Curie-Weiss law is then defined through equation (8): [151, 154]

$$\chi_{CW} = \frac{1}{T - T_0} C_{CW},$$  \hfill (8)

where: $\chi_{CW} =$ Curie-Weiss paramagnetism ($\frac{emu}{mole.Oe}$)

$T_0 =$ Curie-Weiss temperature (K)

$C_{CW} =$ Curie-Weiss constant (s)

The magnitude and sign of the Curie-Weiss temperature, $T_0$, provides information on the nature of magnetic exchange interactions in the system. In particular, $T_0 > 0$ characterizes parallel spin alignment and $T_0 < 0$ indicates antiparallel spin alignment. The Curie-Weiss
constant, \( C_{CW} \), is a measurement of the number of magnetic entities, \( N \), or the average effective atomic moment per magnetic entity, \( \langle \mu_{eff} \rangle \), through the following equation [154, 155]:

\[
\langle \mu_{eff} \rangle = \sqrt{C k_B / N},
\]

Equation (9) is another form of equation (7) by substituting:

\[
\mu_{eff} = \mu_B
\]

where: \( \mu_B = \) Bohr magneton (9.27\times10^{-21} \text{ emu})

Apart from the Curie and Curie-Weiss types of paramagnetism, the conduction electrons which form an energy band in metallic crystals also exhibit a temperature-independent paramagnetism, known as Pauli paramagnetism which originates from the presence of delocalized electrons and corresponds to the electron occupancy at the Fermi level. [149] Thus, the Pauli paramagnetic susceptibility, \( \chi_{pp} \) provides an estimate of the electronic density of states at the Fermi level, \( N(E_f) \), through the following relation [132, 156, 157]:

\[
N(E_f) = \chi_{pp} / 2 \mu_B^2,
\]

(B) Magnetic Measurements:

The magnetic properties of pulverized unsupported nanotubes were studied using superconducting quantum interference device (SQUID) magnetometry (Magnetic Properties Measurement System (MPMS), Quantum Design Inc.). The pulverized flakes of free-standing nanotubes were mounted in evacuated quartz tubes (5 mm OD and 3 mm
ID) prior to carrying out the magnetic measurements, Figure 40, according to the method described by Lewis et al. [158]

![Figure 40: A typical sample of pulverized flakes of free-standing TiO$_2$ NT arrays, sealed in a quartz tube.](image)

SQUID-based magnetometers have high measurement accuracy and capability of providing very high flux sensitivity typically on the order of $10^{-8}$ emu which makes it possible to measure samples with low susceptibility. Besides, the detection coils are relatively large compared to the sample size, resulting in a relatively small sensitivity to the sample geometry. [159] SQUID magnetometer measures magnetic moment of the sample as a function of temperature, magnetic field and time. The MPMS used in this study is capable of measuring the longitudinal magnetic moment of the sample within the field and temperature range of $\pm 5$ T and $1.7 - 400$ K, respectively, under low pressure helium gas. The schematic of MPMS features used to carry out measurements of this Dissertation are shown in Figure 41.
Figure 41: Schematic of the pick-up coils in the SQUID magnetometer and the voltage signal recorded as a function of sample scan length. [160]

The SQUID magnetometer features a set of superconducting pick-up coils within which the sample space is located. The upper and lower coils are wound coaxial to the system’s z-axis and the central coil is wound opposite to these upper and lower coils. The sample, suspended from a rod, is mechanically scanned along the z-axis within the pickup coils, as shown in Figure 41. The sample’s magnetic moment induces currents in the coil set up, which is converted to a voltage signal that is fitted to an equation that produces a quantity that represents the z-component of the magnetic dipole of the sample. A typical voltage signal of an ideal dipole as a function of scan length is also shown in Figure 41.

In this work, the change of the magnetic susceptibility of the nanotubes with temperature was measured under applied magnetic fields of $H = 500$ Oe and $H = 4000$ Oe, in the temperature range of $2 \, \text{K} < \, T < \, 400 \, \text{K}$. The total magnetic susceptibility,
\( \chi_{\text{tot}}(T) \), is fit to an equation (12), which is a combination of Curie-Weiss law (equation (8)) and temperature-independent Pauli paramagnetism:

\[
\chi_{\text{tot}}(T) = \chi_{\text{CW}} + \chi_{\text{PP}} = C_{\text{CW}} / (T - T_0) + \chi_{\text{PP}}, \tag{12}
\]

where: \( \chi_{\text{tot}}(T) \) = Total magnetic susceptibility

\( \chi_{\text{CW}} \) = Curie-Weiss paramagnetism

\( \chi_{\text{PP}} \) = Pauli paramagnetism

Further investigation of the magnetic behavior of the nanotubes was carried out by measuring the nanotube’s magnetic moment as a function of magnetic field in the range of \(-20 \, \text{kOe} < H < 50 \, \text{kOe}\) at various temperatures ranging from \( T = 3 – 300 \, \text{K} \).

The total angular momentum, \( J \), is calculated by fitting the low temperature \( (T = 3 \, \text{K}) \) \( M(H) \) curve to the Brillouin function, equation (13):

\[
B_j(x) = \frac{2J+1}{2J} \frac{1}{\text{ctnh} \left( \frac{(2J+1)x}{2J} \right)} - \frac{1}{2J} \frac{1}{\text{ctnh} \left( \frac{x}{2J} \right)} \tag{13}
\]

in which: \( x \equiv gJ \mu_B H / k_B (T - T_0) \), \( \tag{14} \)

and other parameters are as explained previously. It should be mentioned that in all the graphs and calculations, the raw moment (directly measured by SQUID) was corrected for the quartz tube signal based on the method described by Lewis et al. [160]

3.3.7 Electron Spin Spectroscopy

The chemical nature of the as-anodized and annealed nanotubes was evaluated by room-temperature electron spin resonance (ESR) spectroscopy technique using Bruker EMX ESR spectrometer.
Electron spin resonance spectroscopy, also known as electron paramagnetic resonance (EPR) spectroscopy, is a sensitive and direct technique to investigate the presence and concentration of the paramagnetic species. [161] As described in Section 3.3.6.1, paramagnetism originates from the unpaired spins (electrons) within a material. ESR technique is typically employed to detect and identify unpaired electrons such as free radicals, transition metal ions and color centers.

The principle of operation of ESR is based on the fact that each electron constantly spins around its axes with a specific angular momentum. [162] Electron spin is associated with a magnetic moment equal to $9.27 \times 10^{-21}$ emu, or 1 Bohr magneton, $\mu_B$. In presence of an external magnetic field, the electron is aligned with the direction of the field and precesses about this axis.

![Figure 42: Schematic of the electron spin direction (up and down). [163]](image)

The magnetic field splits the electrons into two groups: (1) a group with magnetic moments parallel to the external magnetic field and (2) a group with magnetic moments antiparallel to the external magnetic field. The spin quantum number of an electron is $S = \pm \frac{1}{2}$, and the two possible orientations of the electron in presence of the external field
corresponds to the projections $M_s = \pm \frac{1}{2}$, each projection with a different level of energy. The lower [higher] energy state is the projection antiparallel [parallel] to the direction of the magnetic field, $M_s = -\frac{1}{2}$ ($+\frac{1}{2}$). These two energy levels are often referred to as the spin $-\frac{1}{2}$ and the $+\frac{1}{2}$ states, Figure 42. If a second, weaker, alternating magnetic AC field is applied to the main DC field using a high frequency microwave-resonant cavity, it can “tip over” the electron when the precession frequency of that electron equals that of the incident microwave frequency, Figure 43. The electron spin resonance absorption occurs when the quanta of the incident microwaves results in transitions between the two states of the unpaired electron. That is, the microwave energy equals the energy-level separation, $E_{1/2} - E_{-1/2}$, between these two states. [162]

![Figure 43: Schematic illustration of the ESR operational principles. As shown on the right hand side of the image, the first derivative of the absorption line is demonstrated as the ESR signal for analysis. [164]](image)

In practice, the applied frequency is maintained constant and the strength of the magnetic field is scanned to locate the values at which the resonance occurs. [162] Electrons at both energy levels absorb the radiation quanta; in the lower energy electrons, this absorption results in jumping to higher energy state and in higher energy electron it
results in stimulated emissions. Absorption and stimulated emission have equal number coefficients (proportionality constant), thus if these two levels have equal distribution of spin population no net value is observed. This equality of spin population happens when there is no unpaired spin in the material. Otherwise, an ESR signal is observed and its intensity is proportional to the population difference between the two spin states.

The resonance condition can thus be explained as:

\[ \Delta E = h\nu = g\mu_\text{B}B \]  

(15)

where: \( \Delta E \) = The energy difference between two spin energy states, \textit{i.e.} parallel or antiparallel to the external magnetic field

\( B \) = The external magnetic field (mT).

\( h \) = Planck’s constant

\( \nu \) = Frequency of electromagnetic radiation (GHz)

\( \mu_\text{B} \) = Bohr magneton.

The \( g \)-factor, is usually \( g = 2.0023 \) for a free electron, which only has a constitution from an electron spin (the orbital momentum, \( l \), is quenched and equals zero). However, the magnetic behavior (and thus the \( g \)-factor) of an electron in a material can be influenced by its surrounding magnetic and electric fields and deviates from the behavior of a free electron. Information on the structure of the material can be obtained by evaluating this deviation from the standard behavior.
In an ESR measurement, the sample is placed in a microwave-resonant cavity between pole pieces of an electromagnetic in a set up shown in Figure 44. The frequency of the microwave source is then adjusted to the resonant value of the cavity. The magnetic field is varied and the amount of the microwave energy that the sample absorbs is recorded for further analysis.

![Figure 44: Block diagram of the electron spin resonance (ESR) spectrometer.][165]

In this work, the nanotube samples were mounted inside evacuated quartz tubes (same configuration as Figure 40) and placed in the microwave-resonant cavity of the ESR machine. The first derivative of the absorption spectrum of each nanotube sample was averaged over 10 scans and presented as the ESR graph. Measurements were carried out at room temperature and a microwave frequency of 9.38 GHz and power of 6.4 mW. The spectroscopic $g$-factor ($g = 2.0023$ for a free electron) was calculated for each nanotube sample based on equation (15). [161]
3.4 Evaluation of the NTs’ Functionality (Catalytic Activity)

The photocatalytic activity of the TiO$_2$ nanotube arrays was investigated via monitoring the photodegradation of 12 µM methyl orange (MO, Sigma-Aldrich) in 10 mL aqueous solution in presence of 0.6 cm$^2$ exposed surface area of titanium-supported nanotubes.

Prior to exposure of the nanotube arrays to the UV-VIS light irradiation, the nanotubes were immersed in the MO solution in a dark environment for 1 h to reach equilibrium in the adsorption-desorption processes of MO molecules on the TiO$_2$ nanotubes. The supported nanotubes were mounted in the reaction cell facing the UV-VIS light source at a distance of 19 cm. The efficient mass transport in the system was ensured by constantly stirring the solution. The UV-VIS light source was a 147 W mercury lamp with 0.5 M copper sulfate solution as the light filter. The experimental set-up, shown in Figure 45, was water-cooled to maintain a constant temperature of 25 °C during the irradiation process.

![Figure 45: Experimental setup for photodegradation of methyl orange.](image)

The absorption spectrum of methyl orange was analyzed by a UV-VIS spectrometer (8452A Diode Array Spectrophotometer, Hewlett Packard) at irradiation
time intervals of 30 min. The absorption peak at 463.8 nm in the MO UV-VIS absorption spectrum was used to monitor the concentration profile of MO in the solution. The change in concentration of MO is evaluated by its fractional conversion,

\[ f_{MO} = \frac{1 - C_t}{C_0}, \]  

(16)

where: \( C_t \) = Absorption at a certain reaction time

\[ C_0 = \text{Absorption at the starting point after reaching equilibrium in dark environment.} \]

A blank control experiment was carried out with Ti foil under the same conditions, the results of which were subtracted from those obtained from the nanotube samples. The error in the measurements was within 5%.

The rate constant of the catalytic MO degradation reaction, \( k \), was calculated assuming a first order reaction, according to the following equation (17):

\[ \frac{dC}{dt} = kC \]  

(17)

\[ \ln\left(\frac{C}{C_0}\right) = kt \]  

(18)

\[ \ln\left(\frac{1}{1 - f_{MO}}\right) = kt \]  

(19)

where \( C \) is the concentration of MO at any point of reaction time and \( f_{MO} \) is the corresponding fractional conversion of the methyl orange (unitless).

As mentioned earlier, the absorption intensity of MO at a wavelength of 463.8 nm is monitored at specific time intervals of the catalytic degradation, using UV-VIS absorption spectroscopy. UV-VIS spectroscopy is an absorption spectroscopy technique
from wavelengths of 160 nm to 780 nm. When absorption of ultraviolet radiation by a molecule occurs, electronic transitions can be stimulated, in which electrons are excited from ground state to a higher electronic state. Based on the energy (or wavelength) at which a molecule (molecular group) absorbs the UV-VIS radiation, the molecular structure can be identified. The absorption intensity is related to the concentration of that molecule in the specimen. Thus, during the degradation of MO to its constituents, decrease in the absorption intensity of this molecule indicates a corresponding decrease of its concentration in the aqueous solution.

(A) Reported Mechanism of Degradation of Methyl Orange in Presence of TiO$_2$

According to the literature report by Ge et al. [166], the catalytic degradation of methyl orange in presence of TiO$_2$ can be described via the following reactions:

\[
\begin{align*}
    TiO_2 + hv & \rightarrow h^+ + e^- \\
    h^+ + OH^-_{(surface)} & \rightarrow OH^* \\
    h^+ + H_2O & \rightarrow OH^* + H^+ \\
    OH^* + MO & \rightarrow Degradation \ products
\end{align*}
\]

Where MO is the methyl orange with a chemical formula of $^-O_3S - Ar - N = N - Ar - N(CH_3)_2$. The last reaction can be then extended through the following suggested degradation mechanism: [166]
\[ (I) \quad \text{H}_3\text{SO} - \text{Ar} - N = N - \text{Ar} - N(CH_3)_2 + OH^* \rightarrow \]
\[ \text{H}_3\text{SO} - \text{Ar} - N = N - \text{Ar'}(OH) - N(CH_3)_2 + H^* \]

\[ (II) \quad \text{H}_3\text{SO} - \text{Ar} - N = N - \text{Ar'}(OH) - N(CH_3)_2 + H^* \rightarrow \]
\[ \text{H}_3\text{SO} - \text{Ar} - N = N - \text{Ar'}(OH) - NH - CH_3 + CH_3^* \]

\[ (III) \quad \text{H}_3\text{SO} - \text{Ar} - N = N - \text{Ar} - N(CH_3)_2 + H^* \rightarrow \]
\[ \text{H}_3\text{SO} - \text{Ar} - N = N - \text{Ar} - NH - CH_3 + CH_3^* \]

\[ (IV) \quad \text{H}_3\text{SO} - \text{Ar} - N = N - \text{Ar} - N(CH_3)_2 + OH^* \rightarrow \]
\[ HO - \text{Ar} - N = N - \text{Ar} - N(CH_3)_2 + SO_3^- \]

\[ SO_3^- + OH^- \rightarrow SO_4^{2-} + H^* \]

where \( \text{Ar} \) and \( \text{Ar'} \) are the aromatic groups of C₆H₄ and C₆H₃, respectively.

### 3.5 Graphing and Mathematical Analyses of Data

Analysis of the x-ray absorption data were done using the open source software, ATHENA, and plotting and curve fitting were done using OriginLab® software v.9.
4.0 RESULTS

The principal objective of this Dissertation research is to obtain fundamental understanding of the interrelations of structural attributes with the magnetic character of nanotubes and their potential relevance to the nanotube functionality. To fulfill this objective, TiO$_2$ nanotubes (NTs) are synthesized and their properties are characterized as functions of the following conditions: (a) Post-synthesis processing conditions – specifically the annealing temperature/duration and the nature of annealing environment, and (b) Introduction of iron (Fe). As a relevant functionality of TiO$_2$ materials, the photocatalytic activity of nanotubes in degrading an organic dye is also examined to further clarify and evaluate the effects of structural attributes and magnetic character on the nanotube functionality.

This Chapter provides details of synthesis and characterization results of the TiO$_2$ nanotubes when they are synthesized as pure and as Fe-doped materials and are subjected to annealing treatments in variety of conditions. The evaluated properties include morphology, crystal structure, electronic structure and magnetic behavior. Results are presented within seven sections. Section 4.1 reports on the synthesis of TiO$_2$ nanotubes. Section 4.2 provides the morphological results when the nanotubes are processed in various conditions. Crystallinity and crystal structure of nanotubes are then characterized in Section 4.3, while Section 4.4 presents results concerning the crystallization behavior of nanotubes. Section 4.5 provides details of results from examination of the structural defects, electronic structure and local order of nanotubes. Section 4.6 is dedicated to magnetic characterization of nanotubes. This Chapter is closed with presenting the results of photocatalytic performance of nanotubes.
4.1 Synthesis of TiO$_2$ NT Arrays

In this section, synthesis results of the short and long pure nanotubes as well as of the Fe-doped nanotubes are presented. These results include description of the morphology of the as-anodized nanotubes as a confirmation of successful nanotube synthesis and information on the composition of these nanotubes.

TiO$_2$ and Fe-doped TiO$_2$ nanotubes are synthesized by the electrochemical anodization of titanium foil and arc-melted Ti(Fe) alloy, respectively, based on the anodization conditions explained in 3.1.1.1. Upon nanotube formation, a brownish oxide layer forms on the titanium substrate which is more visible in case of long nanotubes, as shown in Figure 46 (a), which in case of long nanotubes can be released to form free-standing flakes, Figure 46 (b).

![Figure 46: (a) Titanium foil, as-received and a film of TiO$_2$ NT arrays formed on it after anodization for 6 hrs in the corrosive electrolyte; (b) free-standing flakes of the as-anodized TiO$_2$ nanotubes.](image)

Successful formation of ordered arrays of short and long pure TiO$_2$ nanotubes as well as of the Fe-doped nanotubes is confirmed by their SEM micrographs as shown in Figure 48 to Figure 49.

**Short Pure TiO$_2$ NTs:** Cross-sectional and pore-side SEM images of the as-anodized
short TiO$_2$ nanotube arrays are shown in Figure 47 (a,b). These nanotubes feature an average diameter of 60 nm and an average length of 0.2 µm.

![Figure 47: (SEM) As-anodized short TiO$_2$ NTs: (a) side view and (b) top view.](image)

**Long Pure TiO$_2$ NTs:** The long nanotubes are in a closed-pack arrangement with an average pore size diameter of 100 nm, Figure 48(a, b). The bottom and lateral view of the nanotube arrays are shown in Figure 48 (c, d) after flaking off the titanium substrate with each nanotube surrounded by 6 – 7 adjacent nanotubes.
**Figure 48:** SEM micrographs of the as-anodized TiO$_2$ nanotubes, (a, b) top, (c) bottom, (d) lateral view. [167]

*Fe-Doped TiO$_2$ NTs:* Scanning electron micrographs of the as-anodized Fe-doped nanotubes are shown in Figure 49, confirming the successful synthesis of nanotubes featuring ~ 50 micron length and approximately 100 nm pore size diameter.
Figure 49: (SEM) Fe-doped TiO$_2$ NTs obtained from anodization of the Ti(Fe) alloy for a six-hour anodization; (a) top, (b,c) bottom, (d) lateral view.

The EDS spectrum of the free-standing flakes of as-anodized TiO$_2$ nanotubes (both short and long), Figure 50, confirms that titanium and oxygen are the main components of these nanotubes, with presence of no other impurity within the detection limit of the equipment (~ 0.5 at%). The observed peaks of potassium (K) and fluorine (F) in Figure 50 are due to the presence of residual electrolyte within the nanotubes.
Similar EDS data obtained from pulverized flakes of Fe-doped nanotubes confirmed the presence of approximately $2.1 \pm 0.3$ at% iron (cationic ratio, \( i.e. \ [\text{Fe}] / ([\text{Fe}] + [\text{Ti}] ) \)).

### 4.2 Morphological Features

As described in Section 2.2.3.3, the as-anodized nanotubes are amorphous and do not exhibit useful functionality and post-synthesis processing of the nanotubes via annealing is necessary to crystalize them for functional applications. Considering the importance of geometrical and morphological aspects of nanotubes in determination of their functionality, it is of interest to understand the effect of annealing conditions on development of morphological features in nanotubes. In this section, the short and long pure nanotubes as well as the Fe-doped nanotubes are annealed in various annealing conditions (annealing duration, temperature, gas type) and their morphologies are studied and compared. This section includes three subsections. In Section 4.3.1, morphology of the short nanotubes annealed for two hours at $T = 350$ °C in Ar and O$_2$ is presented. Section 4.3.2 is dedicated to morphological results of long nanotubes annealed at low...
temperatures, \( i.e. T < 270 \, ^\circ\text{C} \), for different time durations from \( t = 5 \) to 180 minutes. Section 4.3.3 is presents results on the morphology of long nanotubes (pure and Fe-doped) annealed for two hours at high temperature \( (T = 450 \, ^\circ\text{C}) \) and in various gas atmospheres (Ar, O\(_2\) and H\(_2\)).

### 4.2.1 Short NTs Annealed at 350 °C

Scanning electron micrographs of the Ar- and O\(_2\)-annealed short TiO\(_2\) nanotube arrays are shown in Figure 51. These nanotubes are annealed for two hours at 350 °C and their as-anodized morphological features are maintained intact as compared to their as-anodized state (Figure 47), regardless of the annealing atmosphere. Annealing in H\(_2\) provided the same results (not shown here).

![Figure 51: (SEM) Top view of the short TiO\(_2\) NTs annealed at 350 °C in (a) oxygen and (b) argon.](image)

### 4.2.2 Long NTs Annealed at Low Temperatures (\( T < 270 \, ^\circ\text{C} \)) for Various Time Durations

In this section, morphological results are provided on the long nanotubes annealed in an inert atmosphere (N\(_2\)) at \( T = 250 \, ^\circ\text{C} \) for various time durations (5 – 180 mins) and at \( T = 270 \, ^\circ\text{C} \) for a time duration of 90 minutes. Results of the transmission electron microscopy on these nanotubes are also provided to clarify the local morphology.
Scanning electron micrographs of free-standing pulverized flakes of pure nanotubes annealed at 250 °C (for various annealing durations) are presented in Figure 52. Faceted nanoparticles are formed and continue to grow as a function of the annealing duration time, at the expense of the nanotube morphology which slowly fragments. The transmission electron micrographs of these nanotubes, Figure 53, confirm that after 30 minutes of annealing at 250 °C the initially-formed grains are already crystalline and appear to be oriented perpendicular to the tube walls, while the bulk of nanotubes are amorphous.

Comparison of the nanotubes’ morphology after 5 minutes of annealing and after 30 minutes of annealing suggests a heterogeneous nucleation process, wherein single crystals grow to large sizes that exceed the nanotube’s wall thickness. Distinct single crystal particles (nanocubes) residing on nanotubular scaffold-like structures can be clearly seen in the micrographs of Figure 52. In addition, the remaining nanotubes appear to be porous and are quite distinct from those present in the as-synthesized condition. The tubular scaffold for long annealing times becomes grainy itself, suggesting internal crystallization.
Figure 52: SEM images of TiO$_2$ NTs annealed in N$_2$ at 250 °C for various durations of time, as indicated on the left side of the images. Note the gradual formation and growth of the nanocubes on the top, bottom and lateral sides of the NTs over the time from 5 to 180 minutes of isothermal annealing.
Figure 53: TEM images of TiO$_2$ NTs annealed in N$_2$ for 30 minutes at 250 °C. (a) A single NT with nanocrystallites formed on it; (b) magnified view of an area of the NT containing the nanocrystallites; (c) a region of the NT free of any nanocrystallites. The dotted squares in (a) indicate the approximate areas to which the zoomed in images in (b) and (c) correspond, and where the corresponding SAED images (insets) have been taken.

When annealed at higher temperatures (i.e. $T = 270$ °C), more elaborate structures with a unique geometrical pattern start to form, originating from the bulk of the nanotubes. The SEM images in Figure 54 show the bottom and lateral view of the TiO$_2$ nanotubes annealed in nitrogen for 90 minutes at 270 °C. These crystallites take the shape of nanobricks of approximate dimensions $150 \times 150 \times 350$ nm$^3$ and continue to grow simultaneously with the formation of a unique geometrical pattern in the bottom and lateral sides of the nanotubes. This geometrical pattern ultimately results in the breakdown of the nanotubular architecture consistent with an earlier report concerning destabilization of the nanotube morphology. [168] Other groups report on this phenomenon but they observed it at significantly higher temperatures ($T > 450$ °C) and mainly attributed it to protrusions that emanate from the original titanium support. [169]
Figure 54: SEM images of other advanced crystallization stages at higher annealing temperature of 270 °C in N₂ for 90 minutes at a heating/cooling rate of 0.5 °C/min, showing a unique geometrical pattern developed during crystallization.

TEM images of nanotubes annealed for 90 minutes in 270 °C are presented in Figure 55 reconfirming (see (a) and (b)) that the nanocubes are single crystals. Furthermore, those nanotubes that were still partially intact after long periods of annealing at lower temperatures, eventually crystallize as shown in Figure 55 (c). In addition, in the final stages of annealing, the measured interplanar distances of the TEM lattice fringes are in reasonable agreement with the literature value reported for the anatase cell parameter $a = 3.78 \, \text{Å}$ (PDF#71-1166), Figure 55 (c).
Figure 55: TEM Images of TiO$_2$ NTs annealed in N$_2$ atmosphere for 90 minutes at 270 °C, demonstrating the crystalline structure. (a) Agglomeration of a few TiO$_2$ nanoparticles on top of a nanotubular scaffold, (b) a higher magnification image clearly demonstrating that the nanoparticles are single crystals and (c) side view of a remaining nanotubular scaffold which is also crystallized.

4.2.3 NTs Processed in Variety of Gas Atmospheres at 450 °C

In this section, the morphology of long nanotubes (pure and Fe-doped) annealed for two hours at 450 °C is studied. First, morphological results of pure nanotube samples processed in O$_2$, Ar and H$_2$ gas atmospheres are presented, followed by those of the O$_2$-annealed Fe-doped nanotubes.

**Pure Long NTs:** These nanotubes are processed in O$_2$, Ar and H$_2$ gas atmospheres for two hours at 450 °C. Annealing the nanotubes in these three different atmospheres transformed their nanotubular morphology to a nanoparticulate morphology, as shown in Figure 56 (a – f), in comparison with the morphology of unannealed amorphous nanotubes (Figure 48).

Note that a few additional larger particles are also observed in the electron micrographs, presumably only on the surface of the nanotubes, Figure 56 (a – d).
Regardless of the annealing atmosphere, the nanotube morphology breaks down into regular faceted nanoparticles during the annealing process, leaving behind a semi-porous nanotubular structure.

Figure 56: (SEM) Perpendicular (left hand side) and parallel (right hand side) views of TiO₂ NTs annealed in: (a, b) oxygen-rich, (c, d) oxygen-deficient (Ar) and (e, f) reducing (H₂) environments.
**Fe-doped TiO₂ NTs:** Similar to the results obtained from pure nanotubes, the Fe-doped nanotubes annealed in oxygen at 450 °C fragmented and formed a connected porous architecture as shown in Figure 57. This morphological transformation which was more significant in Fe-doped nanotubes than the pure nanotube samples annealed in similar conditions (compare Figure 57 with Figure 56 (a, b)).

![Figure 57: (SEM) Lateral and bottom view of the Fe-doped TiO₂ NTs annealed in O₂ at 450 °C. Oxide nanoparticles are developed on the NT scaffold upon annealing and a fragmented architecture is formed.](image)

### 4.3 Crystallinity and Crystal Structure

It is important to understand the crystallographic changes in the as-anodized nanotubes when the morphological features are developed (Section 4.2). In this section, results from a systematic study of the crystallization of TiO₂ nanotubes arrays are provided when these nanotubes are annealed in various conditions (annealing atmosphere, time duration and gas type). This section is divided into three subsections which present the results on the crystal structure (crystal type and lattice parameters) and crystallite size of nanotubes processed in variety of annealing conditions. Section 4.3.1 provides the results from the long nanotubes annealed in an inert atmosphere at various temperatures of $T = 200 – 285$
℃. Results presented in Section 4.3.2 concern the short and long nanotubes annealed in various gas atmospheres at 350 ℃. Results of the pure and Fe-doped nanotubes annealed in various gas atmospheres at 450 ℃ are provided in Section 4.3.3.

4.3.1 NTs Annealed at Variety of Low Temperatures and Time Durations

In this section the results obtained from two sets of experiments are presented. In the first set (part (A)), the nanotubes are isothermally annealed for 90 minutes at temperatures ranging from 200 – 285 ℃ and in the second set of results (part (B)), nanotubes are annealed at 250 ℃ for duration times ranging from 5 to 180 minutes.

(A) NTs Annealed Isochronally at Various Temperatures:

Figure 58 presents the XRD patterns of the nanotubes annealed in N₂, for fixed time intervals of 90 minutes at temperatures ranging from 200 – 285 ℃. The powder diffraction XRD pattern of standard anatase (PDF#71-1166) is plotted in the same graph for comparison. The highest intensity Bragg peak of anatase ((101) reflection plane) starts to emerge when the nanotubes are annealed at 250 ℃, below which they are amorphous. This crystallization temperature onset in an oxygen-deficient atmosphere is thus somewhat lower when compared with the crystallization onset of 280 ℃, reported for the nanotubes annealed in an oxygen-rich atmosphere. [108, 169]
Annealing at progressively higher temperatures produces larger crystallites and smaller unit cell volumes, as indicated in Figure 59 (a, c), where data associated with a commercially available anatase powder (Anatase Reference) are also presented for comparison. Furthermore, as shown in Figure 59 the crystallite size increases almost linearly as a function of the final annealing temperature, which is consistent with previous reports. [15, 170]

A systematic trend is observed in the anatase lattice parameters and in the unit cell volume as a function of the annealing temperature. At the threshold of crystallization (250 °C) the anatase $a$- and $c$-lattice parameters are larger than those for bulk anatase reference data, Figure 59 (b). While both the $a$- and $c$-lattice parameters decrease...
gradually as the annealing temperature increases, a more significant change is observed in the $c$-parameter compared to the $a$-parameter. The overall results of the change in the lattice parameters translate to a gradual decrease in the calculated anatase unit cell volume towards the standard unit cell volume of the bulk standard anatase, Figure 59 (c).

Figure 59: (a) Crystallite size, (b) lattice parameters, and (c) calculated unit cell volume of TiO$_2$ NTs annealed isochronally in N$_2$ for 90 minutes at different temperatures (dotted line is to guide the eye).

(B) NTs Annealed Isothermally for Various Time Durations:

In this part of the study, long nanotubes were annealed at 250 °C for time durations of 5, 30, 90, 120 and 180 minutes. According to the XRD data of nanotubes annealed
isothermally at 250 °C, Figure 60, the anatase structure is obtained even at short times, on the order of 30 minutes. After 30 minutes of annealing at 250 °C, the anatase phase begins to develop and steadily increases even after three hours of isothermal annealing (data not shown here).

![Figure 60: XRD patterns for pure NTs annealed isothermally in N₂ at 250 °C for various duration times at a heating/cooling rate of 10 °C/min. Lines at the bottom of the XRD patterns represent reference anatase powder diffraction pattern.](image)

Correspondingly, study of the dependence of the anatase lattice parameters on the annealing duration at 250 °C (Figure 61 (a)) indicates that the \( a \)-parameter did not change with time, while the \( c \)-parameter gradually decreased over the time (∼ 0.3% decrease from 90 to 180 minutes) reaching the value of \( c \)-parameter of commercially available anatase powder (anatase reference). This trend produces an overall decrease of unit cell
volume (Figure 61 (b)) concurrent with an increase in crystallite size (Figure 61 (c)) as a function of the annealing duration.

Figure 61: (a) Lattice parameters, (b) calculated unit cell volume, and (c) crystallite size of TiO$_2$ NTs annealed isothermally in N$_2$ at 250 °C for various durations (dotted line is to guide the eye).

4.3.2 NTs Annealed in Various Gas Atmospheres at High Temperatures

This section has two parts, A and B. Part (A) is dedicated to the crystal structure and crystallinity results of short and long TiO$_2$ nanotubes, which are annealed in various gas atmospheres for one hour at 350 °C. Part (B) presents the crystal structure and crystallinity results of pure and Fe-doped TiO$_2$ nanotubes annealed for two hours at 450 °C, in various gas atmospheres.
(A) Short and Long NTs, Annealed at 350 °C:

The short and long TiO₂ nanotubes are amorphous in their as-anodized states (figure not shown), consistent with previous reports. [55, 167, 169, 171] The anatase structure develops upon annealing at 350 °C as evidenced by the XRD patterns in Figure 62. The Bragg peaks associated with metallic titanium in these XRD patterns are attributed to the Ti substrate. The highest intensity (101) Bragg peak of anatase is present for all the annealed nanotube samples regardless of the nanotube morphology (short or long) or the annealing atmosphere.

![Figure 62: XRD patterns of the short and long TiO₂ NTs annealed in O₂, Ar and H₂, in comparison with standard anatase and titanium XRD patterns.](image)

(B) NTs Annealed at 450 °C:

*Pure NTs:* The anatase crystal structure develops in all nanotube samples after annealing regardless of the annealing gas, Figure 63. In addition, comparison of the highest intensity anatase Bragg peak of the un-normalized XRD data of the nanotubes annealed
in different gas atmospheres reveals that the H₂-annealed nanotubes are more crystalline than O₂- and Ar-annealed nanotubes, as confirmed by the higher intensity of the Bragg peaks, Figure 63 (b).

![XRD patterns of pulverized TiO₂ NT flakes annealed for 2 h in different gas atmospheres at 450 °C; (b) the un-normalized (raw) XRD data for the highest intensity peak from (101) plane in the annealed crystalline TiO₂ NTs.](image)

The XRD data reveal subtle but significant differences in the anatase \( a \)-axis parameter upon annealing, producing variations in the anatase unit cell volume that are correlated with the type of annealing gas. Specifically, the anatase \( a \)-axis parameter is expanded in H₂-annealed nanotubes relative to those produced in Ar or oxygen-rich annealing environments, Figure 64 (a).
Figure 64: The crystallographic data are displayed for TiO$_2$ NTs subjected to different annealing atmospheres: (a) measured lattice parameters, (b) the anatase unit cell volume and (c) crystallite size (dotted curves are guides for the eye).

Nanotubes annealed in an oxygen-rich environment possess lattice parameters that are very close to those of the commercially available anatase powder (denoted as the anatase reference, shown on the same graph in Figure 64). The anatase c-axis parameter remains constant in all samples, within experimental error. These conditions produce a systematic trend in the anatase unit cell volume of the nanotubes, Figure 64 (b), where annealing the nanotubes in the oxygen-deficient (Ar) or reducing (H$_2$) environments results in a larger unit cell volume as compared to the nanotubes annealed in an oxygen-rich atmosphere. All annealed samples exhibit larger unit cell volumes compared to that
of bulk standard anatase data (PDF#71-1166). Further, application of the Scherrer formula, equation (1) in Section 3.3.3.1, to the anatase (101) Bragg reflection of the annealed nanotubes reveals the presence of larger crystallite sizes in samples annealed in the reducing environment, Figure 64 (c), with a trend that is similar to that of the unit cell volumes, Figure 64 (b).

**Fe-Doped NTs:** The amorphous as-anodized nanotubes crystallize to anatase structure after annealing, Figure 65(a). The few Bragg peaks designated as Cu belong to the copper sample holder on which the nanotubes are mounted for measurements.

![Figure 65: XRD patterns of the nanotubes annealed in oxygen-rich environment in the as-anodized and annealed states. The copper sample holder peaks are designated on the figure. (b) Lattice parameters and (c) unit cell volume of the same nanotube samples, showing a slight expansion of the crystal structure in presence of iron.](image-url)
No crystallographic texture is observed in any of the nanotube samples. The $a$- and $c$-lattice parameters of the Fe-doped nanotubes, plotted in Figure 65(c), are slightly larger than those of the pure nanotubes, resulting in a subtle expansion ($0.1\% \pm 0.05\%$) of the anatase unit cell, Figure 65(c). In addition, the anatase crystallite size in the (101) plane direction is larger in the Fe-doped nanotubes as compared with that of the pure nanotubes (40 nm versus 30 nm, ±1).

4.4 Crystallization Behavior and Activation Energy of Crystallization

This section is dedicated to the results of the crystallization behavior of TiO$_2$ nanotubes that is characterized as function of annealing conditions — specifically, the type of annealing gas and the heating rate — which allowed determination of activation energies for crystallization. As-anodized long nanotubes are thermally processed in reducing (Ar + 2% H$_2$) and inert (Ar) environments, using differential scanning calorimetry (DSC). Details of the processing method are described in Section 3.3.4.

The DSC data of nanotubes annealed at 5 °C/min obtained in reducing and in inert environments are shown in Figure 66 (a). Note that a broad shallow endothermic peak appears at $T \sim 100$ °C and an intense exothermic peak appears at $T > 280$ °C, which can be decomposed and fit to four constituents (starting at $T \sim 220$, 255, 270 and 295 °C, respectively). These four constituents are: a broad peak of low intensity (starting at $T < 270$ °C) followed by three narrow peaks (Figure 66 (a) inset), with parameters summarized in Table 6.
Figure 66: (a) Differential scanning calorimetry (DSC) and (b) thermogravimetry (TG) curves for TiO$_2$ NTs annealed in inert (Ar, solid lines) and reducing (Ar + 2% H$_2$, dotted lines) environments at the heating rate of 5 °C/min. The inset in (a) shows the fitting of the DSC curve of NTs annealed in Ar at heating rate of 5 °C/min.

Table 6: The peak temperatures of crystallization, $T_p$, for the pre-crystallization stage and the three-stage crystallization process of the anodized TiO$_2$ NTs annealed in inert (Ar) and reducing (Ar + 2% H$_2$) environments.

<table>
<thead>
<tr>
<th>Rate ($^\circ$C/min)</th>
<th>Ar</th>
<th>Ar + 2% H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pre-crystallization</td>
<td>Stage #1</td>
</tr>
<tr>
<td>5</td>
<td>262.9</td>
<td>277</td>
</tr>
<tr>
<td>10</td>
<td>285.6</td>
<td>289.3</td>
</tr>
<tr>
<td>15</td>
<td>269.2</td>
<td>313.1</td>
</tr>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>157.5</td>
<td>191.4</td>
</tr>
</tbody>
</table>
These peaks are associated with nanotube crystallization, indicating that the transformation from the as-synthesized amorphous state to the anatase structure proceeds via a pre-crystallization stage (first broad low intensity peak at T ~ 220 °C) followed by a three-stage crystallization process. The first crystallization event is small compared to the second and third events and will not be used here in calculating the activation energy, as described in Section 3.3.4, equation (2). The calculated activation energies are 191 kJ/mol (2nd crystallization event) and 158 kJ/mol (3rd crystallization event) in the reducing environment (Ar + 2% H2) and 162 kJ/mol (2nd crystallization event) and 136 kJ/mol (3rd crystallization event) in the inert gas (Ar), as determined by the Kissinger plots in Figure 67. Other reported activation energy values for crystallization of amorphous titania are based on a single-stage devitrification process and are 208.9 kJ/mol for electrochemically-synthesized titania nanotubes annealed in pure Ar [172] and 147 kJ/mol for amorphous TiO2 nanoparticles annealed in air. [109] These values follow the same trend as those reported here for the multistage crystallization process: larger values of activation energy are obtained in a reducing environment as compared to those achieved in inert gas or oxygen-containing (air) environments. The overall enthalpy change ΔH of the amorphous to anatase crystallization in both inert and reducing gases is ΔH = 18 ± 1 kJ/mol, close to the reported value of 17.3 kJ/mol for the same transformation process occurring in titania powder, [173] which implies that the enthalpy of anatase formation is largely independent of annealing conditions.
Figure 67: Kissinger plots showing the activation energy of the phase transformation (the second and third crystallization stages) from the amorphous as-anodized state to the anatase structure for TiO₂ NTs annealed up to 450 °C in inert (Ar) and reducing (Ar + 2% H₂) environments. β is the heating rate.

Correlation of calorimetric and gravimetric data collected from the nanotubes provides a better understanding of the crystallization behavior in different processing conditions. The thermogravimetric (TG) curves of the nanotubes annealed in reducing and inert environments, Figure 66 (b), shows three zones of mass loss (zones I, II and III) accompanying the annealing process. Zone I (T < 260 °C) and zone III (T > 330 °C) feature a gradual mass loss. Zone II is in the range 230 °C < T < 330 °C, the same temperature range as the crystallization process, and features an abrupt mass loss. At the lowest heating rate (5 °C/min), the total mass loss from room temperature up to T = 345 °C is between 7 and 8 wt% for both reducing and inert annealing atmospheres.
4.5 Structural Defects, Electronic Structure and Local Order

This section consists of two subsections. Section 4.3.1 reports the results obtained from studying the structural defects in long TiO$_2$ nanotubes which are annealed in various gas atmospheres. Section 4.3.2 is dedicated to the results concerning the electronic structure and local order in pure and Fe-doped TiO$_2$ nanotubes.

4.5.1 Bulk Structural Defects

Annealing the nanotubes in a reducing or inert environment alters their crystal structure, as described in Section 4.3, which is anticipated to impact the electronic structure of TiO$_2$. Such annealing-induced changes of the electronic structure may be examined using ESR spectroscopy. The ESR data for TiO$_2$ nanotubes in the as-anodized and annealed states are compared with data obtained from the anatase reference powder, Figure 68.

![Figure 68: Room-temperature ESR intensity for pure TiO$_2$ NTs annealed in a reducing gas and in an inert environment, as compared to that of the as-anodized NTs and commercial anatase powder.](image-url)
It is noted that the anatase powder and the as-anodized nanotubes have a negligible ESR signal. A symmetric ESR signal corresponding to \( g = 1.998 \) is observed for both annealed nanotube samples indicating that similar paramagnetic centers, i.e. unpaired electrons from the same species, are created upon annealing in both gas environments. This \( g \)-value is close to the value \( g = 1.996 \) reported elsewhere that is ascribed to the existence of titanium in the Ti\(^{3+}\) trivalent state. [42, 174, 175] Further, the line shapes from nanotubes annealed in reducing versus oxygen-deficient environments are predominantly Lorentzian, but exhibit a small difference in the derivative peak-to-peak linewidths, \( \Delta B_{pp} \); in the (Ar+2% H\(_2\)) annealing gas \( \Delta B_{pp} = 5.6 \pm 0.1 \) gauss, whereas in the Ar annealing environment \( \Delta B_{pp} = 4.3 \pm 0.1 \) gauss. Also, a higher ESR intensity for the (Ar+2% H\(_2\))-annealed nanotubes compared to that of the Ar-annealed nanotubes indicates a higher concentration of Ti\(^{3+}\) ions when annealing was performed in the reducing environment.

### 4.5.2 Near-Surface, Local Electronic Environment

In this section, the synchrotron-based x-ray absorption spectroscopy results are presented, concerning the element-specific electronic structure and the local order in short and long pure nanotube samples, as well as Fe-doped nanotubes. These studies are carried out on the oxygen K-edge, titanium L-edge and iron L-edge in pure and Fe-doped TiO\(_2\) nanotubes that were processed in various gas atmospheres. The results are provided in two parts, A and B. Part A is dedicated to the short and long pure nanotubes in the as-anodized state and in the annealed state (processed in H\(_2\), Ar and O\(_2\) at 350 °C). Part B focuses on the as-anodized and O\(_2\)-annealed Fe-doped nanotubes.
(A) Short and Long NTs Annealed at 350 °C:

In this part, results obtained from synchrotron-based x-ray absorption spectroscopy on the short and long nanotubes, in the as-anodized and annealed states, are presented. These nanotubes are annealed for one hour at 350 °C in H2, Ar and O2 gas environments. This part of studies was carried out at the U4B beamline at the National Synchrotron Light Source of Brookhaven National Laboratory. Details of the data collection and plotting are provided in Section 3.3.5.

**Ti L3,2-Edge:** A comparison of the Ti L3,2-edge XAS spectra of the TiO2 nanotubes with those of the reference oxides (anatase, rutile and Ti2O3) is presented in Figure 69. These spectra possess two weak pre-edge features followed by series of peaks at higher energies. The Ti L3,2-edge spectra indicate transitions from the Ti 2p3/2 (L3-edge) and 2p1/2 (L2-edge) energy states to the unoccupied Ti 3d states that are modified by spin-orbit interactions and correlation effects. [176-180] Further, the unoccupied Ti 3d band is split into t2g and eg subbands by the crystal field interaction. [176-180] Quantitative information is extracted from the Ti L3,2-edge of the annealed TiO2 nanotubes based on the peak positions and intensities summarized in Table 7.

In the as-anodized state, the Ti L3,2-edge absorption spectra of the short and long TiO2 nanotubes, Figure 69, are quite similar to those of the amorphous TiO2 [181] featuring (1) broad peaks at both L3 and L2 edges, (2) reduced L3-t2g/L3-eg intensity ratios as compared to those of the reference anatase and rutile structures and (3) absence of the L3-eg doublet structure. The shapes and positions of the pre-edge (456 – 457.8 eV) features for all as-anodized nanotube samples are more similar to those of anatase than to those of Ti2O3, which strongly suggests that the dominant oxidation state of near-surface
Ti in the as-anodized nanotubes is Ti$^{4+}$. [182]

Figure 69: Ti $L_{3,2}$-edge XAS of short (red) and long (black) TiO$_2$ nanotubes: (a) as anodized and annealed at 350 °C in (b) O$_2$, (c) Ar, (d) H$_2$ and at 300 °C in (e) Ar, in comparison with (f) anatase, (g) rutile and (h) Ti$_2$O$_3$ reference oxides.
Table 7: The peak fitting parameters of Ti $L_3$-edge XAS spectra of the as-anodized and annealed TiO$_2$ nanotubes and anatase, rutile and Ti$_2$O$_3$ reference oxides.

<table>
<thead>
<tr>
<th></th>
<th>Ti $L_3$-edge</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Peak position/separation (eV)</td>
</tr>
<tr>
<td></td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td>Long TiO$_2$ NTs</td>
<td>As-made</td>
</tr>
<tr>
<td></td>
<td>O$_2$-annealed</td>
</tr>
<tr>
<td></td>
<td>Ar-annealed</td>
</tr>
<tr>
<td></td>
<td>H$_2$-annealed</td>
</tr>
<tr>
<td>Short TiO$_2$ NTs</td>
<td>As-made</td>
</tr>
<tr>
<td></td>
<td>O$_2$-annealed</td>
</tr>
<tr>
<td></td>
<td>Ar-annealed</td>
</tr>
<tr>
<td></td>
<td>H$_2$-annealed</td>
</tr>
<tr>
<td>TiO$_2$ anatase</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$ rutile</td>
<td></td>
</tr>
<tr>
<td>Ti$_2$O$_3$</td>
<td></td>
</tr>
</tbody>
</table>

Annealing the nanotubes did not affect the position of their Ti $L_3$-$t_{2g}$ absorption peak within the resolution of the beamline, Table 7. The Ti $L_3$-$t_{2g}$ and $e_g$ absorption peaks and peaks within the 465 – 480 eV energy range of both short and long nanotubes sharpen upon annealing and resemble those of the anatase structure. The Ti $L_3$-$t_{2g}$ and $e_g$ absorption peaks and peaks within the 465 – 480 eV energy range of both short and long nanotubes sharpen upon annealing and resemble those of the anatase structure, Figure 69. Further, comparison of the XAS spectra of the long nanotubes annealed in Ar but at two different temperatures, *i.e.* at 300 °C and 350 °C as indicated in Figure 69, implies that the annealing temperature is a critical factor in the amorphous-to-anatase transformation.
The Ti-$e_g$ peak exhibits a distinct doublet structure in the annealed short nanotubes (in all annealing atmospheres) and in O$_2$-annealed long nanotubes. The shape of the $e_g$ peak in the Ti $L_{3,2}$-edge spectrum may be considered as a determining “finger print” for various TiO$_2$ polymorphs: the anatase and rutile spectra feature a doublet structure while amorphous TiO$_2$ shows only a single broad asymmetric peak. [178, 179, 181] The separation $d$ between the Ti $L_3$-$e_g$ doublet feature in the as-anodized TiO$_2$ nanotube spectra ($d = 0.8$ eV for both short and long nanotubes) is smaller than those of the annealed nanotubes ($d = 0.9$ to 1.0 eV) and of other reference oxides ($d(\text{anatase}) = 0.9$ eV and $d(\text{Ti}_2\text{O}_3) = d(\text{rutile}) = 1.0$ eV). In addition, as reported elsewhere [181], the overall intensity of Ti-$e_g$ peak of the amorphous TiO$_2$ nanotubes is higher than that characterizing the Ti-$e_g$ peaks of reference anatase and rutile; upon annealing the nanotubes, the intensity ratio of Ti-$e_g$ doublet peaks ($I_{eg(a)}/I_{eg(b)}$) decreases and approaches the value of reference anatase.

The $e_g$ doublet peak intensity ratios in the Ti $L_3$-edge spectra of all annealed nanotubes approach that of the reference anatase, indicating that their local structure and long-range order is similar to that of the anatase structure.

**O K-Edge:** Complementary structural information concerning the TiO$_2$ nanotubes is obtained from the O K-edge x-ray absorption spectra comprising of two groups of peaks, Figure 70. The first group consists of two major peaks within 530 – 536 eV energy range, which are centered at approximately 531 and 534 eV. This group of peaks signals the transition of O-1$s$ core-level electrons to the hybridized O-2$p$ and Ti-3$d$ ($t_{2g}$ and $e_g$) molecular orbitals [178, 183] with a detailed structure that is sensitive to the local symmetry and ligand coordination [178, 180, 184]. The second group of peaks resides in
the higher energy region (537 – 550 eV) and is associated with the O-1s core-level transitions to the hybridized orbitals of O-2p and the Ti-4sp states; this group of transitions is quite sensitive to the long-range crystallographic order [178, 180, 184]. Upon annealing the nanotubes in O₂, H₂ or Ar gas, the O-t₂g and O-e₉g peaks become sharper and their separation increases from 2.1 eV to 2.4 – 2.5 eV (Figure 70) confirming the formation of the anatase structure in the annealed nanotubes. Spectra collected for the annealed short TiO₂ nanotubes are essentially identical and differ only slightly from those of the long nanotubes.
Figure 70: The O K-edge XAS of short (red) and long (black) TiO$_2$ NTs: (a) as-anodized and annealed at 350 °C in (b) O$_2$, (c) Ar, (d) H$_2$ and at 300 °C in (e) Ar in comparison with anatase and rutile as reference oxides.

(B) Fe-Doped NTs Annealed at 450 °C:
Changes in the electronic structure of titanium, iron and/or oxygen upon doping and annealing can be clarified by comparing the element-specific x-ray absorption spectra of the nanotube samples and reference compounds. In this part, results of the x-ray absorption studies on the O K-edge and Ti and Fe $L_{3,2}$-edges in pure and Fe-doped nanotubes and the reference compounds are presented. This part of measurements are
carried out at the U7A beamline at the National Synchrotron Light Source at Brookhaven National Laboratory and details of data collection and plotting methods can be found in Section 3.3.5.

**O K-edge:** The XAS spectra of the O K-edge in the pure and Fe-doped nanotubes consist of two prominent features in the energy range of 527 to 550 eV, Figure 71. The first set of peaks (527 to 535 eV) represent the transition from O 1s core state to the O 2p\(_x\) and 2p\(_\sigma\) states hybridized with Ti 3d bands. The higher energy set of peaks (535 to 550 eV) arises from the delocalization of the antibonding states of the O 2p and Ti 4sp. [185-188]

The peaks features of both pure and doped nanotubes are broad in the as-anodized state; after annealing, however, the first set of peaks become sharper and new features appear. Comparison of the O K-edge peak features of the annealed nanotubes with those of the reference titanium- and iron-based compounds, Figure 71, indicates that anatase structure forms in the nanotubes upon annealing, consistent with the bulk XRD measurements, Figure 65. No significant change in the electronic structure of oxygen in titania was observed in presence of iron, as attested to by the similar peak positions of the O K-edge in the pure and Fe-doped nanotubes.
Figure 71: The O K-edge XAS spectra of the pure and Fe-doped TiO2 NTs in the as-anodized and annealed states and the oxide reference compounds.

**Ti L$_{3,2}$-edge:** The $L_{3,2}$-edge XAS features of titanium can clarify the elemental local structure in titania [184]. Within the energy range of 455 to 470 eV, two main doublet peaks corresponding to the $L_3$ and $L_2$ edges are observed in the absorption spectra of the nanotubes and titania-based compounds, Figure 72. The Ti $L_{3,2}$-edge features arise from Ti $2p^6 \rightarrow 2p^5 3d^1$ transitions (i.e. from Ti 2p core level to the unoccupied 3d energy state), [178, 187, 189] and the strength of the crystal field causes the doublet features for each edge to split into the $t_{2g}$ and $e_g$ subbands. Additional energy splitting of the order of $\sim 1$ eV, more visible at the $e_g$ level (i.e. features D and E in Figure 72), is likely due to breaking degeneration between $d_{x^2-y^2}$ and $d_{z^2}$ sublevels and can be attributed to the off-center displacement of Ti ions, with different configurations and thus peak broadening for different crystal structures (rutile or anatase). It should be noted that no remarkable $e_g$
splitting is observed in the as-anodized (pure and Fe-doped) nanotube samples, highlighting the averaging effect of their amorphous state on the 3d sublevels. Upon annealing, the doublet feature of the $L_3$-$e_g$ peak appears in the nanotubes, Figure 72, and is accompanied with a sharpening of the low energy features (peaks A and B in the same Figure) that resembles those of the anatase spectrum.

![Image](image.png)

**Figure 72:** The normalized Ti $L_{3,2}$-edge XAS for the pure and Fe-doped TiO$_2$ NTs in the as-anodized and annealed states, along with the reference compounds.

Detailed analysis of the Ti $L_{3,2}$-edge peaks through examination of the peak intensities (Figure 73) reveals a variation in the $I(L_3-t_{2g})/I(L_3-e_g)$ intensity ratio, an indication of the change in the empty states. [171] Comparison of the intensities of peak C and (D+E) in Figure 72, quantitatively plotted in Figure 73(a), shows that the $I(L_3-t_{2g})/I(L_3-e_g)$ intensity ratio increases after annealing the pure and Fe-doped nanotubes, which means an increase in the Ti$^{4+}$ content. Furthermore, the intensity ratio of peaks D and E in Figure 72 (subband transitions at the Ti $L_3$-$e_g$ orbital) can signal the type of the
crystal structure, with anatase [rutile] having an $I(e_g)_D/I(e_g)_E$ intensity ratio of larger [smaller] than 1. Both pure and Fe-doped nanotube samples have an $I(e_g)_D/I(e_g)_E$ intensity ratio of > 1, confirming the anatase structure. This intensity ratio for the annealed Fe-doped nanotubes is slightly larger than that of the annealed pure nanotubes, confirming the slightly higher anatase content in the Fe-doped nanotubes.

![Image](image_url)

**Figure 73: Intensity ratios of the Ti $L_3$-edge features for the as-anodized and annealed Fe-doped TiO$_2$ NTs, compared to that of the anatase and rutile structures; (a) $I(L_3-t_{2g})/I(L_3-e_g)$ and (b) $I(e_g)_D/I(e_g)_E$ intensity ratios.**

**Fe $L_{3,2}$-edge:** The Fe $L_{3,2}$-edge is also sensitive to the iron oxidation state. The absorption spectra of the Fe $L_{3,2}$-edge for the Fe-doped nanotubes in the as-anodized and annealed states are shown in Figure 74(a), in comparison with the $L_{3,2}$-edge of reference iron compounds. The multiplets in the Fe $L_{3,2}$-edge spectra, *i.e.* $L_3$ and $L_2$ originate from the spin-orbit coupling of the Fe $2p$ core hole, and are corresponding to the transitions from $2P_{3/2}$ and $2P_{1/2}$, respectively [191], and similar to the Ti $L$-edge, each multiplet can split into $t_{2g}$ and $e_g$ orbitals by the crystal field effect. The fluorine $K$-edge (680 – 705
eV) is also observed in the absorption spectra of the as-anodized nanotubes positioned prior to the Fe $L_{3,2}$-edge, as the result of residual fluorine from the electrochemical anodization synthesis process. The fluorine is substantially removed during the course of annealing [192], as attested to by the disappearance of the F $K$-edge in the Fe $L_{3,2}$-edge spectra of the annealed nanotubes, Figure 74(a).

Figure 74: (a) The XAS spectra of the Fe $L_{3,2}$-edge in the as-anodized and annealed Fe-doped titania nanotubes, as compared to that of metallic Fe confirming that the oxidation state of iron increases upon formation of the nanotubes. (b) Linear combination fit of the Fe $L_{3,2}$-edge spectra of the annealed Fe-doped titania nanotubes (NTs) based on the iron oxide compounds and metallic iron.

The peak features of the Fe $L_{3,2}$-edge in the nanotubes resemble those of the Fe$_2$O$_3$ and Fe$_2$TiO$_5$ with a shoulder positioned prior to the main $L_3$-edge peak. A linear combination fit of the Fe $L_{3,2}$-edge of the annealed Fe-doped TiO$_2$ nanotubes based on the absorption spectra of the $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$ and Fe$_2$TiO$_5$ reference compounds, Figure 74(b), reveals that the local electronic structure of 91.5% of the Fe in the annealed
nanotubes resembles that of α-Fe₂O₃ and 8.5% of it resembles that of the Fe₂TiO₅ structure (fitting error was 5%).

Figure 75: The XAS spectra of the Fe L₃,₂-edge for sequential x-ray absorption scans on the as-anodized and annealed Fe-doped TiO₂ NTs showing the instability of iron oxidation state in the as-anodized NTs.

Extraction of the information from the Fe L₃,₂-edge absorption spectrum of the as-anodized Fe-doped nanotubes is challenging due to two reasons: (1) the significant presence of fluorine in the as-anodized nanotubes and the overlap of the F K-edge with the Fe L₃,₂-edge and (2) the instability of the electronic structure of Fe in the as-anodized nanotubes during the NEXAFS measurements when they were exposed to the x-ray scans in vacuum, Figure 75. The Fe L₂,₃-edge peak of the as-anodized nanotubes clearly shows a split feature designated as peaks α and β in Figure 75, attributed to t²g and e₈ levels. In the species containing Fe²⁺ the intensity of peak α is larger and peak β appears as a weak shoulder, while in the species containing Fe³⁺ this intensity ratio is reversed [193].
first x-ray scan, the peak intensity ratio of $\alpha/\beta < 1$ and when the nanotubes undergo further x-ray scans, peak $\alpha$ increases while peak $\beta$ diminishes. This change in the intensity of the $L_3$-edge peak split features is an indication of the change in the iron electronic structure toward lower oxidation state upon irradiation with x-rays in vacuum, where the iron is reduced. In the annealed nanotubes, however, the electronic state of iron seems to be more stable and no change in the shape of $L_3$ peak is observed by increasing the number of x-ray scans.

4.6 Magnetic Characteristics

This section provides the results on the magnetic characterization of free-standing TiO$_2$ nanotubes as a function of the annealing conditions and composition (pure or Fe-doped), both of which are shown to influence the morphology, crystal structure, crystallinity and electronic structure of the nanotubes (Sections 4.1 to 4.5). All the magnetic measurements are carried out according to the method described in Section 3.3.6 and the results are provided here within two subsections. Section 4.5.1 is dedicated to the magnetic properties of pure long TiO$_2$ nanotubes which are annealed at 450 °C in a variety of gas environments (Oxygen-rich, Oxygen-deficient and reducing). Section 4.5.2 reports the magnetic properties of the as-anodized and annealed Fe-doped nanotubes (annealed in O$_2$ at 450 °C).

4.6.1 NTs Processed in Various Conditions

This section provides the magnetic characterization results of pure TiO$_2$ nanotubes in the as-anodized state and in the annealed state (at 450 °C in O$_2$, Ar and H$_2$).
The total magnetic susceptibility of pure nanotubes $\chi_{tot}(T)$ is shown in Figure 76, as a function of temperature. It can be observed that the total magnetic susceptibility for annealed and as-anodized TiO$_2$ nanotubes is comprised of two major components: a temperature-dependent Curie-Weiss paramagnetism $\chi_{cw}$ that increases with decreasing temperature for $T < 100$ K and a temperature-independent Pauli paramagnetism $\chi_{PP}$ as defined by equation (10) in Section 3.3.6.2. [34]

Figure 76: (a) Temperature dependence of the total magnetic susceptibility, $\chi_{tot}$, for TiO$_2$ NTs in the as-anodized state and annealed (ann.) in different gas environments for 2 h at 450 °C. Data from the anatase reference powder and single crystal rutile is included for comparison. The dotted curves are fit to the total measured susceptibility data using equation (10) in Section 3.3.6.2, encompassing Curie-Weiss and Pauli paramagnetic contributions. The inset shows the low temperature region ($T < 50$ K). (b) Temperature trend of the inverse Curie-Weiss susceptibility for the annealed and as-anodized NTs (same symbols as part (a)), with a linear fit to the data (dashed lines) that highlight a negative Curie-Weiss temperature for the as-anodized and O$_2$-annealed NTs.

Figure 76 (a) and the inset demonstrates that the low-temperature tail of the total susceptibility, dominated by the Curie-Weiss component, is affected by the type of
annealing atmosphere. Evolution of the Curie-Weiss component of $\chi_{\text{tot}}(T)$ is examined through the Curie-Weiss constants obtained from a fit of the magnetic data to equation (3) in Section 3.3.6.2, and summarized in Table 8. Note that the O$_2$-annealed nanotubes exhibit lower values of the Curie-Weiss constant while the H$_2$-annealed nanotubes possess higher values ($C_{CW} = 1.99 \times 10^{-3}$ vs $3.67 \times 10^{-3}$ cm$^3$K.mole$^{-1}$). The commercial anatase powder (anatase reference) shows a significantly lower value for the Curie-Weiss constant, $C_{CW} = 0.60 \times 10^{-3}$ cm$^3$K.mole$^{-1}$, close to that of the Ar-annealed nanotubes, while single crystal rutile has only a temperature-independent magnetic susceptibility within the temperature range of study.

Table 8: Fitting parameters for the measured total magnetic susceptibility, $\chi_{\text{tot}}(T) = \chi_{CW} + \chi_{PP} + C_{CW}(T-T_0)$, equation (12) in Section 3.3.6.2) from data in Figure 76 for TiO$_2$ NTs annealed in different gas environments, as well as for commercially available anatase powder (anatase reference). $C$ is the Curie-Weiss constant, $T_0$ is the Curie-Weiss temperature and $\chi_{PP}$ is the Pauli paramagnetic contribution to $\chi_{\text{tot}}$. The effective moment per Ti ($\langle \mu_{\text{eff}} \rangle_{\text{Ti}}$) and the relative density of states at the Fermi level ($N(E_f)$) are calculated based on equations (9) and (11) in Section 3.3.6.2.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$C_{CW} \times 10^3$ (cm$^3$K.mole$^{-1}$)</th>
<th>$T_0$ (K)</th>
<th>$\chi_{PP} \times 10^5$ (emu.Oe$^{-1}$mole$^{-1}$)</th>
<th>$\langle \mu_{\text{eff}} \rangle_{\text{Ti}}$ ($\mu_B$/Ti)</th>
<th>$N(E_f) \times 10^{22}$ (cm$^3$eV$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$-annealed NTs</td>
<td>1.99 ± 0.10</td>
<td>-1.76 ± 0.1</td>
<td>4.3 ± 0.2</td>
<td>0.073 ± 0.002</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>as-anodized NTs</td>
<td>1.95 ± 0.05</td>
<td>-1.70 ± 0.1</td>
<td>6.2 ± 0.1</td>
<td>0.072 ± 0.001</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td>Ar-annealed NTs</td>
<td>0.44 ± 0.02</td>
<td>-0.66 ± 0.1</td>
<td>0.3 ± 0.01</td>
<td>0.034 ± 0.001</td>
<td>0.13 ± 0.05</td>
</tr>
<tr>
<td>H$_2$-annealed NTs</td>
<td>3.67 ± 0.10</td>
<td>-0.53 ± 0.1</td>
<td>4.5 ± 0.2</td>
<td>0.099 ± 0.001</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>Anatase NPs</td>
<td>0.60 ± 0.02</td>
<td>-1.30 ± 0.2</td>
<td>7.4 ± 0.1</td>
<td>0.040 ± 0.001</td>
<td>3.3 ± 0.2</td>
</tr>
</tbody>
</table>

The inset of Figure 76 displays the temperature-dependent behavior of the inverse Curie-Weiss contribution obtained from the annealed and as-anodized TiO$_2$ nanotubes.
The Curie-Weiss temperatures of the as-anodized and O₂-annealed nanotubes are similar ($|T_0| \sim 2$ K), and negative as it is also in case of the anatase reference ($|T_0| \sim 1$ K), indicating the existence of antiferromagnetic interactions, while Ar-annealed and H₂-annealed nanotubes have $T_0 \sim 0$ K. [194] The magnitude of the Curie-Weiss constant for the as-anodized and O₂-annealed nanotubes is similar and is approximately one-half of that characterizing the H₂-annealed nanotubes. Considering the correlation of the Curie-Weiss constant with the effective magnetic moment based on the equation (9) in Section 3.3.6.2, the average effective magnetic moment per titanium atom, $\langle \mu_{\text{eff}} \rangle_{\text{Ti}}$, for the H₂-annealed sample is higher as compared to those of the other nanotube samples (presented in Table 8 and Figure 77).

![Figure 77: Calculated effective atomic moment per titanium atom, $\langle \mu_{\text{eff}} \rangle_{\text{Ti}}$, (equation (9)) for the as-anodized and annealed NTs (the dotted curve is a guide for the eye).](image)

The measured values of $\langle \mu_{\text{eff}} \rangle_{\text{Ti}}$ for the O₂- and H₂-annealed nanotubes is approximately one order of magnitude smaller than the estimated value reported
elsewhere for undoped defect-rich TiO₂ thin films at \( T = 0 \) K [35]. The value of \( \langle \mu_{\text{eff}} \rangle_{\text{Ti}} \) for the anatase reference powder is less than half of that for the H₂-annealed nanotubes and is close to the value calculated for the Ar-annealed nanotubes, implying that annealing the nanotubes in Ar resulted in a low temperature behavior similar to the commercially available anatase powder.

The magnitude of the temperature-independent magnetic susceptibility \( \chi_{\text{pp}} \) for the H₂-annealed TiO₂ nanotubes (≈ 10⁻⁵ emu/mole.Oe) is one order of magnitude smaller than that of metallic Ti (1.5×10⁻⁴ emu/mole.Oe). [195] According to equation (11), a large \( \chi_{\text{pp}} \) is associated with a large density of states at the Fermi level, \( N(E_f) \), which consequently may result in higher photocurrent values and potentially lead to stronger catalytic activity [196-198]. As summarized in Table 8, the observed trend of \( \chi_{\text{pp}} \) for nanotubes and anatase reference is:

\[
\chi_{\text{pp}}(\text{anatase}) > \chi_{\text{pp}}(\text{amorphous}) > \chi_{\text{pp}}(H_2 - \text{annealed}) \approx \chi_{\text{pp}}(O_2 - \text{annealed})
\]

The calculated density of states at the Fermi level \( N(E_f) \) was also decreased after annealing the nanotubes, Table 8, regardless of the annealing atmosphere.

In addition, the value of the total angular momentum quantum number \( J \) can be calculated, noting that the magnetic moment of the nanotubes at low temperatures (3 to 10 K) follow with Brillouin function (equation (13)), i.e. the plots of \( M \) versus \( H/T \) for various temperatures overlap as shown in Figure 78 (a). Thus, \( J \) of the hydrogen-annealed nanotubes is obtained as \( J = 3/2 \), Figure 78 (b).
Figure 78: (a) Low temperature moment of H₂-annealed TiO₂ NTs at T = 3, 6 and 10 K versus H/T, showing a behavior typical of Brillouin function. The inset shows the corresponding low temperature field dependence of the magnetic moment for the same sample. (b) Brillouin fit on the moment measured at T = 3 K for the same sample, yielding $J = 1.5$ as the best fitting $J$.

4.6.2 Fe-Doped NTs

In this section, magnetic properties of Fe-doped TiO₂ nanotubes are examined in their as-anodized and annealed state (at 450 °C in O₂).

The magnetic susceptibility values of the Fe-doped and pure nanotubes in the as-anodized and annealed states are plotted in Figure 79, as function of temperature under an external magnetic field of $H = 500$ Oe (magnetic properties of pure nanotubes are from Figure 76).
Figure 79: Magnetic susceptibility of the pure and Fe-doped TiO$_2$ NTs at $H = 500$ Oe, in comparison with the commercial anatase nanopowder. The dashed lines are the fits to $$\chi_{\text{tot}}(T) = \chi_{\text{CW}} + \chi_{\text{PP}} = C_{\text{CW}}/(T-T_0) + \chi_{\text{PP}},$$ equation (12) in Section 3.3.6.2.

As compared to the pure nanotubes, the Fe-doped nanotube samples exhibit larger magnetic moments are more significant at low temperatures, \textit{i.e.} at $T < 100$ K. Regardless of the moment magnitude, the susceptibility of all the nanotube samples $\chi_{\text{tot}}(T)$ is comprised of a temperature-independent term, $\chi_{\text{PP}}$ and a Curie-Weiss paramagnetic contribution. Results from the fit using equation (12) in Section 3.3.6.2 are summarized in Table 9. The Fe-doped nanotube samples have one order of magnitude larger Curie-Weiss constant, $C$, as compared with those of the pure nanotube samples. Annealing causes a decrease in the value of Curie-Weiss constant of the Fe-doped nanotubes (from $C = 60$ emu K/Oe/mole to $C = 50$ emu K/Oe/mole). Assuming that all the incorporated iron (\textit{i.e.} 2.1 at\% Fe) is contributing to the magnetic moment, the corresponding effective magnetic moment, $\langle \mu_{\text{eff}} \rangle$ calculated from equation (9) in Section 3.3.6.2 is $\langle \mu_{\text{eff}} \rangle_{\text{Fe}} =$
4.8 ± 0.1 μB/Fe in the as-anodized and \( \langle \mu_{\text{eff}} \rangle_{\text{Fe}} = 4.4 ± 0.1 \) μB/Fe in the annealed Fe-doped nanotubes, in comparison with the reported value of \( \langle \mu_{\text{eff}} \rangle = 2.2 \) μB/Fe for pure bulk iron. [199]

**Table 9:** Curie-Weiss constant, \( C_{\text{CW}} \), and the temperature-independent paramagnetism contributions of the total magnetic susceptibility of the nanotubes under the applied field of \( H = 500 \) Oe, from Figure 79 and Figure 76, fitted to the equation (12) in Section 3.3.6.2.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( C_{\text{CW}} \times 10^3 ) [emu K/Oe mole]</th>
<th>( \chi_{\text{PP}} \times 10^6 ) [emu/Oe mole]</th>
<th>( T_0 ) [K]</th>
<th>( N(E_F) \times 10^{22} ) (cm(^3) eV(^{-1}))</th>
<th>( \langle \mu_{\text{eff}} \rangle_{\text{Fe}} ) ( \mu_B/\text{Fe} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO(_2)</td>
<td>As-made</td>
<td>1.95 ± 0.05</td>
<td>62 ± 1</td>
<td>-1.70 ± 0.1</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>O(_2)-annealed</td>
<td>1.99 ± 0.10</td>
<td>43 ± 2</td>
<td>-1.76 ± 0.1</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>Anatase NPs</td>
<td></td>
<td>0.6 ± 0.1</td>
<td>74 ± 1</td>
<td>-1.3 ± 0.2</td>
<td>3.3 ± 0.2</td>
</tr>
<tr>
<td>Fe-doped TiO(_2)</td>
<td>As-made</td>
<td>60 ± 1</td>
<td>440 ± 30</td>
<td>0.13 ± 0.05</td>
<td>20 ± 1</td>
</tr>
<tr>
<td></td>
<td>O(_2)-annealed</td>
<td>50 ± 0.4</td>
<td>530 ± 10</td>
<td>2.0 ± 0.1</td>
<td>24 ± 1</td>
</tr>
</tbody>
</table>

The Pauli paramagnetic contribution of the moment, \( \chi_{\text{PP}} \), is larger for the Fe-doped nanotubes as compared to the pure nanotubes, and annealing the as-anodized Fe-doped nanotubes in oxygen increases the value of \( \chi_{\text{PP}} \). In addition, the Pauli paramagnetic contribution of the moment is correlated to the density of states at the Fermi level based on the equation (11) in Section 3.3.6.2. The density of states at the Fermi level of annealed nanotubes and anatase nanoparticles are compared in Table 9, showing a higher density of states in the Fe-doped nanotubes as compared to the pure nanotubes and the commercially available anatase nanoparticles.

Assuming that the low temperature magnetic moment in the nanotubes arises from iron cations only, the ionic state of iron can be clarified by determining the angular
momentum quantum number $J$. This can be done through fitting the non-linear part of the low temperature $M(H)$ curve (i.e. the $M(H)$ data after subtraction of the temperature-independent contribution, $M_{PP} = \chi_{PP} \times H$), to the Brillouin function, equation (13) in Section 3.3.6.2, and find the best fitting value of $J$. For a material to be eligible for the Brillouin fit, it should follow Brillouin behavior, that is, its magnetic moment versus temperature-normalized field for all the measuring temperatures should superimpose. As shown in Figure 80(a), the annealed Fe-doped nanotubes follow the Brillouin behavior, Figure 80(b), yielding $J = 5/2$ which corresponds, assuming a sole contribution of the spin moment due to quenching of the orbital component, [200] to Fe$^{3+}$ cations. The same $J$ value was also obtained for the as-anodized Fe-doped nanotubes (data not shown here).

![Figure 80](image)

**Figure 80:** (a) The magnetic moment of the annealed Fe-doped NTs as a function of the temperature-normalized field, confirming that the magnetic moment follows the Brillouin behavior; (b) Non-linear contribution of the low temperature ($T = 3$ K) magnetic moment of the annealed Fe-doped NTs fitted to the Brillouin function, equation (11) in Section 3.3.6.2, which yields the value of $J = 5/2$.

The comparison of low temperature behavior of pure the Fe-doped nanotubes are provided in Figure 81, which shows the non-linear contribution of the magnetic moment
versus magnetic field measured at $T = 3$ K and the corresponding Brillouin fits that gives $J$ values of $3/2$ and $5/2$ for the pure and Fe-doped NTs, respectively.

![Figure 81: Comparison of the Brillouin fits of Fe-doped and pure TiO$_2$ NTs, and the corresponding $J$ values (from Figure 78 and Figure 80).]

4.7 Photocatalytic Activity of TiO$_2$ NTs

In this section, the results of assessment of the photocatalytic activity of the pure short and the long nanotubes are presented. These nanotubes are examined in the as-anodized state and after being annealed for one hour at 350 °C in various gas atmospheres (O$_2$, Ar, and H$_2$).

The photocatalytic activity of the as-anodized (amorphous) and annealed (crystalline) short and long TiO$_2$ nanotubes are examined by the photodegradation of methyl orange (MO) in an aqueous solution. The photodegradation of MO is quantified by the change in its absorption peak intensity as measured by UV-VIS spectroscopy (Section 3.4), Figure 82(a). The MO solution discolored after a few hours of UV-VIS irradiation, Figure 82(b).
Figure 82: (a) UV-VIS absorption of MO dye measured at each time interval, as illustrated by diminishing absorbance peak at 463.8 nm. (b) Discoloring of the Methyl orange solution in presence of Ti-supported TiO$_2$ NTs after 6 hours of exposure to the UV-VIS illumination.

Prior to initiation of the photocatalytic experiment (at time $t = 0$), the initial methyl orange concentration, $C_0$, was similar for all the nanotube samples. Over the course of the experiment the amorphous as-anodized nanotubes (short and long) did not detectably degrade the methyl orange; the annealed short nanotubes also did not detectably degrade the MO, despite their good crystallinity. However, the annealed long nanotubes successfully degraded the methyl orange dye, as depicted in Figure 83 that shows the fractional conversion of MO over the UV-VIS irradiation exposure time in presence of annealed nanotubes.

The initial (first 30 min) fractional conversion rates of methyl orange to the degradation products, $f_{MO,i}$, in presence of crystalline long nanotubes is $f_{MO,i} (\text{H}_2$-annealed) = $(7.23 \pm 0.36) \times 10^{-3}$ min$^{-1}$, $f_{MO,i} (\text{Ar}$-annealed) = $(6.07 \pm 0.30) \times 10^{-3}$ min$^{-1}$ and $f_{MO,i} (\text{O}_2$-annealed) = $(3.64 \pm 0.18) \times 10^{-3}$ min$^{-1}$. The conversion rates and the concentration of MO in the presence of the annealed nanotubes gradually decreased as a
function of UV-VIS exposure time, independent of the annealing gas type. After a 240-min exposure of the long crystalline nanotubes to UV-VIS light, the fractional conversion of methyl orange reached values of $f_{MO}(H_2\text{-annealed}) = 86.3\% \pm 4.3\%$, $f_{MO}(Ar\text{-annealed}) = 80.3\% \pm 4.0$ and $f_{MO}(O_2\text{-annealed}) = 62.2 \pm 3.1\%$.

Figure 83: The fractional conversion for the photodegradation of methyl orange, $f(MO)$, under UV-VIS illumination in presence of TiO$_2$ nanotubes annealed in O$_2$, Ar and H$_2$.

The catalytic degradation reaction of MO resembles a first order chemical reaction, as defined in section 3.4, equation (17) and shown in Figure 84 (b). The rate constant, $k$, of the reaction is calculated from Figure 84 and equation (19) in section 3.4, and plotted in Figure 84 (a), showing that the reaction rate in presence of H$_2$-annealed NTs is higher compared with the reaction rate constants in presence of Ar- or O$_2$-annealed NTs.
Figure 84: (a) Plot of the ln(1/(1-\(f_{MO}\))) of the photodegradation of methyl orange, under UV-VIS illumination in presence of TiO\(_2\) nanotubes annealed in O\(_2\), Ar and H\(_2\), showing a first order reaction. The solid lines are linear fits to the data points based on equation (19) in section 3.4, which allows the calculation of the reaction rate constant, \(k\), as plotted in (b).
5.0 DISCUSSION

This Dissertation research is focused on understanding of relationships between the microstructure, crystal structure, electronic structure and magnetism in TiO$_2$ nanotubes that may influence their functionality. These properties were examined as functions of (a) post-synthesis processing conditions (specifically, annealing temperature/duration and the nature of annealing environment) and (b) introducing an external dopant (Fe). Details of the characterization results are provided in Chapter 4.0. As a relevant functionality of TiO$_2$ materials, the photocatalytic activity of nanotubes was examined to understand and evaluate the effects of structural attributes and magnetic character on the nanotube functionality.

This Chapter provides discussion of the results presented in Chapter 4.0, within two sections. Section 5.1 is dedicated to the discussion of the structure-magnetic property correlations in TiO$_2$ nanotubes. Section 5.2 discusses the photocatalytic activity of nanotubes, evaluated as a function of the structural and magnetic attributes. In each section, a summary of results is presented with the associated discussion.

5.1 TiO$_2$ NTs Processed in Various Conditions (Processing- and Dopant-Induced Changes in Morphology, Structure and Magnetic Properties)

In this section, a summary of results from characterization of the pure nanotubes is presented along with the associated discussion. The as-anodized nanotubes are amorphous with no long range crystallographic order and are predominantly paramagnetic. Results from Chapter 4.0 demonstrate that the crystal structure, electronic structure, and magnetic behavior of the as-anodized nanotubes change (a) when they are
subjected to annealing processes, and (b) when iron is introduced into their structure. Based on these observations, two subsections are provided here that discuss the following matters: effects of processing conditions – specifically, a variety of annealing atmospheres, time durations and temperatures, and effects of iron-incorporation on the properties of nanotubes as well as the correlations of these properties.

(A) Discussion: Processing-Induced Changes in Morphological, Structural and Magnetic Properties of NTs

The as-anodized TiO$_2$ nanotube arrays are amorphous and transform to the anatase crystal structure when they are subjected to thermal treatments up to 450 °C in different gas atmospheres (oxygen-rich, oxygen-deficient and reducing gases). The amorphous-to-anatase phase transformation is concurrent with development of unique morphological features when nanotubes are annealed in oxygen-deficient or reducing gas atmospheres. Regardless of the type of annealing gas, however, a three-stage crystallization behavior is observed, with concomitant mass loss (see Figure 66). The lowest temperature threshold for long range order crystallization in an oxygen-deficient annealing environment was found as $T = 250$ °C (see Figure 53 and Figure 58). Meanwhile, the anatase structure that formed from processing the nanotubes in such environments has a reduced tetragonality and a larger unit cell volume as compared to that of the commercial nanosized anatase powder reference (see Figure 64). Furthermore, this crystallization process is accompanied by formation of Ti$^{3+}$ ions in oxygen-deficient or reducing gas, and the electronic states of titanium and oxygen in the structure of TiO$_2$ nanotubes are greatly influenced by the annealing conditions (see Figure 69). In addition, pure nanotubes annealed in reducing gas atmosphere possess a higher effective magnetic moment per
titanium atom as compared to nanotubes annealed in an oxygen-rich gas (see Figure 76 and Figure 77).

(i) Annealing-induced development of morphological features and the proposed crystallization sequence: Unique morphological features, such as nanobrick-decorated tubes, are developed during the annealing of nanotubes in reducing or oxygen-deficient gas atmospheres. Development of these morphological features is concurrent with the crystallization of nanotubes which occur during a three-stage crystallization process in reducing or oxygen-deficient gas atmospheres. Based on observations of the morphological features (Section 4.2.2), and results from simultaneous differential scanning calorimetry/thermogravimetric measurements (Section 4.4) and x-ray diffraction (Section 4.3.1) of the nanotubes, the following crystallization sequence is proposed. First, pre-crystallization structural relaxation leads to a slight rearrangement of the atoms. [201] After structural relaxation, small crystalline nanoparticles are formed. This is followed by the highly-exothermic crystallization of the nanotube walls [202], which then leads to impingement of the nanoparticles within the nanotube wall to form linked nanocrystallites. It was observed that annealing amorphous TiO$_2$ nanotubes in inert environment causes crystalline nanoparticles to form on the amorphous nanotube wall at temperatures as low as $T \sim 250 \, ^\circ$C (Figure 52 to Figure 55), which is consistent with the temperature range at which the DSC crystallization peak is noted ($T \sim 260$ to 280 °C).

The initial mass loss when heated to $T < 230 \, ^\circ$C is due to the elimination of residual fluorine ions [169, 192] and adsorbed water, consistent with the observation of the broad endothermic DSC peak at $T \sim 100 \, ^\circ$C. In the temperature range 230 °C $< T <$
330 °C, the mass loss is concurrent with the exothermal DSC crystallization peak that is attributed to the removal of anodization electrolyte remnants and associated rearrangement of the atoms. A porous morphology (Figure 56) may appear at this stage. The intense crystallization of the nanotubes is completed when the temperature reaches about 330 °C (Figure 66(a)); heating above this temperature ($T > 330 \, ^\circ C$) in the inert/reducing environments results in subsequent crystallite growth which may be accompanied by additional loss of oxygen (as will be discussed later) as revealed by the TG curves (Figure 66(b)).

(ii) Evidence of structural defects in annealed NTs, obtained from structural characterizations: Expansion of the unit cell volume in nominally-pure anatase nanotubes (see Figure 64(b)) is consistent with the creation of non-stoichiometric crystalline anatase-type TiO$_2$ containing structural defects such as oxygen vacancies ($\tilde{V}_o$) [203] which are arranged in a manner that elongates the $a$-axis and compresses the $c$-axis directions. While stoichiometric TiO$_2$ contains only Ti$^{4+}$ ions and is considered to have a temperature-independent magnetic susceptibility [39, 204], annealing in oxygen-deficient or reducing environments produces charged structural defects, such as oxygen vacancies. Two titanium ions are reduced from the Ti$^{4+}$ state to the Ti$^{3+}$ state for each oxygen vacancy created in order to achieve localized charge neutrality. [205-207] The electronic orbital structure surrounding the vacancy is deformed to foster donation of electrons from adjacent Ti$^{3+}$ ions and thus provide localized charge neutrality. [35, 194, 206, 208] Conversion of quadrivalent Ti$^{4+}$ cations to trivalent Ti$^{3+}$ cations is accompanied by an increase in the titanium ionic radius (0.61 Å vs 0.67 Å, or ~ 10% increase). [195] Moreover, there is electrostatic repulsion between the two mutually-exposed cations in
the absence of the bridging oxygen anions in the crystal structure. All of these effects can contribute to the observed unit cell volume expansion. [209-211] Such an expansion in the crystal unit cell upon the introduction of oxygen vacancies is also reported for other nanostructured transition-metal oxides such as cerium oxide nanoparticles. [210, 212] Meanwhile, the larger crystallite size in the bulk of nanotubes obtained during annealing in a reducing environment, Figure 64(c), is consistent with the enhanced growth conditions that are facilitated in such an environment, with larger, more defective unit cells donating higher atomic mobility pathways for crystallite growth. [109, 213]

(iii) Evidence of structural defects in annealed NTs, obtained from electron spin resonance spectroscopy: ESR spectroscopy results on the annealed nanotubes confirm the presence of Ti$^{3+}$ species, which are found to be of higher concentration in the nanotubes annealed in a reducing environment and are associated with a higher concentration of oxygen vacancies. Meanwhile, the predominantly Lorentzian line shape of the ESR signal from the annealed nanotube samples, Figure 68, indicates that the lineshape is primarily determined by spin relaxation arising from dynamic motion of the spins (electron delocalization). The slightly larger linewidth from nanotubes annealed in the reducing gas environment indicates slightly more rapid motion in this sample, consistent with the presence of higher concentration of oxygen vacancies associated with Ti$^{3+}$.

(iv) Evidence of structural defects and local order in annealed NTs, obtained from synchrotron-based absorption spectroscopy: Clarification of the relationships between the structural attributes and magnetic behavior of the nanotubes can be facilitated by understanding different aspects of their near-surface local order and electronic structure,
by referring to the analysis of their Ti L-edge and O K-edge x-ray absorption spectra (Section 4.5.2). According to the Ti-e\textsubscript{g} (in L\textsubscript{3}-edge) doublet peak features and the values of intensity ratio in the annealed long nanotubes (Figure 69), their local structure [176, 177] and long-range order [181, 214-216] resembles that of the anatase structure. The more significant appearance of anatase features at 537 – 550 eV energy region of the O K-edge spectrum of the O\textsubscript{2}-annealed nanotubes confirms an improved anatase formation at the surface of these nanotubes versus the Ar- and H\textsubscript{2}-annealed nanotube samples. In other words, annealing in oxygen promotes the anatase formation at the surface of the nanotubes, as compared to annealing in Ar or H\textsubscript{2}. A lower oxidation state (lower than 4\textsuperscript{+}) of near-surface Ti was observed in nanotubes annealed in reducing and inert gas atmospheres, but not in those annealed in the oxidizing environment. Reduction of Ti\textsuperscript{4\textsuperscript{+}} to lower oxidation state such as Ti\textsuperscript{3\textsuperscript{+}} due to loss of lattice oxygen by thermal treatment of TiO\textsubscript{2} in oxygen-deficient or reducing atmospheres is consistent with the results from the ESR measurements. Presence of these structural defects, i.e. Ti\textsuperscript{3\textsuperscript{+}} associated with \(\hat{\nu}_O\), in the H\textsubscript{2}- and Ar-annealed nanotubes is evident from observation of the smaller energy separation between their \(t_{2g}\) and \(e_g\) peaks of the O K-edge spectra when compared with the O\textsubscript{2}-annealed nanotubes (Table 7). [112, 178, 180, 181, 217-221]

\(v\) Evidence of vacancy-induced magnetic properties in NTs

The observed changes in the magnetic moment per titanium atom in the TiO\textsubscript{2} nanotubes upon annealing in a reducing environment (Table 8) are consistent with the creation of oxygen vacancies, accompanying the reduction of Ti\textsuperscript{4\textsuperscript{+}} to Ti\textsuperscript{3\textsuperscript{+}}. [203, 222, 223] These vacancies can produce a localized magnetic moment, due to magnetic interactions such as double exchange, [35, 208] or from Ti\textsuperscript{3\textsuperscript{+}} ions coupled ferromagnetically in donor bound
magnetic polarons. [122, 224] The obtained total angular momentum, $J = 1.5$ for the H$_2$-annealed nanotubes can be assigned to the Ti$^{3+}$, confirming the presence of these species that give rise to the magnetism. Observation of such magnetic behavior arising from oxygen vacancies is reported for other pure transition metal oxide nanostructures such as defective TiO$_2$ single crystals, thin films of TiO$_2$ and hafnium oxide. [35, 225, 226]

In summary, it was observed that post-synthesis processing of nanotubes can alter their crystal structure and induce creation of structural defects, which in turn can influence the electronic structure and magnetic character of the nanotubes.

(B) Discussion: Dopant-Induced Changes in Structural and Magnetic Properties of NTs

This section is dedicated to the discussion of the results from characterization of the TiO$_2$ nanotubes in presence of Fe. Results from Sections 4.2.3, 4.3.2, 4.5.2 and 4.6.2 demonstrated that the electrochemical anodization of the Ti(Fe) alloy creates Fe-doped TiO$_2$ nanotubes with a cationic Fe concentration of approximately 2.1 at%. The amorphous as-anodized pure/Fe-doped nanotubes transform into the anatase crystal structure (both in the bulk and at the near-surface region) by annealing in oxygen, which is accompanied with defragmentation of the nanotube wall to form a connected porous architecture. In addition, annealed Fe-doped nanotubes have a slightly larger unit cell and larger crystallite size than the pure nanotubes. Meanwhile, the local electronic environment of iron in TiO$_2$ nanotubes resembles those of the Fe$_2$O$_3$ and Fe$_2$TiO$_5$. The Fe-doped nanotubes exhibit larger magnetic moment than the pure nanotubes and based on low-temperature magnetic measurements, Fe contributes to the magnetic moment most likely in form of Fe$^{3+}$. 
(i) Evidence of iron-incorporation in NTs, obtained from structural characterization:
The slight expansion observed in the lattice structure of the crystalline Fe-doped nanotubes versus that of the pure nanotubes can be attributed to the Fe ions substituting for some of the Ti ions in the anatase crystal structure. Even though the Fe\(^{3+}\) cationic radius is smaller than that of Ti\(^{4+}\) (0.55 Å versus 0.61 Å for coordination number of 6) [195], this substitution may cause lattice expansion due to bonding alterations and possible formation and stabilization of structural defects such as oxygen vacancies, [70, 167] which form to maintain the charge neutrality. [227]

(ii) Clarification of the bonding state of Fe in NTs, based on the synchrotron-based absorption spectroscopy results: The Fe \(L_{3,2}\)-edge absorption spectroscopy results suggest that the local electronic structure of Fe most likely resembles those of the Fe\(_2\)O\(_3\) and Fe\(_2\)TiO\(_5\), both containing Fe\(^{3+}\) ions. Synthesis of a \(\alpha\)-Fe\(_2\)O\(_3\) nanoporous membrane is reported by direct anodization of iron foil in a comparable electrolyte composition as is used in this study [228], suggesting that Fe can oxidize to Fe\(^{3+}\) as in \(\alpha\)-Fe\(_2\)O\(_3\) during the anodization of Ti(Fe) foil. The absorption spectra of the Fe \(L_{3,2}\)-edge also confirmed that Fe is already in the oxidized state in the as-anodized nanotubes.

In addition, the change in the electronic structure of Fe in the as-anodized nanotubes from Fe\(^{3+}\)-dominant to a Fe\(^{2+}\)-dominant state during the x-ray irradiation may be explained by x-ray-induced inter-valence charge transfer between the Fe\(^{3+}\) and Fe\(^{2+}\) [229, 230]: the as-anodized nanotubes have a mixed valence state of Fe\(^{2+}\) and Fe\(^{3+}\) within the anatase structure and upon x-ray irradiation charge transformation from Fe\(^{2+}\) to Fe\(^{3+}\) may occur.
(iii) Evidence of dopant-induced magnetic properties in NTs: Results from the magnetic characterization of Fe-doped nanotubes are in agreement with the x-ray spectroscopy results. The obtained values of $\langle \mu_{\text{eff}} \rangle_{\text{Fe}}$ as 4.8 and 4.4 $\mu_B$/Fe in the as-anodized and annealed Fe-doped nanotubes can be assigned to the Fe$^{3+}$ ions. The deviation from the reported value of $\langle \mu_{\text{eff}} \rangle_{\text{Fe}} = 5.92$ $\mu_B$/Fe$^{3+}$ [231] can indicate short-ranged correlations between the Fe$^{3+}$ moments. The 8% decrease in the magnitude of the effective magnetic moment of Fe-doped nanotubes from 4.8 $\mu_B$/Fe in the as-anodized state to 4.4 $\mu_B$/Fe in the annealed state may be due to a partial formation of Fe$_2$TiO$_5$ during the process of annealing the nanotubes at 450 °C [232]. Fe$_2$TiO$_5$ is paramagnetic at room temperature [13] and can possibly add slight disorder to the magnetic moment orientation of the nanotubes and reduces the net magnetic moment. In addition, the obtained total angular momentum quantum number of $J = 5/2$ further confirms that the observed magnetic moment arises from Fe$^{3+}$ ions.

(iv) Evidence of increased metallic-like behavior in annealed Fe-doped NTs (versus pure state): Despite the decrease in the effective magnetic moment after annealing the Fe-doped nanotubes, the Pauli paramagnetic contribution of the total magnetic susceptibility and thus the density of states at the Fermi level increases. The x-ray absorption spectroscopy results indicate an increase in the oxidation state of Fe upon annealing from Fe$^{2+}$-dominant state to a Fe$^{3+}$-dominant state. As discussed earlier to explain the observed expansion of the anatase unit cell upon annealing, the presence of Fe$^{3+}$ may form/stabilize oxygen vacancies to maintain charge neutrality. The presence of oxygen vacancies can contribute to itinerant electrons [167] which are stated to contribute
to the increase in the metallic-like behavior (increase in the Pauli paramagnetic contribution of the total magnetic susceptibility).

5.2 Evaluation of the Property-Functionality Correlations in TiO$_2$ NTs

Correlations of the morphological, structural (crystal structure and electronic structure), defect state and magnetic character of pure nanotubes processed in various conditions can contribute to the understanding of the photocatalytic behavior of nanotubes processed in different annealing conditions. Results from Section 4.7 showed that the photoactivity of the as-anodized amorphous nanotube samples was negligible, regardless of the nanotube morphology. In addition, the photoactivity of the annealed nanotubes was dependent on the nanotube morphology (short versus long tubes) and the annealing conditions: the catalytic degradation of methyl orange was faster (larger reaction rate constant) in presence of H$_2$-annealed nanotubes than in presence of Ar- or O$_2$-annealed nanotubes.

Based on the literature reports, the negligible photoactivity of the as-anodized amorphous nanotubes is ascribed to a high density of defects in the amorphous state which can serve as recombination centers. [233-237] The lack of photoactivity of the crystalline short nanotubes is presumably due to the low nanotube content on the titanium substrate. Among the long crystalline nanotubes, however, the photoactivity is a function of the annealing atmosphere, with H$_2$-annealed nanotubes exhibiting the best performance followed by the Ar-annealed and O$_2$-annealed nanotubes. The difference in photocatalytic activity of the long nanotubes annealed in different gas atmospheres is hypothesized to be related to the differences in their (I) degree of local structure and long-range order (a length scale of 1 nm) [216] and (II) density of structural defects, both in bulk and at the near-surface region considering that surface is critical in catalytic
functionality. An oxygen-rich annealing environment more effectively induces the local crystalline structure and long-range order in the nanotubes with fewer structural defects [167, 205, 206, 221] as compared to that obtained in the reducing or inert annealing atmospheres. Interestingly, despite the higher near-surface crystallinity of O₂-annealed long nanotubes, they exhibit lower photocatalytic activity relative to that of the Ar- and H₂-annealed nanotubes. Such observation suggests that the local defects near the surface, along with the bulk crystalline structure, play a more critical role in determining the photocatalytic activity of TiO₂ nanotubes. [221] These changes in the defect state of the nanotubes are anticipated to affect the electronic band-gap which consequently influences the light absorption. [23] The higher amount of local defects near the tube surface generated by the reducing annealing gas (H₂) is anticipated to facilitate the charge separation and thereby may affect the production of hydroxyl radicals which can contribute to the catalysis by serving as reactive sites for degradation of organic compounds. [235, 238, 239]

Overall, the superior performance of the H₂-annealed long nanotubes in degrading methyl orange is attributed to the larger concentration of bulk and local surface defects (Ti³⁺ associated with oxygen vacancies) and the anticipated decrease in the electronic band-gap due to the presence of oxygen vacancies, along with the crystalline structure. [167, 205, 206, 221] In addition, magnetic characterizations confirmed the presence of slightly higher density of states at the Fermi level, which consequently may affect the photocurrent values and thus the catalytic activity. [196, 197] Considering the significant effect of iron on the structural and magnetic properties of TiO₂ NTs, it is anticipated that iron-incorporation would also influence the catalytic behavior of NTs.
6.0 CONCLUSIONS

Results obtained from this Dissertation research demonstrated correlations between the microstructure (morphology and crystallinity), crystal structure, electronic structure and magnetic properties of TiO$_2$ nanotubes, with potential relevance to their functionality. These properties were influenced by variations of the (a) post-synthesis processing conditions (e.g. annealing temperature and gas environment), and (b) composition (dopant-free or Fe-doped).

In this Dissertation, arrays of nominally-pure (short and long) and Fe-doped (Fe cationic concentration of 2.1 at%) TiO$_2$ nanotubes were synthesized by the electrochemical anodization of titanium foil and arc-melted Ti(Fe), respectively. The as-anodized amorphous nanotubes were then subjected to annealing treatments in variety of gas atmospheres and temperatures to transform into the anatase structure. Unique morphological features, such as porous walls and nanobrick-decorated tubes, are developed during the amorphous-to-anatase phase transformation in both inert and reducing atmospheres, which can hypothetically correlated to the three-stage nature of the crystallization process.

Furthermore, annealing of nanotubes in reducing and oxygen-deficient environments results in a slight expansion in the anatase unit cell, that can potentially translate into bonding alterations in TiO$_2$ crystal structure. In addition, annealing-induced structural defects – specifically, oxygen vacancies accompanying reduction of Ti$^{4+}$ to Ti$^{3+}$, are evident in crystalline nanotubes. These structural defects produce a localized magnetic moment, and affect the magnetic behavior of these nominally-pure nanotubes with a parallel change in the electronic density of states at the Fermi level. The structural
defects are known to influence the electronic structure (such as the band-gap) of TiO$_2$ nanomaterials and consequently affect their functionality. Evaluation of the photocatalytic activity of TiO$_2$ nanotubes processed in different environments demonstrated that there are positive correlations between the functionality of nanotubes and their bulk crystallinity, density of structural defects, and local electronic environment.

Apart from the approach of post-synthesis processing in altering the properties of TiO$_2$ nanotubes, proper incorporation of iron was also found as a successful approach in inducing changes in the structural and magnetic properties of nanotubes. Iron was resided in TiO$_2$ nanotubes in form of Fe$^{3+}$, most likely substituting the Ti$^{4+}$ ions in the anatase structure and contributed to formation/stabilization of oxygen vacancies. The effect of Fe-incorporation in the anatase structure was observed as an expanded anatase unit cell volume, larger crystallite size, increased localized magnetic moment and higher density of states at the Fermi level of TiO$_2$. These changes in the crystal structure, magnetic behavior and electronic structure of TiO$_2$ nanotubes may also be associated with alterations in the functionality of TiO$_2$ nanotubes for energy-related applications.

In summary, it was observed that post-synthesis processing of nanotubes and introducing Fe into their structure are two approaches that can alter the crystal structure of nanotubes and induce creation of structural defects, which in turn can influence the electronic structure and magnetic character of the nanotubes. Optimization of these approaches is thus expected to lead to enhanced photocatalytic activity of TiO$_2$ that originates from such tailored structural and magnetic characteristics.
7.0 RECOMMENDATIONS FOR FUTURE WORK

Results of this Dissertation provided fundamental knowledge on the correlations of structural-magnetic properties in TiO2 nanotubes with potential relevance to their functionality. However, there are still questions to be addressed, specifically:

1) What is the impact of process-induced morphological features on the functionality of nanotubes?
2) How is the functional response of the Fe-doped nanotube arrays compared with pure nanotubes?
3) How does the iron concentration affect the properties (and functionality) of nanotubes?
4) How does the method of iron incorporation affect the properties of nanotubes?

This section presents recommendations for future research in an effort to address the above questions. Accomplishment of these recommendations would provide an enhanced insight into the various aspects of property-functionality relationships in TiO2-based nanomaterials, which can be generalized to other transition-metal oxides and provide paths to engineer oxide-based materials for an enhanced functionality and potential multifunctionality in energy-related applications.

**Recommendation 1: Evaluate the impact of the process-induced morphological features on the functionality of TiO2 nanotubes.**

TiO2 nanostructures are promising materials for employment in photocatalytic devices. In catalysis, surface area and geometrical attributes are known to play an important role. As reported in Chapter 4, Section 4.3.2, unique morphological features, such as nanobrick-
decorated tubes and porous interconnected tubular morphology, are developed on TiO$_2$ nanotubes when they are annealed at low temperatures or in reducing/oxygen-deficient environments (for example, see Figure 54). These morphological features that are predominantly crystalline (see Figure 53 and Figure 55 in Section 4.3.2) may contribute to an increase of the active surface area of nanotubes and consequently affect their catalytic performance. In addition, they may alter the pathways for charge transport and affect the recombination process by introducing grain boundaries. To understand these potential effects, it is recommended to measure the active surface area of the processed nanotubes using the related techniques such as the BET (Braunauer-Emmett-Teller) method [240]. This evaluation, in conjunction with the characterizations and evaluations that are carried out in this Dissertation, would provide the opportunity to realize if variations of these morphological features can be a practical approach to be considered for enhancement of nanotube functionality. Some other typical morphologies which were observed in the annealed nanotubes in the course of this Dissertation research are shown in Figure 85.

Figure 85: (SEM) The annealed TiO$_2$ NTs: (b) bottom and (c) lateral bottom view showing formation of nanoparticles atop the nanotubes and a double-layer wall morphology.
Recommendation II: Evaluate the functional response of the Fe-doped nanotube arrays.

In this Dissertation, correlations of structural – magnetic properties with the functionality were verified by monitoring the degradation of an organic dye in presence of photoactivated differently-processed pure nanotubes. As it was discussed in Chapter 5, the effect of processing on the pure nanotube properties was to induce structural changes through for instance, expanding the anatase unit cell and introducing structural defects such as oxygen vacancies and Ti\(^{3+}\) which in turn resulted in change in the magnetic response of nanotubes. Doping these nanotubes with iron similarly affected these properties but in other orders of significance, for instance, larger localized magnetic moment was observed in the Fe-doped nanotubes than in the pure nanotubes. It is anticipated that the doping the nanotubes with iron would affect their functionality, and this can be verified by carrying out similar experiments as the pure nanotubes in measuring their photoactivity (see Section 3.4)

Recommendation III: Evaluate the effect of Fe content on the properties (and functionality) of TiO\(_2\) nanotubes.

In this Dissertation the concentration of Fe in TiO\(_2\) nanotubes was fixed (cationic concentration of \(~ 2.1\) at\%). It would be of interest to evaluate how the dopant concentration may affect the crystal structure, electronic structure and magnetic character of the nanotubes. To this end, it is recommended that Ti-\(\alpha\)Fe \((\chi = 2, 6, 10, 15\) at\%) alloys are fabricated using the arc-melting technique (see Part (B) in Appendix I) for subsequent anodization, processing and characterizations.
There is one challenge in this method which should be addressed. There is a limit in the weight limit of the arc-melted shot in the laboratory-scale arc-melting machine, and thus the size of the arc-melted shots would be limited. The amounts of nanotubes that can be obtained from anodization of these shots depend on the size of these precursors. Considering the small size of the shots, the amount of anodized nanotubes most likely would not be sufficient for the bulk magnetic measurements (e.g. SQUID magnetometry), especially when the iron content and thus the anticipated magnetic moment is low. To address this challenge, the surface-sensitive element-specific x-ray magnetic circular dichroism (XMCD) spectroscopy technique is recommended, as an alternative to the bulk SQUID magnetometry. Details of the principles of XMCD spectroscopy technique can be found in an article by Scheinfein et al. [146]

**Recommendation IV (Ongoing work): Evaluate the effect of fabrication method in creating the precursors of Fe-doped NTs.**

The method of iron-incorporation in TiO$_2$ nanotubes may influence the functional properties of these nanostructures, considering that the bonding state, stability of the electronic structure and distribution of Fe may be dependent on the incorporation technique. In this Dissertation, Fe-doped nanotubes were prepared from anodization of an arc-melted Ti(Fe) alloy. Another approach to fabricate Ti(Fe) alloy is melt-spinning which is a rapid solidification technique and can fabricate thin ribbons of Ti(Fe) for subsequent anodization and production of nanotube arrays. Rapid solidification allows metastable retention of Fe in the Ti metal, a result that is not possible to attain with equilibrium synthesis techniques. To best of the author’s knowledge, there is no report on the fabrication of TiO$_2$ nanotubes by anodization of melt-spun ribbons. This approach is
currently an ongoing work and preliminary experiments demonstrated successful fabrication of these precursors (Figure 86) with nominal atomic composition of $\text{Fe}_{4.4}\text{Ti}_{95.6}$.

![Figure 86](image)

**Figure 86:** Typical SEM images of both sides of the Ti(Fe) melt-spun ribbons, showing a smoother surface on the wheel-side of the ribbon. The cross-section view of a typical ribbon shows the ~ 30 micron thickness.

Due to the small size of the ribbons a practical anodization set up was developed by mounting a number of ribbons (typically 10 to 12 ribbons) side by side on the conductive carbon tape attached to a piece of aluminum foil, as shown in Figure 87.

![Figure 87](image)

**Figure 87:** (a) Anodization set up for the synthesis of NTs from Ti(Fe) melt-spun ribbons; (b) The Ti(Fe) ribbons immersed in the electrolyte under anodization.

Proper anodization of these ribbons resulted in fabrication of the nanotubes, as shown in Figure 88. More work regarding the characterization of these nanotubes is ongoing.
Figure 88: A typical anodized Ti(Fe) ribbon and the SEM image of as-anodized Fe-doped TiO$_2$ NT ordered arrays formed on the ribbon.
8.0 NOMENCLATURE

$2\theta$  
Angle of detector arm in XRD, degree

$a, b, c$  
Crystallographic axes

$a$  
Crystal lattice constant, Å

A  
Amperes

ann.  
Annealed

at%  
Atomic percent

$B$  
The external magnetic field, mT

$B (2\theta)$  
Average grain size in Scherer formula, Å

BCC  
Body-centered cubic (crystal structure)

BNL  
Brookhaven National Laboratory

c  
Crystal lattice constant, Å

$C$  
Curie constant, $\frac{\text{emu}}{\text{mole.Oe.K}}$

$C_0$  
Absorption at the starting point after reaching equilibrium in dark environment

$C_{CW}$  
Curie-Weiss constant, $\frac{\text{emu}}{\text{mole.Oe.K}}$

$C_t$  
Absorption at a certain reaction time

CNF  
Center for Nanomaterial and Nanotechnology

d  
Interatomic spacing (nm)

DC  
Direct current

DI  
De-ionized
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>DMS</td>
<td>Dilute magnetic semiconductor</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye-sensitized solar cells</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation Energy (of crystallization)</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band-gap energy, eV</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>emu</td>
<td>Electromagnetic unit</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron paramagnetic resonance</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron spin resonance</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>$f(\text{MO})$</td>
<td>Fractional conversion for photodegradation of methyl orange</td>
</tr>
<tr>
<td>$f_{\text{MO},i}$</td>
<td>The initial (first 30 min) fractional conversion rates of methyl orange</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>$g$</td>
<td>the $g$-factor or Landé $g$-factor</td>
</tr>
<tr>
<td>G</td>
<td>Gauss</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck’s constant</td>
</tr>
<tr>
<td>$H$</td>
<td>Magnetic field, Oe</td>
</tr>
<tr>
<td>HCP</td>
<td>Hexagonal closed pack (crystal structure)</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric acid</td>
</tr>
<tr>
<td>IMA</td>
<td>International Mineralogical Association</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>ID</td>
<td>Inner diameter, mm</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$j, J$</td>
<td>The total angular momentum number</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee of Powder Diffraction Society</td>
</tr>
<tr>
<td>$k$</td>
<td>Scherer constant</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant, $1.38 \times 10^{-16} \frac{m^2kg}{s^2K}$</td>
</tr>
<tr>
<td>$l, L$</td>
<td>The orbital angular momentum quantum number</td>
</tr>
<tr>
<td>$L$</td>
<td>Full width half max (FWHM) in Scherer formula, Radian</td>
</tr>
<tr>
<td>M</td>
<td>Molar</td>
</tr>
<tr>
<td>MO</td>
<td>Methyl Orange</td>
</tr>
<tr>
<td>$M_s$</td>
<td>Saturation moment, emu/g</td>
</tr>
<tr>
<td>MPMS</td>
<td>Magnetic Properties Measurement System</td>
</tr>
<tr>
<td>$N$</td>
<td># of the magnetic atoms per unit volume with the magnetic moment, $\mu$</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near edge x-ray absorption fine structure spectroscopy</td>
</tr>
<tr>
<td>NSLS</td>
<td>National Synchrotron Light Source</td>
</tr>
<tr>
<td>NTs</td>
<td>Nanotubes</td>
</tr>
<tr>
<td>OD</td>
<td>Outer diameter, mm</td>
</tr>
<tr>
<td>Oe</td>
<td>Oersted, the unit of magnetizing field</td>
</tr>
<tr>
<td>PC</td>
<td>Personal computer</td>
</tr>
<tr>
<td>PDF</td>
<td>Powder diffraction file</td>
</tr>
<tr>
<td>PEY</td>
<td>Partial electron yield</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>R</td>
<td>Ideal gas constant, 8.314 J/mol.K</td>
</tr>
<tr>
<td>$s, S$</td>
<td>The spin momentum quantum number</td>
</tr>
</tbody>
</table>
SAED  Selected-area electron diffraction
SEM  Scanning electron microscopy
SQUID  Superconducting quantum interference device

\( t \)  time

\( T \)  Tesla, unit of the applied magnetic field (1 T = 10^4 Oe)

\( T_0 \)  Curie-Weiss temperature, K

\( T_C \)  Curie temperature, K

\( T_p \)  Crystallization peak temperature, K

TEM  Transmission electron microscopy

TEY  Total electron yield

TG  Thermogravimetry

Torr  Non-SI unit of pressure with the ratio of 760 to 1 standard atmosphere

UV  Ultraviolet

UV-VIS  Ultraviolet-visible

\( V_{DC} \)  Direct current voltage

vol\%  Volume percent

wt\%  Weight percent

XMCD  X-ray magnetic circular dichroism

XPS  X-ray photoemission spectroscopy

XRD  X-ray diffraction

\( \dot{V}_O \)  Oxygen vacancy

\( \alpha, \beta, \gamma \)  Crystallographic angles

\( \beta \)  Heating rate, degrees/min
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi$</td>
<td>Magnetic susceptibility, emu/g.Oe</td>
</tr>
<tr>
<td>$\chi_{CW}$</td>
<td>Curie-Weiss paramagnetism, $\frac{emu}{mole.Oe}$</td>
</tr>
<tr>
<td>$\chi_{PP}$</td>
<td>Pauli Paramagnetic component</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength of x-ray radiation in Scherer formula, Å</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Magnetic moment, $\mu_B$</td>
</tr>
<tr>
<td>$\mu_B$</td>
<td>Bohr magneton, unit for an electron magnetic dipole moment, $9.27 \times 10^{-21}$ emu</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Angle of incident x-ray beam, degrees</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Frequency of electromagnetic radiation, GHz</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>The energy difference between two spin energy states, i.e. parallel or antiparallel to the external magnetic field</td>
</tr>
</tbody>
</table>
9.0 REFERENCES


[58] K. Shankar, J. I. Basham, N. K. Allam, O. K. Varghese, G. K. Mor, X. Feng, M. Paulose, J. A. Seabold, K.-S. Choi and C. A. Grimes, Recent Advances in the Use of


10.0 APPENDIX

(A) Fabrication and Characterization of the Ti(Fe) Arc-Melted Alloy Sheet, the Fe-Doped NTs’ Precursor

As described in Chapter 3, pieces of titanium foil are anodized in presence of corrosive ions for nanotube synthesis. Understanding the characteristics of the titanium foil as the nanotubes’ precursor, such as the surface smoothness, crystal structure and magnetic behavior can provide information on the potential differences when the nanotubes are synthesized from an iron-incorporated starting material.

**Morphology:** Scanning electron micrograph of the titanium foil, Figure 89, reveals some elongated features on the titanium surface that are typical topography resulted from hot or cold rolling of these foil during the fabrication process.

![Figure 89: (SEM) Surface of Ti foil.](image)

*Composition and Crystal Structure:* Within the detection limit of EDS spectroscopy, no impurity (including Fe) was detected in the titanium foil. Structural studies on the titanium foil confirmed the hexagonal structure as plotted in Figure 90, compared to the powder diffraction data of standard hexagonal titanium (PDF#44-1294). A preferred orientation is observed at the (103) plane positioned at $2\theta = 70.6^\circ$. The $a$ and $c$ lattice parameters of the titanium foil were calculated as $a = 2.940 \pm 0.005$ Å and $c = 4.670 \pm$
0.005 Å which are 0.37% and 0.27% larger as compared to those of the standard hexagonal titanium ($a = 2.951$ Å, $c = 4.683$ Å).

**Figure 90:** XRD Pattern of titanium foil, showing its hexagonal structure with preferred orientation at (103) plane.

**Magnetic Behavior:** The titanium foil exhibited a magnetic behavior typical of paramagnetic materials in response to change in magnetic field (a positive slope, $R^2 = 0.99$) and a largely temperature-independent moment resembling that of the Pauli paramagnetic behavior for $T = 10 – 400$ K. The molar susceptibility of titanium foil was calculated as $\chi_m = 147$ (μemu/Oe.mole) which is approximately similar to the reported molar susceptibility value of 151 (μemu/Oe.mole) for titanium. [195]
Figure 91: Magnetic behavior of titanium foil as a function of (a) magnetic field and (b) measurement temperature, showing a paramagnetic response to field and a largely temperature-independent behavior.

(B) Fabrication and Characterization of the Ti(Fe) Arc-Melted Alloy Sheet, the Fe-Doped NTs’ Precursor

In this section the fabrication technique of the Ti(Fe) alloy sheet is explained and the characterization results of this alloy are presented.

(i) Fabrication of Ti(Fe) Alloyed Sheet

Ti(Fe) sheets (5 wt% equivalent to 4.4 at% Fe) was purchased from ACI Alloy, USA. According to the manufacturer, these pieces (2.54 cm × 2.54 cm and 1 mm thick) were made by vacuum arc melting of 5 wt% iron in Ti(Fe) followed by cold rolling to obtain sheets with the desired thickness. These sheets were subsequently anodized for 6 hours to form Fe-doped nanotubes. The anodized nanotubes were then removed from the sheet by sliding a glass slide to prepare the Ti(Fe) sheet for further anodization sets. The nanotubes that characterized and studied in this Dissertation are from the 4th anodization set of this alloy sheet.
Arc melting is an alloying method that provides an elevated mechanical homogeneity. In this alloying method, the metallic shots in proper weight ratio (herein, 5 wt% Fe \textit{wrt} Ti) are brought to a vacuum environment in a water-cooled crucible plate (typically made from copper), Figure 92. An electrode (typically from tungsten) is brought to the vicinity of the shots to start the melting process. Several kiloamperes of DC current is then applied through the electrode to form an arc between the electrode and the metallic shots to initiate the melting.

![Figure 92: Schematic illustration of the arc melting equipment. [241]](image)

(ii) Characterization of Ti(Fe) Al loyed Sheet

The morphology, composition and crystal structure of this alloy is studied along with its magnetic behavior.

**Morphology and Composition:** Surface morphology of the Ti(Fe) alloy (Figure 93) looks similar to that of titanium foil, showing lines of aligned texture most likely due to the fabrication process (cold-rolling). The thickness of the sheet is measured as 1 mm. Compositional study on the Ti(Fe) alloy using EDX confirms the presence of 5 wt% iron, corresponding to ~ 4.4 at% iron in the alloy (Figure 93 (b)).
Crystal Structure: Structural examination of the Ti(Fe) sheet revealed the presence of two crystalline phases in the alloy (two sets of Bragg peaks, Figure 94). The first crystalline phase is identified as the hexagonal (HCP) crystal structure of titanium when it is compared to the powder diffraction pattern of standard HCP titanium. The second crystalline phase have peaks at 2θ positions of 39.33°, 57.15°, 71.35°, 84.66° and 98.34°. Detailed analysis of these peaks confirmed that they belong to a body-centered cubic (BCC) or β-titanium, with a shift toward higher 2θ degrees in compared to the standard BCC Ti. This shift is an indication of a compressive strain probably due to two reasons: 1) incorporation of iron in the structure of titanium during the alloying and 2) residual stress due to the manufacturing method. In the solid state, titanium alloys are arranged in either hexagonal closed-packed (HCP or α-titanium) or body-centered cubic (BCC or β-titanium). Pure titanium undergoes a transformation from HCP structure to BCC structure.
at \( T > 882 \, ^\circ C \). Presence of iron may have contributed to the stability of the BCC structure of titanium when it was cooled to the room temperature where titanium is most stable in the hexagonal structure.

![XRD pattern of Ti(Fe) alloy showing the presence of two crystallographic phases.](image)

The \( a \) lattice parameter of this strained BCC phase is calculated as \( a = 3.282 \pm 0.147 \, \text{Å} \) which indicates a slightly compressed unit cell (-0.72\%) as compared with the standard BCC titanium \( (a = 3.306 \, \text{Å}, \text{PDF#44-1288}) \). Considering that atomic radius of Fe is smaller than Ti (1.26 versus 1.76 Å) iron may have substituted the Ti atoms in the BCC structure, leading to a smaller unit cell.

**Magnetic Behavior:** Ti(Fe) alloy shows a paramagnetic behavior at both room and low temperatures, Figure 95. The Ti(Fe) calculated magnetic molar susceptibility at room temperature is \( \chi = 168 \, \mu\text{emu/mole} \cdot \text{Oe} \), slightly larger than that of the reported value for Ti, \( \chi = 151 \, \mu\text{emu/mole} \cdot \text{Oe} \). [195] This 11\% difference would be due to the presence of iron in form of diluted atoms which gave rise to an additional paramagnetic behavior.
Further, the magnetic susceptibility of Ti(Fe) alloy is largely temperature-independent, within the temperature range of 10 to 350 K, Figure 95.

Figure 95: Magnetic behavior of the cold-rolled arc-melted Ti(Fe) alloy as a function of (a) field, and (b) temperature.