X-ray Absorption Spectroscopy, X-ray Diffraction and Optical Luminescence Studies of Phase Transition of Titania Nanotubes

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Abstract

The one-dimensional (1D) TiO$_2$ nanotubes (NTs) and their derivatives have been extensively studied due to their wide applications, such as photocatalysts, solar cell, paints and so on. Since TiO$_2$ has a wide band gap (~3.0 eV), its photo-absorption as the photocatalyst only occurs in the UV region that wastes mostly solar energy. Therefore, the solution to higher photocatalytic efficiency has been sought for some time. This thesis presents a study of the size-dependent phase transitions of TiO$_2$ NTs using synchrotron-based X-ray techniques. The chemical environment including local symmetry and the luminescence origin of the TiO$_2$ NTs can be tracked by X-ray absorption near-edge structures (XANES) and X-ray excited optical luminescence (XEOL) technique. As a result, the anatase-to-rutile transition highly depended on the sizes of NTs with the same annealing treatment. Additionally, the shortest NTs require a lower temperature to start the amorphous-to-anatase transition.

Keywords

TiO$_2$ nanotubes, X-ray absorption near-edge structure, X-ray excited optical luminescence, In-situ X-ray diffraction, phase transition
Since titania (TiO$_2$) was discovered as a photocatalyst for splitting water by Fujishima and Honda in 1972, it has been developed and widely used in water splitting, supercapacitors, solar cells, photocatalytic degradation of pollutants, sensors and lithium-ion batteries. Furthermore, more attention has been concentrated on one-dimensional (1D) TiO$_2$ nanotubes (NTs) among the TiO$_2$ materials family, which is due to their low cost, non-toxicity, excellent stability. However, the large band gap (~3.0 eV) limits the photo-absorption of TiO$_2$ to act as a photocatalyst, which only occurs in the near-ultraviolet range and wastes 95% of solar energy. Therefore, the solution to higher photocatalytic efficiency has been sought for some time and this thesis explores and combines two possible solutions. It presents a study of the size-dependent phase transitions of TiO$_2$ NTs by synchrotron-based X-ray spectroscopy, which involves precise control of size (length, diameter, and thickness) by a two-step electrochemical anodization under various conditions and achievements of desirable phases of TiO$_2$ NTs by subsequent thermal-annealing treatments with different temperatures. In the characterization, there are four techniques used in this thesis. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) are used to track the surface morphology and the crystalline structure of the TiO$_2$ NTs. Importantly, the synchrotron-based techniques are also applied to provide valuable structural information of TiO$_2$ NTs. The synchrotron is the facility that accelerates electrons to nearly the speed of light and emits light with a continuous and wide range of wavelengths from the infrared to gamma rays, which is a powerful tool to probe the structural and electronic information of various materials. The chemical environment including local symmetry and the luminescence origin of the TiO$_2$ NTs can be tracked by X-ray absorption near-edge structures (XANES) and X-ray excited optical luminescence (XEOL) technique. As a result, the size features of TiO$_2$ NTs can be controlled by the electrochemical anodization method. The anatase-to-rutile transition highly depended on the sizes of NTs with the same annealing treatment. Additionally, the shortest NTs require a lower temperature to start the amorphous-to-anatase transition.
Co-Authorship Statement

The X-ray absorption near-edge structures (XANES) and X-ray excited optical luminescence (XEOL) measurements of TiO$_2$ nanotubes (NTs) in Chapter 3 were carried out with the help of Dr. Tom Regier and Mr. Zachary Arthur at the spherical grating monochromator (SGM) beamline of Canadian Light Source (CLS). The in-situ X-ray diffraction (XRD) experiments with increasing temperatures were performed with the help of Dr. Yu-Chun Chuang at 09A X-ray diffraction beamline of Taiwan Photon Source (TPS). The ex-situ XRD measurements at TPS are carried out with the help of Lo-Yue Zhang at TPS.

The lab XRD data in Chapter 3 and Chapter 4 were collected with the help of Ms. Kim Law at Department of Earth Science, University of Western Ontario (UWO). The scanning electron microscopy (SEM) images of TiO$_2$ NTs in Chapter 3 and Chapter 4 were collected with the help of Mr. Todd Simpson and Mr. Tim Goldhawk at Nanofabrication Faculty, UWO.
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<td>0D</td>
<td>Zero dimensional</td>
</tr>
<tr>
<td>1D</td>
<td>One dimensional</td>
</tr>
<tr>
<td>AP</td>
<td>As-prepared</td>
</tr>
<tr>
<td>BSEs</td>
<td>Backscattered electrons</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>CLS</td>
<td>Canadian Light Source</td>
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<tr>
<td>CNTs</td>
<td>Carbon Nanotubes</td>
</tr>
<tr>
<td>DCM</td>
<td>Double-crystal monochromator</td>
</tr>
<tr>
<td>DI</td>
<td>De-ionized</td>
</tr>
<tr>
<td>EA</td>
<td>End-station area</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
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<tr>
<td>FLY</td>
<td>Fluorescence yield</td>
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<tr>
<td>FWHM</td>
<td>Full width at half maximum intensity</td>
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<tr>
<td>LINAC</td>
<td>Linear accelerator</td>
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<tr>
<td>NTs</td>
<td>Nanotubes</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SEs</td>
<td>Secondary electrons</td>
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<tr>
<td>SGM</td>
<td>Spherical Grating Monochromator</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<td>-----------</td>
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<tr>
<td>SR</td>
<td>Synchrotron radiation</td>
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<tr>
<td>TEY</td>
<td>Total electron yield</td>
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<tr>
<td>TPS</td>
<td>Taiwan Photon Source</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<td>UWO</td>
<td>University of Western Ontario</td>
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<tr>
<td>VB</td>
<td>Valence band</td>
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<td>Visible</td>
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<tr>
<td>XAFS</td>
<td>X-ray absorption fine structure</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
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<td>X-ray excited optical luminescence</td>
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<td>XRD</td>
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Chapter 1

1 Introduction

1.1 Titanium dioxide

1.1.1 Background

As the earth's limited natural fossil resources are being voraciously used and excessive CO\textsubscript{2} is causing global warming, the generation and development of renewable and clean energies are taken to a higher level. Among various methods, photo-electrocatalysis, as a green technology, aimed to generate hydrogen from water-splitting and reduce CO\textsubscript{2} to renewable fuels has attracted much attention [1-4]. Meanwhile, rechargeable batteries such as lithium and sodium batteries are popular objectives as storage devices for clean energies [5, 6].

Titania (TiO\textsubscript{2}) has been discovered as a photocatalyst for splitting water by Fujishima and Honda in 1972 [7]. During the few decades since then, TiO\textsubscript{2} has been developed and widely used in water splitting, supercapacitors, dye-sensitized solar cells, photocatalytic degradation of pollutants, sensors, self-cleaning and lithium-ion batteries [8-10]. More importantly, much more attention has been paid to one-dimensional (1D) tubular nanomaterials since the discovery of carbon nanotubes (CNTs) by Iijima et al. in 1991 [11]. Among these nanotubular materials, TiO\textsubscript{2} nanotubes (NTs) have become a popular object to study for wide applications due to their high specific surface area, strong ion-exchanging ability, especially for robust photocatalyst [1, 2, 12] and solar cells [8-10]. In addition, TiO\textsubscript{2} NTs have great potential for large-scale commercialization due to their low cost, non-toxicity, high rate performance, excellent stability, and cyclability.

1.1.2 Crystal structures

In nature, there are three crystal structures of TiO\textsubscript{2}, i.e., anatase (tetragonal, space group I4\textsubscript{1}/amd), rutile (tetragonal, space group P4\textsubscript{2}/mmn) and brookite (orthorhombic, space group Pbca) [13]. As shown in Figure 1-1, these three polymorphs present similar distorted structures of TiO\textsubscript{6} octahedra with six-fold oxygen coordination to titanium...
cations. More specifically, anatase shows TiO$_6$ octahedra jointed by sharing corners and its unit cell has tetragonal structure with $a = 0.54$ nm and $c = 0.95$ nm. Rutile shows sharing octahedral edges and its unit cells have a tetragonal structure with $a = 0.46$ nm and $c = 0.30$ nm. Brookite shows both corners sharing and edges sharing of octahedra and orthorhombic structure exists in the unit cell with $a = 0.92$ nm, $b = 0.54$ nm and $c = 0.51$ nm parameters.

![Crystal structure of TiO$_2$ polymorphs: anatase, rutile and brookite.](image)

**Figure 1-1** Crystal structure of TiO$_2$ polymorphs: anatase, rutile and brookite. [14]

Among these three TiO$_2$ crystal phases, rutile is regarded as the most stable bulk phase while anatase and brookite are more stable phases in nanoscale due to their lower surface energy than that of rutile. Among them, anatase and rutile are more popular research objects due to their superior photocatalytic activities than brookite [1, 2, 8, 15]. Besides, it is reported that mixed-phase TiO$_2$ NTs with a specific ratio of anatase and rutile (Degussa P25, rutile/anatase 80:20) have extraordinary photoelectric properties that showed much better photocatalytic performance than single-phase TiO$_2$ (anatase, rutile, and brookite). [16]

### 1.1.3 Limitations and solutions

There are still limitations of TiO$_2$ for applications requiring high efficiency. Firstly, anatase and rutile are wide band gap semiconductors with band gap at 3.2 eV and 3.0 eV, respectively [17, 18]. In the solar spectrum in **Figure 1-2**, the band gaps of anatase (3.2 eV) and rutile (3.0 eV) are marked by vertical lines, indicating that the photo-absorption and photoactivity of TiO$_2$ occurred in the near-ultraviolet (UV) range. Since the UV light
only constitutes approximately 5% of solar energy, most of the solar energy in the visible (Vis) and infrared (IR) regions are wasted [2, 19].

![Solar Spectrum Diagram](image)

**Figure 1-2** The solar spectrum showing the radiation power at different photon energies. The visible range is labelled corresponding to the light colours. [20]

Secondly, the rapid combination rate between photo-generated electrons in the conduction band (CB) and associated holes in the valence band (VB) is an obstacle of TiO$_2$ in regard to superior photoactivity [1, 2, 15]. Photocatalysts take advantage of the photo-excited holes and electrons to participate in the reaction. Fast electron-hole (e-h) recombination is not desirable for photocatalytic or photovoltaic effects. In other words, the short lifetime of electron-hole pairs decreases the photo-efficiency of TiO$_2$. 
To address these issues, many solutions and methods have been sought and reported [1, 2, 16]. The key methods are summarized below. Firstly, introducing a secondary species to the TiO$_2$ lattice (doping) has been developed to narrow the band gap by modifying the energy levels of CB and VB [13]. Two types of TiO$_2$ heterostructures induced by doping methods were proposed - with non-metal and transition metal elements. The introduction of non-metal species to TiO$_2$ can reduce the band gap via raising the energy level of VB (Figure 1-3 (a)), shifting the absorption range to visible and even IR regions [1, 12, 21]. The first reported non-metal species doping of TiO$_2$ was N [12], followed by neighbouring elements including C, F, and S [22-24]. For transition metal species (such as Cr, Fe, and Ni), the doping can reduce the band gap by adjusting the CB (Figure 1-3 (b)), which also shifts the photoabsorption into the visible and infrared regions [25, 26]. However, they can promote the recombination of electron-hole pairs by inducing trap states, which leads to lower photoactivity [1].

Another solution to improve the photo-efficiency is to extend the electron-hole pair lifetime, and there are three ways to achieve it (Figure 1-4): (i) morphology engineering, (ii) phase control and (iii) noble-metal sensitizing. In (i), one-dimensional (1D) nanostructure has drawn attention due to its large surface area as well as rapid charge transferring compared to zero-dimensional (0D) meterial [13, 15, 27]. So far, various 1D nanostructures have been synthesized with different morphologies: nanowire, nanotube, nanorod, and nanobelt [27-30]. Here, the focus is on 1D nanotube due to its easy
controllability in tube sizes (length, diameter, and thickness) and excellent uniformity and rapid transferring of charge carriers along the longitudinal direction [31]. In (ii), transforming amorphous TiO$_2$ into the mixed-phase (anatase and rutile) structure can help separate the photo-excited electrons and holes. It has been reported that anatase/rutile heterostructures with a specific ratio contribute to an extraordinary photocatalytic activity due to the extended lifetime of electron-hole pairs; this is due to the mismatching of the top of the valence band and the bottom of the conduction band between the two phases, which greatly reduces the rate of electron-hole recombination [16, 32]. Another route (Figure 1-4 (iii)) to prevent electrons and holes from recombining is to introduce noble-metal (such as Ag, Au, Pd, and Pt) sensitizing to TiO$_2$ [1, 32, 33]. In this case, the noble metals can be attached to nanostructures and then serve as an electron sink or holder, forbidding the electrons to recombine with the holes [2, 15, 32].

Figure 1-4 Schematic illustration of suppression of the electron–hole recombination by: (i) ordering the TiO$_2$ nanostructures, (ii) forming mixed-phase (anatase and rutile) structures, and (iii) constructing metal/TiO$_2$ heterostructures.

This study involves precise control of the size (length, diameter, and thickness) of TiO$_2$ NTs via electrochemical anodization method and transformation of phases of TiO$_2$ via annealing treatments; thus methods (i) and (ii) listed above are used. For characterization, synchrotron-based techniques are used to investigate the electronic and structural properties of TiO$_2$ nanotubes as a function of morphology and annealing temperature.
1.2 Synthesis methods of TiO$_2$ nanotubes

There are many methods developed to synthesize TiO$_2$ nanotubes structures, such as hydrothermal method, electrochemical anodization, chemical vapour deposition (CVD) method, template-assisted method and sol-gel method. In this thesis, the TiO$_2$ NTs are synthesized with the electrochemical anodization method. Its history and recent developments will be introduced below. In this method, the type of electrolyte, the pH of electrolyte, anodization time, anodization potential and temperature can influence the size of TiO$_2$ nanotubes (length, diameter, and wall thickness). Furthermore, the mechanism for the formation of TiO$_2$ nanotubes will be discussed at the end of this section.

1.2.1 Development of electrochemical anodization method

Highly ordered TiO$_2$ NTs arrays can be synthesized by a two-step electrochemical anodization of titanium metal, which creates decorative oxide layers on the metal surface [1]. This synthesis method has been conducted for several decades since anodized TiO$_2$ was first reported in 1984 by Assefpour-Dezfuly et al. [34] In the early years of TiO$_2$ nanotubes synthesis, titanium was etched with alkaline peroxide, followed by anodization using chromic acid as an electrolyte, resulting in porous TiO$_2$ NTs. Since then, significant progress has been made via synthesizing ordered anodized TiO$_2$ NTs with fluorine-containing electrolytes in 1999 by Zwilling and coworkers [35]. Since this breakthrough in the fabrication of tubular TiO$_2$, plenty of attempts have been made to optimize the electrolyte to obtain highly-ordered TiO$_2$ NTs arrays. Five main generations of electrolytes have been developed, as summarized in Table 1-1.

The first-generation of electrolytes used in anodization was reported by Gong et al. in 2001 [36], who obtained TiO$_2$ NTs via anodization of titanium foil with HF/H$_2$O electrolyte at room temperature [37]. However, the anodized product of this electrolyte showed obvious length limitation of tubes (200-500 nm). The second-generation electrolytes consist of Na$_2$SO$_4$(NH$_4$)$_2$SO$_4$/NH$_4$F fluoride-based buffered solution, which increased length limitation of nanotubes while nanotubes showed rough external surface with ripples on the wall resulting from electric current oscillation during anodization process. [38, 39] After that, the third-generation with NH$_4$F/H$_2$O in ethylene glycol
organic electrolyte with fluoride ions was developed, which overcame ripple problem and smoother and longer TiO$_2$ NTs have been fabricated. [40] In later work, the fluoride-free electrolytes have been attempted, such as HClO$_4$ solution, which represents the fourth-generation electrolyte. Finally, Macak et al. fabricated highly ordered hexagonal nanotube close-packed arrays by a multistep anodization method, which has been considered as the fifth-generation electrolyte. [41] The 5$^{th}$ generation electrolytes consisting of NH$_4$F (0.5 wt%), H$_2$O (0.1-5 wt%) and ethylene glycol have been widely used in research due to their easy control of the tube size and tunability via multi-step approaches [2, 42], where additional anodization can enhance the weak adhesion between Ti substrate and TiO$_2$ NTs to achieve longer tube lengths.

Table 1-1 Five generations of electrolytes of anodization method to synthesize TiO$_2$ NTs. [31]

<table>
<thead>
<tr>
<th>TiO$_2$ NTs</th>
<th>Electrolyte</th>
<th>Morphology: Length, diameter, thickness</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^{st}$ generation: HF electrolytes</td>
<td>0.5 wt% HF</td>
<td>200-500 nm, 10-100 nm, 13-27 nm</td>
<td>[36, 37]</td>
</tr>
<tr>
<td>Short nanotubes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2$^{nd}$ generation: F-based buffered electrolytes</td>
<td>1M Na$_2$SO$_4$(NH$_4$)$_2$SO$_4$ + 0.5 wt% NH$_4$F</td>
<td>0.5-2.4 μm, 100 nm, 12 nm</td>
<td>[38, 39]</td>
</tr>
<tr>
<td>Rough wall with wing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3$^{rd}$ generation: F-containing organic electrolytes</td>
<td>0.5 wt% NH$_4$F + 2 vol% H$_2$O in ethylene glycol</td>
<td>5-1000 μm, 100 nm, 12 nm</td>
<td>[40]</td>
</tr>
<tr>
<td>Smooth and ultra-long tubes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4$^{th}$ generation: F-free electrolytes</td>
<td>0.01-3M HClO$_4$</td>
<td>30 μm, 20-40 nm, 10 nm</td>
<td>[41]</td>
</tr>
<tr>
<td>Disordered tubes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5$^{th}$ generation: multiple-step anodization in F-containing organic electrolytes</td>
<td>0.5 wt% NH$_4$F + 2 vol% H$_2$O in ethylene glycol</td>
<td>2-10 μm, 100 nm, 15-20 nm</td>
<td>[2, 43]</td>
</tr>
<tr>
<td>Smooth and hexagonal tubes</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
To date, the electrolyte has been further optimized, which fabricated highly order TiO$_2$ NTs arrays with long tube length and high adhesion between TiO$_2$ NTs and Ti substrate. The development is ongoing.

### 1.2.2 Mechanism for the formation of anodic titania nanotubes

![Figure 1-5 Schematic illustration of the mechanism of formation of anodic titania nanotubes by an electrochemical anodization method [44].](image)

During the electrochemical anodization process (Figure 1-5 (a)), the oxidation of titanium metal occurs in the anode, which frees Ti$^{4+}$ at the metal/oxide interface and then it migrates to the top of the oxide layer (Equation 1-1). After that, Ti$^{4+}$ can combine with OH$^-$ provided by water dissociation under the electric field and the hydrated oxide is produced over several steps, and these chemical reactions are summarized in a single reaction (Equation 1-2). In the meantime, an oxide layer is formed on the titanium metal substrate (Equation 1-2b). The O$^{2-}$ also provided by water dissociation moves to the
Ti/TiO\textsubscript{2} interface and reacts with the Ti\textsuperscript{4+} to produce the TiO\textsubscript{2} layer on the metal substrate. Furthermore, an additional TiO\textsubscript{2} oxide layer can be produced subsequently due to the condensation reaction of the hydrated anodic layer, which contributes to formation and oxide and water (Equation 1-3). These four equations illustrated above are the possible reactions that occur at the anode during the field-assisted oxidation process, in which the applied potential determines the rate of ion migrating through the Ti/TiO\textsubscript{2} interface. Here, the electric field is defined by the voltage across the oxide layer $\Delta U$ and the layer’s thickness $d$, which can be expressed by the equation $F = \Delta U / d$. [44] It is worth mentioning that the growth of the oxide layer is self-limited since the field would decrease as the oxide layer grow thicker, and it would be too small to assist the migration of ions. Additionally, hydrogen is released at the cathode where H\textsuperscript{+} meets electrons (Equation 1-4). When all reactions abovementioned are taken into consideration, the overall reaction can be represented by Equation 1-5.

**Oxidation of titanium**

\[
Ti \rightarrow Ti^{4+} + 4e^+ \quad (1-1)
\]

**Formation of the oxide layer**

\[
Ti^{4+} + 4OH^- \rightarrow Ti(OH)_4 \quad (1-2)
\]

\[
Ti^{4+} + 2O_2^- \rightarrow TiO_2 \quad (1-2b)
\]

\[
Ti(OH)_4 \rightarrow TiO_2 + 2H_2O \quad (1-3)
\]

**Hydrogen evolution**

\[
2H^+ + 2e^- \rightarrow H_2 \quad (1-4)
\]

**Overall reaction**

\[
Ti + 2H_2O \rightarrow TiO_2 + 2H_2 \quad (1-5)
\]

In the following, fluoride ions from the electrolyte play an important role in forming the nanotube structure during the etching process. The chemical dissolution of oxide
(Equation 1-6) and the hydrated layer (Equation 1-7) occur by fluoride ions, which results in the formation of the soluble hexafluoro titanium complex, [TiF$_6$]$^{2-}$ (Figure 1-5 (b)). In this step, the F$^-$ ions compete with O$_2^-$ in the oxide in the presence of H$^+$, or with the OH$^-$ in Ti(OH)$_4$. In addition, the fluoride ions can react with Ti$^{4+}$ ions as well to form the fluoro-complex (Equation 1-8), assisted by the applied potential, under which the Ti$^{4+}$ is injected from the metal/metal oxide interface and F$^-$ migrates towards metal. It is worth mentioning that the chemical dissolution of the oxide by the F$^-$ and field-assisted dissolution that weakens the Ti-O band probably have a combined impact on the formation of this stable complex [TiF$_6$]$^{2-}$ [31]. It is evident that the [TiF$_6$]$^{2-}$ has a large negative Gibb’s free energy of formation, which is -2118.4 kJ/mol at room temperature. [45] The Gibb’s free energy of formation for TiO$_2$ is higher ( $\Delta G_{298}^\circ = -821.3$ kJ/mol ) than that of the [TiF$_6$]$^{2-}$ complex, which indicates the latter is more stable. [45] In addition, the evolution of oxygen occurs at the anode during the anodization (Equation 1-9), which can be considered as a side reaction.

Etching process

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + H_2O$$ (1-6)

$$Ti(OH)_4 + 6F^- \rightarrow TiF_6^{2-} + 4OH^-$$ (1-7)

$$Ti^{4+} + 6F^- \rightarrow TiF_6^{2-}$$ (1-8)

Oxygen evolution

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+$$ (1-9)

During the etching process, the equilibrium between oxide layer formation at the inner interface and dissolution (by the effect of F$^-$ ions) at the outer interface can be achieved. As shown in Figure 1-5 (c), the initial nanotubes (nanopores) are created on the oxide surface due to the mutual effect of the steady-state between formation and dissolution of oxide and compressive stress, which contributes to oxide layer and fluoride-rich layer (fluoride migrates to Ti/TiO$_2$ interface under the electric field) into rounding shapes. With the process of the etching, the size and depth of pores increase rapidly. The
nanotubes morphology is formed by the dissolution of the soluble fluoride-rich layer (disappearance of adjacent tube walls), as shown in Figure 1-5 (d). [44]

1.2.3 Influence of anodization parameter on the size of nanotubes

The electrolyte plays an important role in the morphology, structure and growth rate of TiO$_2$ NTs. Different electrolytes determine different electric field strengths and dissolution rates of the oxide layer during the anodization process. More specifically, the higher electric field would lead to a bigger breakdown site, which leads to a larger diameter of TiO$_2$ NTs. Furthermore, a faster dissolution rate of the oxide layer could lead to a shorter length of TiO$_2$ NTs. Basically, there are two different types of electrolytes: organic and aqueous electrolytes. Usually, longer and better organized TiO$_2$ NTs would be fabricated with organic electrolytes due to lower diffusibility of ions in organic electrolytes.

The pH of the electrolyte shows a significant influence on the growth of the high-aspect-ratio nanotubes. Different diameters and thicknesses of anodized TiO$_2$ NTs can be achieved with different pH conditions due to different oxide dissolution rates. The lower pH of the electrolyte, the higher the dissolution rate of TiO$_2$ layer and the smaller thickness of nanotubes.

The anodization potential can influence the morphology (length and diameter) of anodized TiO$_2$ NTs via determining the electric field strength applied to the oxide layer. Usually, a static potential is applied to the experiment and the potential range is from 10-50 V for F-containing electrolytes. If the applied potential is too low, it cannot form the nanotube structures by starting to oxidize Ti metal to Ti$^{4+}$. When the anodization potential is too high, breakdown events would occur in the TiO$_2$ NTs due to the high reaction rate of the field-assisted process.

The anodization time mainly affects the length of nanotubes. It is recognized that the longer the time, the longer the nanotubes. However, when the equilibrium between the formation and the dissolution of the oxide layer is reached, the length of the nanotube cannot increase even though the anodization time is prolonged. The optimal anodization
time depends on electrolytes. Generally, anodization with organic electrolytes is so gentle that the anodization time could be 4 h-10 h to achieve highly ordered organized TiO$_2$ while that for HF-containing electrolytes could be as short as 30 min.

1.3 Synchrotron radiation overview

Synchrotron radiation (SR) is a bright light source producing a wide continuous range of electromagnetic radiation from infrared to gamma rays. In a synchrotron, electrons are accelerated to a speed close to the speed of light in the storage ring. SR is emitted in the tangential direction of the orbit when the relativistic electrons are bent under the external magnetic field.

Synchrotron radiation was first observed in the General Electric Research Laboratory in Schenectady, New York, on April 24, 1947 [46], and it has been recognized as a powerful tool since the 1960s [47]. There had been significant progress in the development of synchrotron when the first dedicated synchrotron radiation source, Tantalus I, was operated in 1968 [48]. Then, the synchrotron was widely used to probe the structural and electronic information of various materials and synchrotron radiation facilities have been developed and built all around the world. With the development of instrumentation, the second-generation SR facilities such as BESSY I (Germany), NSLS (US) and Aladdin (US) came into researchers’ sight in the 1980s. After that, the third-generation SR has been developed due to their introduction of insertion devices such as undulators and wigglers that generate more bright light. In this thesis, synchrotron experiments were carried out in two third-generation synchrotrons - Canadian Light Source (CLS) and Taiwan Photon Source (TPS).
**Figure 1-6 The schematic diagram of the Canadian Light Source (CLS) synchrotron radiation facility [49]**

**Figure 1-6** shows the schematic diagram of a synchrotron radiation facility. Firstly, electrons are ejected by heating a cathode to a very high temperature (almost 1000 °C) under direct current high voltage. These emitted electrons are put into the linear accelerator (LINAC), where electrons are accelerated to a speed close to the speed of light with the energy of the order of MeV. After that, accelerated electrons are inserted into the booster ring to obtain further acceleration until the energy of electrons reaches the order of GeV. Then, electrons are transferred to the storage ring and circulate in the orbit with almost speed of light. In this process, there are a couple of magnets located in the storage ring aimed to control the direction of electrons, such as bending magnets (red components in **Figure 1-6**) and quadrupole magnets (green components in **Figure 1-6**). In addition, a radio-frequency (RF) cavity is in the straight section of the storage ring, which is used to replenish the energy loss during the synchrotron radiation process. It achieved boost electrons and remain the same travel speed by applying a time-varying electric field.

As illustrated above, the synchrotron radiation process occurs since the trajectory of the accelerated electron is changed by various magnets. The bending magnets are dipole magnets, which are in the curved section of the storage ring. As known as the “insertion
devices”, undulators and wigglers are arrays of magnets with alternating polarity, which are located in the straight section of the storage ring. Different type of magnets contributes to different spatial distribution radiation, which can be determined by the opening angle ($1/\gamma$) with $\gamma$ expressed by the following equation (Equation 1-10),

$$\gamma = \frac{E}{m_0 c^2}$$  \hspace{1cm} (1-10)

where $\gamma$ is the ratio of the mass of a relativistic electron to its rest mass $m_0$, $c$ is the speed of the light and $E$ is the energy. Figure 1-7 shows the configurations of the bending magnet, wiggler and undulator. There is a sharp cone sweep produced in the bending plane under the bending magnet. Compared to the bending magnet, the wiggler leads to a large opening angle ($\gg 1/\gamma$) while the undulator a smaller opening angle ($1/\gamma\sqrt{N}$) due to its lower magnetic field. [50] Basically, there is a short period in the wigglers and large bend structure that can result in a continuum of radiation. For the undulator, the longer period and small bend structure are desirable for experiments to need a collimated beam with higher brightness (number of photons per second per source area per unit angle).

![Figure 1-7 The schematic layout of spatial (a) and the spectral distribution (b) of bending magnet, wiggler and undulator. [50, 51] The $1/\gamma$ is the opening angle and N is the atomic number.](image)
Since the synchrotron can generate the radiation which covers a broad energy range from infrared (IR) to hard X-ray, the monochromators can be used to select energies to satisfy various experiment requirements. In this case, a grating monochromator can be used to select soft X-rays while a double-crystal monochromator can be employed to choose hard X-rays.

**Figure 1-8** Schematic diagram of a grating monochromator with rotated position (a) and diffraction results from a typical Echellette-type grating (b).

**Figure 1-8 (a)** shows a schematic diagram of the soft X-ray selected by the grating monochromator. When the incident light hits the grating monochromator at a grazing angle, it gets diffracted at different diffraction angles (different energies). To keep the exit beam at a fixed angle, energy with a specific value can be selected by rotating the grating (rotatable) or moving the optical aperture (movable). The physical theory of grating diffraction is expressed by **Equation 1-11**, which also is illustrated in **Figure 1-8 (b)**.

\[
\nu = d \left( \sin \alpha \pm \sin \beta \right) \quad (1-11)
\]

where \( \alpha \) is the angles of incidence, \( \beta \) is the angle of diffraction, \( n \) represents the order of the diffraction, \( \lambda \) represents the wavelength of the diffraction light and, and \( d \) is the distance between the grating lines.
To operate hard X-ray experiments at beamlines, a double-crystal monochromator (DCM) is usually applied which includes two identical crystals. Two perfect crystals are set parallel to each other in a DCM and both crystals have the same physical parameters with the same element and same d-spacing value. An X-ray beam with specific energy and a fixed exit angle can be achieved by rotation and translation of the two paralleled crystals. As shown in Figure 1-9, the first crystal is installed that can be rotated to have different incident beam angles (θ). Meanwhile, the second crystal can direct the Bragg diffracted beam to the fixed exit point (Figure 1-9 (b)) by rotation and translation. Thus, the mono-energy X-ray with constructive interference can be selected following Bragg’s law (Equation 1-12).

\[ n\lambda = 2d\sin\theta \] (1-12)

where \( n \) means the order of diffraction, \( \lambda \) represents the wavelength of the diffracted light, \( d \) means the lattice spacing of the crystal and, \( \theta \) is the Bragg angle. Usually, the crystals used are Si (111), Si (333), InSb (111), etc. Depending on the measurement requirements for energy range, the type of crystal with different d-spacing values can be chosen. More specifically, the inter-planar distance can be determined by their miller indices (h, k, l) and lattice constant a, and the relationship between them is expressed by the Equation 1-13 (applied to cubic crystal). For example, Si (333) has a better resolution due to its smaller inter-planar distance calculated compared to that of Si (111).
Between the InSb (111) and Si (111), the smaller lattice constant of the latter contributes to a higher resolution.

\[ d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \]  

(1-13)

The difference between grating and crystal monochromator is the distance between the line; in soft X-ray gratings, it can vary from 600 to 1800 lines per millimeter or microns separation between lines. Smaller gratings cannot be fabricated for hard X-rays which have wavelengths on the order of 0.1 nm or Å; so crystal with lattice spacing on the order of Å must be used.

Overall, synchrotron radiation has several advantages comparing to the traditional X-ray source [52]. Firstly, the synchrotron radiation can provide the tunable energy range within IR to hard X-ray by using the monochromators. Moreover, there are 12 orders of magnitude higher brightness of flux (number of photons per second per milliradian of horizontal angle per 0.1% bandwidth integrated over all vertical angles) of SR than that of the traditional X-ray source. Furthermore, the high spatial resolution spectra can be achieved by a highly collimated beam of SR. In addition, the SR can produce the photon that is linearly polarized in the orbit plane or elliptically polarized out of the orbit plane. Finally, pulsed wave with a few nanoseconds between pulses is due to bunched electrons generated by the RF cavity, which provides an opportunity to conduct time-resolved spectroscopy experiments.

1.4 Thesis outline

The outline of this thesis is in the following. Chapter 1 gives the general introduction of TiO₂ nanostructures, synthesis of TiO₂ nanotubes via an electrochemical anodization method, an overview of synchrotron radiation, and the objective of this thesis. Chapter 2 describes details of synchrotron-based characterizations including XANES and XEOL techniques and laboratory characterization including XRD and SEM. Chapter 3 presents a study of the phase transition (anatase to rutile) of two series TiO₂ NTs (anodization time-dependent and anodization voltage-dependent) by XANES and XEOL. Chapter 4 shows a synchrotron-based in-situ XRD study to reveal the temperatures of annealing treatments.
when phase transitions of a given morphology of TiO$_2$ NTs occur, and the process of phase transformations (amorphous to anatase) as a function of tube morphology. Chapter 5 includes the conclusions of this thesis and proposes future work.

1.5 References


Chapter 2

2 Instrument and Techniques

In this chapter, the two synchrotron radiation facilities, Canadian light source (CLS) and Taiwan Photon Source (TPS), and their beamlines are described firstly. Then, the synchrotron-based techniques are introduced including X-ray absorption near-edge structures (XANES) and X-ray excited optical luminescence (XEOL). Furthermore, the details of laboratory characterization including Scanning electron microscopy (SEM) and X-ray diffraction (XRD) are described.

2.1 Synchrotron radiation facilities and beamlines

2.1.1 Canadian Light Source (CLS)

![Figure 2-1 Schematic layout of the CLS experimental hall. [1]](image)

The Canadian light source (CLS) is one of Canada’s largest scientific projects as a third-generation synchrotron light source, which is located in Saskatoon, Saskatchewan, Canada. It consists of a storage ring with the energy of 2.9 GeV and a linear accelerator that used to inject electrons to the ring. The circumference of the ring is 170.88 meters with a maximum current of 220 mA, and the horizontal emittances of 18 nm-rad. [1]
**Figure 2-1** shows the schematic layout of the CLS experimental hall, which indicates the beamlines in the CLS SR facility. There are 12 straights (9 available for insertion devices), 24 bending magnets, and over 40 possible beamlines in the CLS. Currently, there are 17 available beamlines (and 2 under construction) that can provide photon energy range from Far IR to hard X-ray.

2.1.1.1 SGM beamline at CLS

![Diagram of SGM Beamline](image)

**Figure 2-2** The layout of the SGM beamline at CLS. [2]

The high-resolution spherical grating monochromator (SGM) beamline (11ID-1) at CLS can provide the tunable and bright photon energy within the range of 250 eV-2000 eV, which is desirable for studying the K-edges of low-Z elements and the L-edges of transition metals. **Figure 2-2** shows the layout of the SGM beamline, which indicates that a dragon-type monochromator at the beamline. Three gratings can be used to choose for the desired energy range; low energy grating with 250-700 eV, medium energy grating with 450-1250 eV, and high energy grating with 740-2000 eV. The resolution E/ΔE is greater than 5000 at energies below 1500 eV with the spot size of 1000 μm×100 μm. The beamline flux (photons/s) at 100 mA is >10^{12} at 250 eV and >10^{11} at 1900 eV [2]. The beamline contains two end-stations areas (EA), referred to as the EA1 and EA2, respectively, in **Figure 2-2**. EA1 is designed for photoemission studies, and EA2 is desired for X-ray absorption measurement. XANES and XEOL experiments in this thesis
were conducted at EA2 for measuring the Ti L-edge and the O K-edge of various samples.

2.1.2 Taiwan Photon Source (TPS)

![Figure 2-3 The schematic layout of the TPS beamline map. [27]](image)

The Taiwan Photon Source (TPS) is one of the world’s brightest synchrotron X-ray sources, which is located in Hsinchu, Taiwan, China. The accelerator consists of a low-emittance synchrotron 3.0 GeV storage ring with a circumference of 518.4 meters and it comprises 24 double-bend achromats (DBA) cells, with six straight sections of 12 meters and eighteen straight sections of 7 meters in length. The booster ring of the accelerator is designed concentrically and housed in a donut-shaped building. The maximum ring current can is 500 mA in a top-up injection mode by using two sets of KEKB type superconducting RF cavities. **Figure 2-3** shows the schematic layout of the TPS beamlines map. There are 7 insertion-device (ID) beamlines in TPS phase-I; 3 beamlines of 12 meters straight sections and 4 of 7 meters straight sections. To date, all 7 beamlines at Phase I and 9 beamlines (1 beamline under construction) at Phase II are available for
users that can provide photon energy range from far IR to hard X-ray, and beamlines at phase III are under construction.

**Figure 2-4** The layout of the in-situ PXRD (09A) beamline at TPS. [28]

The in-situ powder X-ray diffraction beamline (09A) at TPS is desirable for the study of the static and dynamic structures of hard condensed matter with hard-X-ray diffraction. Figure 2-4 shows the layout of the 09A beamline at TPS, which indicates that a pair of IU22 undulators at this beamline, one behind the other. They serve as the X-ray source with the photon energy ranging from 5.6 to 25 keV, which covers the K-edge of most transition metals and the L-edge of rare earth and actinides. There are two operating modes in this beamline to accommodate the diverse scientific programs and experimental techniques. In Mode 1, a double-crystal monochromator is employed to provide a beam with the energy resolution of \( \Delta E/E \sim 10^{-4} \). The photon flux in this mode under regular operation is about \( 3 \times 10^{13} \) photons/s at 8 keV. A set of K-B mirrors will be applied to focus the beam to a few tens of micrometers for the investigation of magnetic structures with X-ray magnetic scattering. In-situ XRD experiments with increasing temperature in this thesis were conducted in Mode 1 to collect data of various TiO\(_2\) NTs samples with 15 keV photon energy. In Mode 2, for the development of X-ray cavities and atomic structures and investigation with the obtained temporally coherent X-rays, an ultrahigh-
energy resolution monochromator is inserted into the beam path to provide energy resolution of $\Delta E/E \sim 10^{-8}$. The photon flux at this mode is about $5 \times 10^9$ photons/s at 14.4 keV. In-situ XRD experiments with controlled temperatures in this thesis were conducted in Mode 1 with 15 keV photon energy to collect data of various TiO$_2$ NTs samples.

2.2 Synchrotron-based technique

2.2.1 The X-ray absorption fine structures (XAFS)

X-ray absorption occurs when the X-ray interacts with matter. The relationship between the intensity of the transmitted X-ray ($I_t$) and the incident X-ray ($I_0$) follows the Beer-Lambert Law (Equation 2-1) where $t$ is the thickness of samples and $\mu$ is the absorption coefficient.

$$\frac{I_t}{I_0} = e^{-\mu t} \quad (2-1)$$

The $\mu$ can be expressed by Equation 2-2 and Equation 2-3. In Equation 2-2, $\rho$ is the density of the sample, $Z$ is the atomic number of the element, $A$ is the atomic mass, and $E$ is the X-ray energy. It can be noted that the absorption coefficient $\mu$ is highly dependent on $Z$ and $E$, which indicates that the X-ray absorption spectroscopy is an element-specific technique. In Equation 2-3, $\mu$ is described by the X-ray absorption cross-section $\sigma$ and density $\rho$ of any given specimen.

$$\mu \approx \frac{\rho Z^4}{AE^3} \quad (2-2)$$

$$\mu = \sigma \cdot \rho \quad (2-3)$$

When the energy of the incident photon ($E$) is equal to or higher than the binding energy of a core electron, there is an abrupt increase of X-ray energy absorption resulting from the abrupt increase of absorption cross-section. The absorption cross-section can be considered as the probability of absorption of a photon and producing an electron transition from the initial to the final state. When the core electron is excited, it can transit
to other states, such as an unoccupied bond state, quasi-bound state and even the continuum. Here, the specific energy where a dramatic increase in the absorption coefficient $\mu$ can be observed is known as the absorption edge. Figure 2-5 shows several absorption edges of various elements in the plot of the absorption cross-section as a function of photon energy. For Pb, five absorption edges (labelled as L₁, L₂, L₃, K and M) show up at various energies corresponding to the excitation of various core electrons. Specifically, the nomenclature of the absorption edge depends on the shell of the excited core electrons. For example, the K-edge of Pb represents the excitation of an electron from 1s orbital (K-shell). The L₁-edge, L₂-edge, and L₃-edge are corresponding to the energy that the excitations of the 2s, 2p¹/₂ and 2p³/₂ electrons, respectively. Furthermore, the M₅-edge of Pb refers to the excitation of an electron from 3d₅/₂ orbital (M-shell). It should be noted that the variation of cross-section shows high energy dependence, which indicates its energy-specific and element-specific properties.

![Figure 2-5](image)

**Figure 2-5** The absorption edges of four elements in the plot of the absorption cross-section (in cm²/g) versus photon energy (in keV). [3]

The X-ray absorption fine structures (XAFS) describe the variation of the X-ray absorption coefficient $\mu$ as a function of X-ray energy $E$ in a certain chemical environment. [4] Generally, the XAFS show up once the outgoing electrons interfere with the neighbouring atoms in the chemical environment via single or multiple scattering.
Usually, XAFS consists of two parts: X-ray absorption near edge structure (XANES) with energy from 20 eV below and 50 eV above the edge, and the extended X-ray absorption fine structure (EXAFS) with energy from 50 eV to 1000 eV above the edge. This separation of XAFS is based on the different kinetic energy of electrons associated with different scattering behaviours. More specifically, low kinetic energy electrons favour multiple scattering (XANES) and high kinetic energy electrons favour single scattering (EXAFS).

XANES comes from electronic transitions into bound and quasi-bound states as well as multiple scattering interferences from neighbouring atoms, which makes it a powerful tool to probe the local environment of the absorbing element. It can provide electronic and local information including unoccupied electronic states, oxidation states, and local symmetry. [5] For the EXAFS, single scattering dominates, and it also can track the local structure of materials by providing information of bond length within second or third atomic shells and coordination number. [6-8] In this thesis, the study of TiO₂ NTs is focused on XANES spectra and more details are described in the following.

**Figure 2-6** shows the schematic illustration of XAFS of a free atom and that within a chemical environment (a diatomic system in this case). In a free atom system, shown in **Figure 2-6 (a)**, the photo-electron can be created when a core-level electron absorbs an incident photon with energy higher than the core-level binding energy. The wavenumber of the photon-electron can be considered that is proportional to $\sqrt{E - E_0}$ ($E$ is the energy of incident X-ray and $E_0$ is the binding energy of the core-level electron). It can be noted that $\mu$ (on the right side of figure) decreases monotonically above the edge, and there are no oscillations (chemical modulation) of $\mu$ due to scattering with neighbours, and no XAFS [3]. The atom in a diatomic shows a different story, as shown in **Figure 2-6 (b)**. When the incident X-ray that equal to or higher than the absorption edge is absorbed with binding energy, the photon-electron can fill the unoccupied bound states and quasi-bound states. The outgoing photoelectron from the absorbing atom can scatter from the neighbouring atom (scattering atom). The backscattered wave from the neighbouring atom can return to absorbing atom. There are possible constructive and destructive
interferences between the outgoing waves and backscattered waves. It leads to modulations of absorption coefficient $\mu$ and this is the origin of XAFS.

Figure 2-6 Schematic illustration of X-ray absorption of a free atom via the photoelectric process (a) and X-ray absorption fine structure of a diatomic system via scattering of photo-electron with neighboring atom (b). [3] For a free atom in its chemical environment, $\mu$ decrease monotonically above the edge, and there is no XAFS.
Figure 2-7 Schematic illustration of multiple scattering processes via several multiple scattering paths. The $\chi_n$ represents the scattering pathways between the absorbing atoms and n-1 neighbouring atoms.

In a certain chemical environment (an atomic cluster), there are several multiple scattering paths between absorbing atom and all neighbor atom (scattering atom). Figure 2-7 shows the schematic illustration of several multiple scattering pathways in the process. The total absorption coefficient can be expressed by the absorption coefficient of a single atom ($\mu_0$) and the contribution from its several multiple scattering pathways ($\chi_n$).

$$\mu(E) = \mu_0[1 + \sum_{n\geq2}\chi_n(E)]$$  \hspace{1cm} (2-4)

The equation indicates that the structural factor of the samples including bond length, local symmetry and ligands have a significant impact on the amplitude and spectral profile of XAFS (XANES).
2.2.2 Detection modes

Figure 2-8 Schematic illustration of detection modes of XANES: transmission (a) and total electron yield and fluorescence yield (b).

In the XANES experiments, there are three detection modes: transmission, total electron yield (TEY) and fluorescence yield (FLY). Basically, the transmission (Figure 2-8 (a)) is the most direct mode and the absorption coefficient $\mu$ can be determined by Equation 2-5,

$$\mu t = \ln\left(\frac{I_0}{I_t}\right)$$

where transmitted X-ray ($I_t$) and the incident X-ray ($I_0$) would be measured in the experiment. However, the thickness of the sample should be suitable to achieve a reliable outcome. This thickness should be around the so-called one-absorption-length ($\mu t = 1$), which leads to $36.8\%$ transmission. Samples that are too thick would lead to almost total absorption and no transmission while the ultra-thin samples would result in non-reliable absorption coefficients. Usually, the transmission mode is desired for hard X-rays with thin-film samples.

For the materials requiring soft X-ray, total electron yield (TEY) and fluorescence yield (FLY) are desirable once it is assumed that these yields are proportional to the absorption coefficient $\mu$. As illustrating above, when the electron is excited and then core-hole is left, the electron at a shallower level can occupy the core-hole and another electron can be ejected via the secondary or Auger process. [10] The TEY mode (Figure 2-8 (b)) can detect these electrons ejected from the sample in the XANES experiments, such as
photoelectrons, secondary electrons and Auger electrons. The TEY is a surface-sensitive detection mode that can detect within a few nanometers into the sample. The electron escape length can be determined by its kinetic energy via the universal curve (Figure 2-9). It is worth mentioning that TEY is a popular detection mode in the measurement with the soft X-ray since electrons’ extremely short attenuation length can avoid the thickness effect.

![Figure 2-9 Attenuation lengths extracted from the SR measured spectra.][9]

![Figure 2-10 X-ray attenuation length of anatase TiO$_2$ (density = 3.78 g/cm$^3$) within the photon energy range of 250-5500 eV with the incident angle of 90 degrees. It covers the Ti L-edge, the O K-edge and the Ti K-edge][9]
When the electrons from the shallower levels fill the core-hole, there are X-ray fluorescence emitted. Fluorescence yield (FLY) is another detection mode (Figure 2-8 (b)), which can collect fluorescent X-rays from the inside the TiO$_2$ nanotubes at least 2 orders of magnitude deeper than electron yield [11]. Thus, it can be considered as bulk-sensitive technique comparing to TEY. Figure 2-10 shows the X-ray attenuation length of TiO$_2$ (in this case) within the photon energy range of 250-5500 eV. It can be noted that the attenuation length varies with photon energy (element measured) and the penetration length of FLY is from hundreds of nanometers to approximately 10 microns. For example, the X-ray attenuation length is around 1 micron just below the Ti L-edge while it is around 0.2 microns just below the O K-edge. Furthermore, it can penetrate even 10 microns deeper of the samples with ~4970 eV photon energy (Ti K-edge). In the measurement, experimental data is current (X-ray photons) which detected by the MCP (microchannel plates). The MCPs are used to collect fluorescence X-rays only via applying a high negative voltage to the first channel plate to prevent electrons hitting on the MCPs. In addition, there are four FLY detectors located at various angles regarding the sample and each detector can collect partial fluorescence yield. In the thesis, the FLY represents total fluorescence yield, which sums these four partial fluorescence yields.

2.2.3 X-ray excited optical luminescence (XEOL)

Once a core electron is excited during the process of X-ray absorption, the core-hole is left, and a couple of de-excitation processes could take place to re-fill the core-hole. Figure 2-11 shows a schematic illustration of the de-excitation process after the X-ray absorption, including Auger and fluorescence decay process. The Auger electrons and fluorescence X-ray photons are products as the result of two de-excitation processes; the former is non-radiative by ejecting Auger electrons while the latter is radiative via the emission of fluorescence. More specifically, the core-hole left when a core electron is excited to the continuum (Figure 2-11 (a)). On one hand, an electron at a shallower level tends to fill the core-hole and release energy that excites another electron to continuum, which is the de-excitation process via ejecting Auger electrons (Figure 2-11 (b)). On the other hand, the electron can fill the core-hole and emit X-ray fluorescence (Figure 2-11 (c)), which is an alternative de-excitation process.
These are the two processes that are following X-ray absorption and are related to the core-hole left, which leads to the Auger electron yield and fluorescence yield proportional to the absorption coefficient. Furthermore, it should be noted that these two processes are in competition, and the Auger process is dominating the low Z elements while the X-ray fluorescence decay is the dominant-channel in the high Z elements. [12]

**Figure 2-11 Schematic illustration of the de-excitation processes following the X-ray absorption (a): Auger decay process (b) and X-ray fluorescence (c). In the diagram, the solid circles mean electrons while the open circles are holes.**

As the de-excitations such as the Auger process and fluorescence occur following the X-ray absorption and core-holes are filled, the holes at outer shells left and addition energy would excite electron at shallower levels (secondary excitation). This kind of excitation will take place in a cascade process and produce electron-hole pairs until no additional energy can support the further electrons excitations. In a semiconductor, for example, a chain decay process (thermalization), which involves the elastic scattering of energetic electrons (and hole), would be achieved when the holes transfer to the top of the valence band (VB) and photoelectrons would migrate to the bottom conduction band (CB). Since then, the electrons and holes will recombine and release energy radiatively or non-radiatively.
Among them, the X-ray excited optical luminescence (XEOL) is generated via optical photoemission from the radiative recombination process. There are three possible paths of this recombination showed in Figure 2-12. After the thermalization process, the electron in CB and the hole in VB can combine directly via emitting light with energy close to the band gap (Figure 2-12 (b)). It normally takes place via the formation of excitons (a hydrogen-like atom with the hole and the electron), this exciton has some binding energy (of the order of 10 meV below the bottom of the conduction band), usually small compared with the band gap of several eV and is often called near band gap or optical emission. Another combination path is in-direct, which is assisted by phonon (Figure 2-12 (c)). The third path is achieved via producing optical photons from defect states between the band gap (Figure 2-12 (d)), which is generally due to defects, impurities, and trapped holes.

Figure 2-12 Schematic diagram of (a) electron-hole excitation and electron-hole radiative recombination by (b) direct path, (c) indirect path assisted with phonon and (d) defect path.

Essentially, XEOL is an X-ray photon in, optical photon out technique. In the XEOL, certain energy can be used to excite core electrons and detect the corresponding de-excitation channels selectively, which makes it element-specific. As illustrated above, the
XEOL measures a specific de-excitation channel associated with the energy redistribution upon the absorption of an energetic photon. In this way, the variation of the absorption coefficient is usually consistent with XEOL. [13, 14] Combining with XANES, XEOL can be both element-specific and site-specific. These advantages are coupled effectively to the luminescence channel when the incident photon energy is scanned across an absorption edge of an element, probing the responsible sites for X-ray energy transfer to optical emission [13, 14].

2.3 Other characterization techniques

2.3.1 Powder X-ray diffraction (XRD)

Since it has been discovered that the spacing of planes in a crystalline structure can serve as three-dimensional grating to diffract X-ray in 1912 [15], the X-ray diffraction technique draws a lot of attention. It is a common technique now to exploit the scattering of X-ray from the material, which can identify the crystalline structure and atomic spacing of the material.

![Figure 2-13 An illustrating diagram of Bragg's diffraction.](image)

When the crystal suffers X-ray, the electrons vibrate with the frequency of the incident radiation in its path. Then, the energy is scattered by these electrons as X-rays with the same frequency of the incident beam. In this step, most of scattering waves interfere destructively while some scattering waves in a certain direction interfere constructively. In the latter condition, the scattered waves are reinforced, leading to a cooperative scattering effect known as diffraction. [16] In the crystal structure, every atom in each
plane can act as the center of the radiating spherical wave. W.L. Bragg noted that X-ray is diffracted by the crystal lattice which contributes to constructive interference if the condition satisfies the following equation, which is known as the Bragg Law.

\[ n\lambda = 2dsin\theta \]  

(2-6)

where \( n \) is an integer (1, 2, 3, …, \( n \)), \( \lambda \) is the wavelength of the X-rays, \( d \) is the interplanar spacing between successive parallel planes, and \( \theta \) is the diffraction angle. **Figure 2-13** shows the geometry of Bragg diffraction, in which the incident X-ray strikes the planes at an angle \( \theta \) and is reflected at an angle \( \theta \) as well. It can be noted that the travel distance of DEF is larger than that of ABC, and the difference between them is the distance of IF. In order to the diffracted X-ray with a larger number of sites remain in-phase, the distance of IF should be an integer multiple of the wavelength of the X-ray, \( n\lambda \).

X-ray powder diffraction is the most common technique to identify the unknown crystalline material. **Figure 2-14** shows an X-ray powder diffraction setup and the diffractometer plane of a conventional \( \theta \) to \( 2\theta \) diffractometer. Generally, it consists of an X-ray tube (X-ray source), a sample positioning stage (sample holder) and the X-ray detector. [17]

![Diffraction patterns in 3D space from a powder sample and the diffractometer plane of a conventional 0-20 diffractometer.](image)

The X-rays are generated in the X-ray tube by heating a filament to produce electrons and then accelerate them to a target material at the applied voltage. The accelerated electrons knock electrons in the core level of target metal and vacancies left will be filled by
dropping down electrons from the outer orbitals, in which the X-rays are emitted. Thus, the \( K_\alpha \) emission of the target materials (usually Cu, Fe, Mo and Cr) determines the wavelength of accident X-ray in the measurement.

The conventional diffractometer is confined within a plane known as the diffraction plane. The two diffraction cones represent forward diffraction and backward diffraction, and each crystallite in the powder produces its diffraction cone. In the diffraction measurement, a position-sensitive detector (PSD) is mounted on the detection circle, which can be rotated by the angle of 2\( \theta \) along a detection circle to collect the diffracted X-ray. When the collimated X-ray beam hits the sample, the intensity of the diffracted X-ray is collected as the detector rotates. Intensity peaks will appear as the detector scans when the incident and diffracted X-rays satisfy the Bragg’s Law, which indicates constructive interferences occur. The detector records the intensity of the diffracted X-ray signal versus the angle 2\( \theta \).

The position (2\( \theta \)) of a diffraction peak is corresponding to a certain inter-plane distance in the Bragg’s equation. [19] Another feature of the peak worth mentioning is the peak width. There is a relationship between the broadening of the peaks and crystallite size, which is known as the Scherrer equation (Equation 2-7). [20]

\[
\beta_{hkl} = \frac{K\lambda}{L_{hkl}\cos\theta_{hkl}}
\]  

(2-7)

where the \( \beta_{hkl} \) is the full width at half maximum intensity (FWHM) of the peak for a certain phase (hkl), the Scherrer constant \( K \) is varies based on how the width measured, \( \lambda \) is the wavelength of incident X-ray, the \( \theta_{hkl} \) is the angle of the peak position and \( L_{hkl} \) is crystallite length. This equation can be interpreted that the width of the peak is inversely proportional to the size of the crystallite [20].

2.3.2 Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) image is one of the most convenient tools to look into the morphology of nanostructure, which provides valuable information on its favourable properties to researchers. [21, 22]
**Figure 2-15** shows a schematic diagram of the SEM setup. Firstly, electrons are emitted from the electron gun on the top. These electrons are accelerated at an applied voltage and then pass through the condenser lens and objective lens to form an electron beam with a few nanometer diameters. When the beam hits the surface of the specimen, the interaction between the beam and specimen occurs to produce the electron signals. During the scanning of the specimen surface, the electron signals are collected and processed by the detector, in which the signals are converted into brightness points based on the number of detected electrons and then display corresponding electron image on the screen. [22]

![Schematic diagram of the SEM](image)

**Figure 2-15 The schematic diagram of the SEM. [23]**

Due to the interaction between the incident electron beam and specimen surface, there are kinds of electrons signals emitted (**Figure 2-16**), such as secondary electrons (SEs), backscattered electrons (BSEs), Auger electrons, X-ray, absorption electrons, transmission electrons and so on. [23, 24]
Figure 2-16 The interactions between the electron beam and the specimen (a) [22] and the generation of these electrons(b) [25].

Among these electrons, the secondary electrons and backscattered electrons are two main detection means for morphology imaging. The BSE shows lower resolution for morphology due to its related to chemical elements properties. However, the SEs exhibit better resolution due to its topographies with an optimal signal-to-noise ratio. In this way, SE is usually used in SEM to obtain surface morphology images. [26]

In addition, absorption electrons and BSEs can provide chemical composition information. The Auger electrons and X-rays usually are used to analyze the chemical composition in a specimen. Transmission electrons can be used in the transmission electron microscope (TEM), which can provide better resolutions to characterize surface morphology. [22]

2.4 References


Chapter 3

3 XANES and XEOL studies of TiO\textsubscript{2} nanotubes

3.1 Introduction

The one-dimensional (1D) TiO\textsubscript{2} nanotube and its derivatives have been extensively developed due to their potential use in water-splitting, and lithium-ion batteries. [1-4] More importantly, TiO\textsubscript{2} is one of the solar-driven substrates for photovoltaics. The solution to optimize their morphology with increasing the photocatalytic efficiency has been sought for some time. [5, 6] Three phases of TiO\textsubscript{2} are existing in nature: anatase, rutile and brookite. Based on previous studies [7, 8], the mixed-phase TiO\textsubscript{2} (anatase and rutile) with a specific ratio (Degussa P25, rutile/anatase 80:20) shows a higher efficiency for photocatalysis, which motivates further study on optimizing TiO\textsubscript{2} structure via the mixed-phase method.

As a key to designing the desirable TiO\textsubscript{2} NTs with mixed phases towards their applications, the phase transition, from anatase to rutile, has drawn much attention. This irreversible phase transition can be induced by annealing at a proper temperature. Furthermore, the 1D TiO\textsubscript{2} nanotubes have attracted much attention due to their easy controllability in tube sizes (length, diameter, and thickness) and excellent uniformity, which enables rapid transferring of charge carriers along the longitudinal direction. [9] To date, many types of research are focused on the size dependence of the anatase-to-rutile phase transition TiO\textsubscript{2} nanocrystals. Generally, there is a proportional relationship between phase transition temperature and size. [10, 11] The phase transition of TiO\textsubscript{2} nanoparticle (8-21 nm) occurs with annealing at the temperature within the range from 520 to 600 °C. [12] The TiO\textsubscript{2} nanoparticle with around 10 nm diameter showed the anatase-to-rutile phase transition from 550 °C. [13] In addition, the phase transition temperature of TiO\textsubscript{2} nanoparticles with 200 nm is between 750 °C and 850 °C, which is significantly higher than that of phase transitions in bulk TiO\textsubscript{2} (~600 °C). [14]

However, the clear relationship between the size of TiO\textsubscript{2} NTs and annealing temperature when phase transition has not yet been reported. In this chapter, highly ordered
amorphous TiO$_2$ nanotube arrays are synthesized via an electrochemical anodization method, which allows the control of the size of the nanotubes under various conditions. Subsequent thermal-annealing treatments at different temperatures are used to obtain desired phases of TiO$_2$ nanotubes. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) are used to track the morphology and phase transformation of the nanotubes, respectively. The chemical environment including local symmetry and the luminescence origin of the TiO$_2$ NTs can be tracked by X-ray absorption near-edge structures (XANES) and X-ray excited optical luminescence (XEOL) technique.

3.2 Experimental section

3.2.1 TiO$_2$ nanotubes synthesis

Highly ordered TiO$_2$ nanotubes are prepared via a two-step electrochemical anodization method (Figure 3-1), which includes two electrodes. In the experiments, the Ti foil (Goodfellow, 0.1 mm thick, ~1 cm × 2.5 cm) is the anode and the Pt wire is the cathode. A fluoride-containing solution (0.3 wt.% NH$_4$F, 2 vol% water and ethylene glycol) is used as the electrolyte. In the first-step of anodization, the Ti foil is anodized at a potential of 50 V (Hewlett-Packard 6209B DC power supply) for 4 hours at room temperature (21 °C). After that, TiO$_2$ NTs formed on the Ti foil are removed by the ultrasonic rinse in 1 M HCl solution with nanoconcaves left behind. Before the next step, the TiO$_2$ NTs are rinsed by de-ionized (DI) water and ethanol for 3 times. In the second-step of anodization, the cleaned Ti foil with nanoconvaves is anodized again to produce highly ordered TiO$_2$ nanotubes with different anodization time. The anodization time is 15 min, 30 min, 60 min and 120 min for #1, #2, #3 and #4 TiO$_2$ NTs, respectively. After that, the TiO$_2$ NTs are rinsed by DI water and ethanol three times to clean the residual electrolyte on the surface of TiO$_2$ NTs samples. Finally, thermal-annealing treatments are applied to TiO$_2$ NTs optionally to induce phase transformations. In this step, samples were annealed at 500 °C, 750 °C, 900 °C for 2 hours in ambient air with a ramping rate of 15 °C/min using a KSL-1100X high temperature muffle furnace.
Figure 3-1 Schematic of electrochemical anodization. [15]

3.2.2 Characterization

Scanning electron microscopy (SEM, LEO 1540XB and 1530XB) is used to provide morphology information especially size information of different TiO$_2$ NTs. X-ray diffraction (XRD, Rigaku Ru200BVH, Co K$_\alpha$ radiation with $\lambda=1.8\text{Å}$) is used to determine the phase of TiO$_2$ NTs. The synchrotron experiments data was collected at CLS (Saskatoon, SK, Canada). The X-ray absorption near edge structure (XANES) on Ti L$_{3,2}$-edge and O K-edge is aimed to track the local and electronic structures. The XANES spectra are collected at the Spherical Grating Monochromator (SGM) beamline (resolving power $E/\Delta E > 5000$). [16] Before the measurement, the TiO$_2$ NTs samples standing on the Ti metal substrate were mounted on a sample holder normal to the incident beam. In the measurement, the data of the energy range of Ti L$_{3,2}$-edge XANES and O K-edge XANES is collected at 453–474 eV and 520–575 eV, respectively. Furthermore, the total electron yield (TEY) and fluorescence yield (FLY) modes are applied and corresponding specimen current and fluorescence are recorded at the same time, respectively.

Furthermore, the X-ray excited optical luminescence (XEOL) was conducted at the SGM beamline to probe defect emission. The excitation energy was selected across the Ti L$_{3,2}$-edge (453–474 eV) and O K-edge (520–575 eV). During the experiment, the excitation energy can be fixed to excite below, at and above the edge of interest (Ti L$_{3,2}$-edge and O K-edge in this case). The wavelength of the luminescence can be recorded from 200 to
1000 nm. All XANES and XEOL spectra in this study are normalized to the incident photon flux, I₀.

**Results and discussions:**

### 3.3 Anodization time-dependent TiO₂ NTs

#### 3.3.1 Morphology

The SEM images of TiO₂ NTs on the Ti metal substrate prior to and after annealing at various temperatures are shown in Figure 3-2 (a-d). As-prepared TiO₂ NTs show highly ordered nanotube arrays (Figure 3-2 (a)), in which nanotubes are stacking together from top to bottom with homogeneous hollow structures while each nanotube is amorphous. The round cap structure appears on the bottom side and an additional TiO₂ oxide layer shows on the top side.

With annealing treatments, TiO₂ NTs achieve phase transitions according to their XRD patterns (Figure 3-2 (e)). After annealing at 500 °C (for 2 hours), as-prepared TiO₂ NTs achieved their first phase transformation, from amorphous to anatase. There is a sintering effect in anatase structure (Figure 3-2 (b)), which shows cracks throughout the wall of nanotubes. These cracks are due to the diffusion of bulk defects to the surface of nanotubes during the crystallization and strain-relief from the bulk of nanotubes during the annealing treatments. When the annealing temperature is increased to 750 °C, the rutile phase appears while the anatase phase still partly remains based on their XRD patterns. Therefore, it indicates a mixed-phase (anatase and rutile) structure of TiO₂ NTs was induced by annealing at 750 °C for 2 hours. These results agree with the results reported previously. [17] It also offers the hope that the controlled mixed-phase structure can be obtained by annealing between 500 °C and 750 °C.
Figure 3-2 SEM images of as-prepared (AP) amorphous TiO$_2$ NTs (#2 sample: anodized at 50 V for 4h in the first step and 30 min in the second step) (a) and annealed at different temperatures (c-d) together with their XRD patterns (e). All scale bars in SEM images are 200 nm.
In Figure 3-2 (c), although partial nanotube structure is maintained, the smooth morphology of each nanotube has been destroyed. However, increasing the annealing temperature to 900 °C, the nanotube morphology of TiO$_2$ entirely disappear. According to the XRD patterns (Figure 3-2 (e)), the TiO$_2$ NTs completes the second phase transformation, from anatase to rutile, at 750 °C annealing for 2 hours. Figure 3-3 (a-d) shows the side view and cross-sectional images of as-prepared TiO$_2$ NTs anodized at 50 V for 4 h in the first anodization step. In the second anodization step, samples #1-#4 were grown at the same static potential (50 V) for 15 min, 30 min, 60 min and 120 min, respectively. It can be seen that there is a good control of the size of TiO$_2$ with nanotube morphology. These four samples show well-aligned nanotube arrays. Their size information, as well as fabrication condition, are summarized in Table 3-1.

According to their size information (Figure 3-3 (e)), the lengths of TiO$_2$ NTs show an obvious increasing trend with increasing anodization times (from 15 min to 120 min). More specifically, the lengths of NTs are generally proportional to the anodization times that are within the range from 15 min to 60 min. After that, the increasing rate of length becomes slower and NTs achieve a length of around 3420 nm after 120 min-anodization. However, the outer diameter and thickness of the nanotubes’ wall show a slight decrease with increasing reaction time. More importantly, the calibration curve of size (Figure 3-3 (e)) can be used to synthesize the NTs with a specific size. As mentioned above, the TiO$_2$ NTs are products of oxide layer formation and the etching process. With anodization time increasing, it allows nanotube to grow before they achieve equilibrium. Basically, the longer anodization time, the longer the TiO$_2$ nanotubes. However, the length of NTs cannot increase all the time in the anodic process and their length is self-limited. More specifically, the electric field across the oxide layer is defined as Equation 3-1, where the U is the potential applied and d is the thickness of the oxide layer. [18] This field can control the ion migration in the anodic process, and it will decrease when oxide layer is thicker. Finally, it is too small to force ion to migrate and the grow of the length of NTs will be stopped.

$$F = \frac{U}{d}$$  \hspace{1cm} (3-1)
The increasing lengths of all nanotube samples, in this case, indicate that these four reaction times have good control for the length of nanotubes. Furthermore, the inner diameter shows a slight increase and the thickness of the nanotubes’ wall is decreased with anodization time increasing, which is due to the dissolution rate is slightly higher than the formation rate of oxide layer. In addition, the anodization time has a smaller impact on the diameter or the thickness than the length of nanotubes.

![SEM images of as-prepared TiO_2 NTs samples (a-d) anodized for various times together with their size information (length, outer diameter and thickness of nanotube wall) (e). All scale bars in SEM images are 200 nm.](image-url)
### Table 3-1 Size of the as-prepared (amorphous) TiO₂ NTs anodized at various times.

<table>
<thead>
<tr>
<th>NTs</th>
<th>Voltage (V)</th>
<th>1st time (min)</th>
<th>2nd time (min)</th>
<th>Electrolyte</th>
<th>Length (nm)</th>
<th>Outer diameter (nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>240</td>
<td>15</td>
<td>0.3%NH₄F+EG</td>
<td>572±30</td>
<td>167±9</td>
<td>60±7</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>240</td>
<td>30</td>
<td>0.3%NH₄F+EG</td>
<td>1250±66</td>
<td>162±9</td>
<td>52±6</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>240</td>
<td>60</td>
<td>0.3%NH₄F+EG</td>
<td>2340±120</td>
<td>160±7</td>
<td>50±5</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>240</td>
<td>120</td>
<td>0.3%NH₄F+EG</td>
<td>3430±175</td>
<td>152±4</td>
<td>45±4</td>
</tr>
</tbody>
</table>

Figure 3-4 XRD pattern of four TiO₂ NTs samples (#1-#4) annealed at 750 °C for 2 hours. The peaks marked with A and R indicate the peaks from anatase crystal structure and rutile crystal structure, respectively.

To track the relationship between the phase transition behaviour and their sizes, these four samples with different sizes under the same annealing treatment (750 °C for 2 hours) have been investigated, as shown in Figure 3-4. At first glance, some samples have both anatase and rutile phases, which suggests they are mixed-phase structures. Sample #1 shows mostly the rutile phase while sample #2 exhibits a dominant-rutile structure with a minor anatase phase. XRD results also indicate that sample #3 has anatase features and #4 shows the anatase phase as well. These different phase compositions under the same annealing treatment provide evidence for different phase transition behaviour of samples of different morphology.
Table 3-2 Weight composition of the rutile phase in four TiO$_2$ NTs samples (#1-#4) annealed at 750 °C for 2 hours. The $A_R$ and $A_A$ are intensities of integrated diffraction peaks from rutile (110) and anatase (101), respectively. The $W_R$ is weight composition of the rutile phase

<table>
<thead>
<tr>
<th>NTs</th>
<th>A (101) position</th>
<th>Peak intensity</th>
<th>$A_A$</th>
<th>R (110) position</th>
<th>Peak intensity</th>
<th>$A_R$</th>
<th>$W_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.60</td>
<td>152.67</td>
<td>27.24</td>
<td>32.14</td>
<td>7250.6</td>
<td>1245</td>
<td>98.1%</td>
</tr>
<tr>
<td>2</td>
<td>29.66</td>
<td>455.85</td>
<td>111.4</td>
<td>32.24</td>
<td>3503.8</td>
<td>1035</td>
<td>91.3%</td>
</tr>
<tr>
<td>3</td>
<td>29.66</td>
<td>1512.5</td>
<td>486.4</td>
<td>32.18</td>
<td>114.82</td>
<td>10.93</td>
<td>2.50%</td>
</tr>
<tr>
<td>4</td>
<td>29.72</td>
<td>1811.8</td>
<td>630.3</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

More importantly, the XRD pattern can be used to determine the phase composition in the mixed-phase TiO$_2$ NTs by the ratio of the areas under the anatase (101) and rutile (110) peaks. The phase composition (rutile) can be expressed by the following equation [13, 19],

$$W_R = \frac{A_R}{0.884A_A + A_R}$$

where the $W_R$ is weight composition of the rutile phase, $A_R$ and $A_A$ are intensities of integrated diffraction peak from rutile (110) and anatase (101), respectively. Noted that the peak area of anatase is corrected by a factor of 0.884. [19] The weight compositions (rutile) of sample #1 to #4 TiO$_2$ NTs annealed at 750 °C determined by Equation 3-1 are summarized in Table 3-2.

It can be noticed that the rutile phase shows decreasing proportions from sample #1 to #4 (from smaller size to a bigger size of TiO$_2$ NTs). Recall that phase transformation of TiO$_2$ is from amorphous to anatase and then to rutile. TiO$_2$ NTs with a smaller grain size can start phase transition at a lower annealing temperature with the same annealing time. [6] In this case, smaller NTs have a higher composition of the rutile phase compared to bigger samples. It indicates that smaller NTs start phase transition at a lower temperature and convert to a higher proportion of the rutile phase than bigger NTs under the same annealing treatment (at 750 °C for 2 hours). In this way, bigger TiO$_2$ retains more anatase characters and needs a higher temperature to achieve a complete phase transition.
3.3.2 XANES spectra and XEOL analysis

To conduct a comprehensive study on the dependence of the phase transition of the highly ordered TiO$_2$ NTs upon their morphology (size), the electronic structure and defect of mixed-phase samples are tracked by X-ray absorption near-edge structure (XANES) together with X-ray excited optical luminescence (XEOL). The former tracks the unoccupied electronic states at the bottom of the conduction band the latter technique tracks the defect emission states characteristic of the anatase and rutile phases. [20, 21]

Fine structure at the Ti L$_{3,2}$-edge XANES and the O K-edge XANES of TiO$_2$ NTs samples annealed at 750 °C as well as standard anatase and rutile are shown in Figure 3-5. In general, XANES tracks X-ray absorption when electrons transit to unoccupied states in their local environment from core states. As mentioned, there are two detection modes for XANES measurement: total electron yield (TEY) and total fluorescence yield (FLY). TEY is a surface-sensitive technique due to the short escape depth of electrons from nanotubes while FLY is bulk-sensitive by collecting fluorescent X-rays from inside the tubes at least 2 orders of magnitude deeper than electron yield. [22] Combining these two detection modes, the phase transformation direction (e.g. inside out or the other way around) can be investigated.

As mentioned above, surface information of TiO$_2$ NTs is monitored by TEY spectra at the Ti L$_{3,2}$-edges as well as the O K-edge. In the TEY spectra of Ti (Figure 3-5(a)), two pre-edge features (p1 and p2) are from core-hole-d-electron interactions [8]; peaks a-c (at the Ti L$_3$-edge) and peaks f-g (at the Ti L$_2$-edge) come from electron transitions from the Ti 2p$_{3/2}$ and 2p$_{1/2}$ to the unoccupied Ti 3d states, respectively. At both the Ti L$_3$-edge and Ti L$_2$-edge, peaks are split into 3d-t$_{2g}$ state (a at the Ti L$_3$-edge and d at the Ti L$_2$-edge) and 3d-e$_g$ state (b-c at the Ti L$_3$-edge and e at the Ti L$_2$-edge) resulting from crystal field splitting, which destroys the degeneracies of electron orbital states (usually d orbitals) by the effect of attraction between transition metal cations (Ti) and its ligands (O) with negative charge. In addition, the 3d-e$_g$ state at the Ti L$_3$-edge shows further splitting into peak b and c, which is generated by the local [9] or long-range [10] tetragonal distortion at the Ti site of the TiO$_6$ from octahedral symmetry. More importantly, these different splitting behaviours due to different distortion can be used to identify crystal structure.
The intensity ratio between peak b and peak c indicates the unique features of anatase (D_{2d}) and rutile (D_{2h}). For example, it has been established both by experiment and theory that more intense features of peak b than that of peak c indicates that anatase phase is dominant character in the structure, while a more intense peak c suggests a rutile-dominant structure.

Figure 3-5 Ti L_{3,2}-edge XANES of TiO_2 NTs samples (#1-#4) collected in total electron yield (TEY) mode (a) and in fluoresce yield (FLY) mode (b). O K-edge XANES collected in TEY mode (c) and FLY mode (d). The standard anatase and rutile powder samples (Sigma-Aldrich) are also recorded for the reference in each spectroscopy.
Based on Ti TEY spectra (Figure 3-5 (a)), TiO$_2$ NTs samples with the same annealing treatment (at 750 °C for 2 hours) show different intensity ratios between features b and c which indicates different phase transition behaviour and dominant phase. Compared to standard anatase and rutile spectra, #1 TiO$_2$ NTs show a rutile-dominant structure while #2 NTs indicate a mixed-phase structure with a higher rutile proportion (higher peak c). In addition, #3 TiO$_2$ NTs and #4 NTs show both anatase-dominant crystal structure. If their morphology features especially size are considered, an important trend (from sample #1 to #4) that more anatase and fewer rutile features is obtained with increasing nanotube size. To provide a semi-quantitative analysis of the mixed-phase structure, the linear combination fitting is conducted on the TEY XANES spectra based on standard anatase and rutile (shown in Figure 3-5 (a)). The fitting results are summarised in Table 3-3, which presents the anatase and the rutile ratio in sample #1-#4 TiO$_2$ NTs. Noted that all anatase transformed to rutile in #1 NTs while there is 24.4% anatase composition left in the #2 NTs with the same annealing treatments (750 °C for 2 hours). Furthermore, the #3 TiO$_2$ NTs show a different ratio mixed-phase that the anatase phase counts 82.9% and the rutile phase counts 17.1%, which indicates an anatase-dominant structure. There is an anatase structure in #4 NTs and no rutile composition detected. These results are consistent with the phase contents (rutile) of each sample calculated via their XRD patterns.

### Table 3-3 Linear combination fitting results of peaks b and c in TEY XANES spectra at the Ti L$_{3,2}$ edge (Figure 3-5(a))

<table>
<thead>
<tr>
<th>NTs</th>
<th>Length (nm)</th>
<th>Outer diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Annealing temperature (°C)</th>
<th>Anatase (%)</th>
<th>Rutile (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>572±30</td>
<td>167±9</td>
<td>60±7</td>
<td>750</td>
<td>0.000</td>
<td>1.000</td>
</tr>
<tr>
<td>2</td>
<td>1250±6</td>
<td>162±9</td>
<td>52±6</td>
<td>750</td>
<td>0.244</td>
<td>0.756</td>
</tr>
<tr>
<td>3</td>
<td>2340±1</td>
<td>160±7</td>
<td>50±5</td>
<td>750</td>
<td>0.829</td>
<td>0.171</td>
</tr>
<tr>
<td>4</td>
<td>3430±1</td>
<td>152±4</td>
<td>45±4</td>
<td>750</td>
<td>1.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

As illustrated above, the TiO$_2$ NT achieves its phase transformation from amorphous to anatase and then to rutile with increasing annealing temperature. Based on the TEY spectra, a smaller sample needs a lower temperature to start phase transition to rutile while a bigger TiO$_2$ NTs requires a higher temperature to achieve phase transition to
rutile. It indicates that the phase transition highly depends on their size and annealing temperature. It should be noted that the smaller the structure the larger the fraction of atoms on the surface. Since the cohesion energy of surface atoms is less than that of the bulk due to unsaturated coordination, the melting point (temperature of occurring phase transition) of nanostructures is always lower than that of bulk materials, which explains the lower transition temperature for smaller nanotubes.

One the other side, TEY at the O K-edge also provides valuable information to understand the electronic structure. In the TEY spectra of O (Figure 3-5 (c)), the peaks A and B result from the electronic transitions from O 1s to O 2p covalently hybridized with 3d-t$_{2g}$ and 3d-e$_g$ states of Ti, respectively. The t$_{2g}$ and e$_g$ states are split from the Ti 3d band due to crystal field splitting. [23] Furthermore, the electronic transition from O 1s to O 2p covalently hybridized with Ti 4sp states contributes to peaks C and D. In specifically, peak C is from the antibonding state while peak D the bonding state between O 2p and Ti 4sp hybridized state. [23, 24] Peak E at the higher energy region suggests that TiO$_2$ crystalline structure has long-range order. [25] Comparing the spectra of standard anatase, the peak D further split into D$_1$ and D$_2$ and they are assigned to b$_{2u}$ and b$_{3u}$ states in rutile structure, respectively. [24] It is also noted that a blueshift in energy for peak C and E of rutile structure (D$_{2h}$), which indicates it is different from local symmetry in anatase (D$_{2d}$). However, peak C and D are assigned to b$_3$ and e energy level in the anatase structure. [24]

According to Figure 3-5 (c), the #1 and #2 TiO$_2$ NTs show a rutile-like structure while the #3 and #4 NTs indicate anatase-like features according to their reference generally. #1 TiO$_2$ NTs show almost the entirely rutile phase. However, it can be noted that peaks D$_1$ and D$_2$ of #2 NTs are not well resolved compared to peaks D$_1$ and D$_2$ of standard rutile. Furthermore, there is a redshift of peak E in the spectra of #2. These two observations demonstrate that the anatase feature also exists in #2 TiO$_2$ NTs and thus #2 showed mixed-phase structure with a higher rutile proportion. For #3, it is worth mentioning that a slightly broader peak D compared to standard anatase suggests that a very small amount of rutile features remain in its structure. #4 shows almost entirely anatase structure shown
by a perfect match to standard anatase reference. These results from the Ti L\(_{3,2}\)-edge TEY and the O K-edge XANES are consistent to each other.

The electronic structure of TiO\(_2\) NTs in the bulk is investigated by FLY XANES spectra at the Ti-L\(_{3,2}\)-edge and O K-edge (Figure 3-5 (b) and (d)). As illustrated in Chapter 2, the attenuation length of X-ray in anatase and rutile are 0.14 \(\mu\)m and 0.13 \(\mu\)m above the Ti L\(_{3,2}\)-edge (454.4 eV) and O K-edge (547.5 eV), respectively, which are much deeper than surface- sensitive (0.1 nm) TEY detection.

At first glance, Ti L\(_{3,2}\)-edge FLY spectra show a damped and broader trend compared with TEY spectra, which is owing to the self-absorption. [7] It usually occurs in the soft X-ray region (photon energy range: 250 eV–1000 eV), especially for the thick sample. [21] There are similar spectra for TEY and FLY at the Ti Ti-L\(_{3,2}\)-edge, which indicates that not only surface but also bulk of TiO\(_2\) NTs undergo phase transitions. On the other side, TEY and FLY at the O K-edge also show the same story; phase transition happens in both the bulk and surface of the samples.

From XANES, the local environment, including local symmetry and Ti oxidation were tracked. The relationship between the luminescence and related elemental and chemical environment can be detected and predicted by X-ray absorption near-edge structures (XANES) and X-ray excited optical luminescence (XEOL) technique.[26]

As illustrated in Chapter 2, XEOL is the result of the recombination of electrons and holes near the bandgap via transition or energy transfer to defect states associated with the thermalization process. The intensity of luminescence can decrease due to less efficient energy transfer (to the optical channel). For example, the decreasing of sampling depth (increasing absorption) above the edge reduces the thermalization path.

Furthermore, the intensity of XEOL is very sensitive to the excited edge, which indicates the elemental specificity of XEOL. Based on previous studies [21], the visible emission (at 520 nm wavelength) is from defects in the anatase structure while near-IR emission (at 820 nm wavelength) results from the rutile detect. This information be used as the fingerprint to distinguish different crystalline structures. Usually, the defects in anatase are considered oxygen vacancies in the lattice. For the rutile, the emission is due to an
intrinsic defect where recombination happens between deep electron trap and holes. [26, 27]

Figure 3-6 The XEOL maps of #1 TiO$_2$ NTs annealed at 750 °C for 2 hours at the Ti L$_{3,2}$-edge (a) and O K-edge (b). The XEOL maps of #4 TiO$_2$ NTs annealed at 750 °C for 2 hours at the Ti L$_{3,2}$-edge (c) and the O K-edge (d). The x-axis is wavelength (in nm) of emission, the y-axis is excitation energy selected and the z-axis is the intensity of emission. The intensity of emission is colour-coded.

Based on studies [21], crystalline TiO$_2$ NTs are light-emitting while amorphous TiO$_2$ NTs do not show any luminescence. Thus, XEOL results are collected from annealed samples, which are measured at fixed excitation energy across the interesting edges. The
excitation energies are selected across the Ti L$_{3,2}$-edge and O K-edge, which are marked (with *) in Figure 3-5 (a) and (b).

**Figure 3-6** shows the Ti L$_{3,2}$-edge and O K-edge excited XEOL of #1 and #4 TiO$_2$ NTs after annealing. The #1 TiO$_2$ NTs (**Figure 3-6(a) and (b)**) indicate a rutile-dominant structure based on their emission band in the near-IR region. It also can be noted there is a very weak emission at 520 nm wavelength from both Ti XEOL and O XEOL perspectives, which provides evidence that anatase also exists in its structure. These results are in good accordance with their X-ray absorption spectroscopy. However, the #4 TiO$_2$ NTs are almost entirely anatase phase according to the emission band at 520 nm wavelength only.

As illustrated above, the XEOL intensity is sensitive to the excited energy across the edges, which indicates the specificity of the element. In our case, the K-edge of O (531 eV) is higher in energy than the Ti L$_{3,2}$-edge (458 eV). When the O K-edge is excited, the Ti L$_{3,2}$-edge is also excited. It contributes to a higher intensity of the emission in the XEOL across the O K-edge than that of the Ti L$_{3,2}$-edge for both #1 and #4 TiO$_2$ NTs. Additionally, the XEOL intensity variation from rutile shows different behaviour from anatase structure based on the Ti XEOL (**Figure 3-6(a) and (c)**). More specifically, the intensity of emission from the rutile structure of #1 TiO$_2$ NTs (at 820 nm wavelength) is more obviously reduced when excitation energy is tuned above the threshold (458 eV), while increasing trend of the intensity was observed at 520 nm wavelength (from anatase) of #4 TiO$_2$ NTs. This different change trend probably indicates the different region of anatase and rutile center. It can be considered that the X-ray penetrates deeply (sampling mainly the bulk) when the excitation energy is set below the Ti L$_{3,2}$-edge. The probe depth will decrease abruptly above the edge and sampling the surface or near surface region. The obvious decrease of rutile intensity with excitation energy above the Ti L-edge (458 eV) indicates that the surface has less contribution to the rutile defect. In addition, the anatase-dominant #4 NTs sample (**Figure 3-6(c) and (d)**) shows a wider emission band than the rutile-dominant structure. In the mixed-phase structure, it is worth mentioning that there is a competition between the two optical decay channels (associated with anatase or rutile defect) to archive recombination of electron and hole pairs.
Furthermore, electron or hole scavengers from rutile may quench the anatase emission and the recombination rate of electron-hole in rutile is dramatically faster than that of anatase. [28] Thus, the rutile emission in the structure can be produced more efficiently, which showed a narrower emission band in XEOL spectra.

### 3.4 Anodization potential-dependent TiO$_2$ NTs

#### 3.4.1 Morphology

The other series are anodization potential dependence of TiO$_2$ NT, which are synthesized at the different potentials for the same reaction time. Figure 3-7 (a-c) show SEM images of amorphous #7, #2 and #8 TiO$_2$ NTs samples anodized at 35 V, 50V and 65 V for 30 min, respectively. These three samples show highly-ordered TiO$_2$ NTs arrays with different sizes (length, diameter and thickness). It is worth noting that there is a good control of the size of TiO$_2$ with nanotube morphology. Figure 3-7 (d) demonstrates the relationship between their size and the anodization potentials applied to the experiments. More details in the fabrication condition and their size information are summarized in Table 3-4.

At first glance, highly ordered TiO$_2$ NTs are formed at all anodization potentials applied. The length, outer diameter and thickness of TiO$_2$ NTs show an increasing trend as the anodization voltage increases. The #7 TiO$_2$ exhibits a 296-nm-long nanotube morphology with a diameter of 58 nm and a thickness of 21 nm after anodizing at 35 V for 30 min. With a higher anodization voltage (50 V) for the same anodization time, the #2 NTs achieve a length of approximately 1250 nm, a diameter of 162 nm and a thickness of 54 nm. However, the #8 TiO$_2$ shows slight increases in their size (a length of 1333 nm, a diameter of 198 nm and a thickness of 71 nm) with 65 V anodization potential (. In addition, the inner diameters can be calculated by the outer diameters and thicknesses, which show an increasing trend.

**Figure 3-7 (d)** indicates the length increase fast when the potential within the range of 35 V to 50 V and then tend to be saturated. These results thus imply that it is efficient to increase the size of NTs by increasing anodization potential within the range of 35 V to 50 V. However, this efficiency drops when the anodization voltage is above 50 V. The
consideration of this sequence is related to the growth mechanism of NTs. More importantly, there is an almost linear relationship between outer diameter or thickness and anodization voltage, respectively. It is in good agreement with previous studies. [9, 29]

![SEM images of as-prepared #7 (a), #2 (b) and #8 (c) TiO$_2$ NTs samples anodized at the different potentials for the same anodization time together with their size information (length, outer diameter and thickness of nanotube wall) (d). All scale bars in SEM images are 200 nm.](image-url)
Table 3-4 Size of the as-prepared (amorphous) TiO\textsubscript{2} NTs anodized at the different potentials.

<table>
<thead>
<tr>
<th>NTs</th>
<th>Voltage (V)</th>
<th>1\textsuperscript{st} time (min)</th>
<th>2\textsuperscript{nd} time (min)</th>
<th>Electrolyte</th>
<th>Length (nm)</th>
<th>Outer diameter (nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>35</td>
<td>240</td>
<td>30</td>
<td>0.3%NH\textsubscript{4}F+EG</td>
<td>296±22</td>
<td>58±8</td>
<td>21±3</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>240</td>
<td>30</td>
<td>0.3%NH\textsubscript{4}F+EG</td>
<td>1250±66</td>
<td>162±9</td>
<td>54±6</td>
</tr>
<tr>
<td>8</td>
<td>65</td>
<td>240</td>
<td>30</td>
<td>0.3%NH\textsubscript{4}F+EG</td>
<td>1333±90</td>
<td>198±16</td>
<td>71±7</td>
</tr>
</tbody>
</table>

As illustrated above, the TiO\textsubscript{2} NTs are products of oxide layer formation and the etching process. The anodization voltage governs the electric field strength applied on the oxide layer, which determines the rate of the field-assisted oxidation of the metal. In addition, the Ti\textsuperscript{4+} can be injected from the metal/metal oxide interface to react with F\textsuperscript{-} migrating towards metal under the application of anodization potential. The product of this reaction is [TiF\textsubscript{6}]\textsuperscript{2-}, which is a stable and soluble complex. It is worth noting that this field-assisted reaction will compete with the chemical dissolution of TiO\textsubscript{2} by the effect of F\textsuperscript{-}. From this point, the anodization voltage has an efficient range to control the morphology of TiO\textsubscript{2}. If the voltage applied is too high (> 240 V) [30], it will drive the Ti\textsuperscript{4+} into the electrolyte [31] and the F\textsuperscript{-} towards the metal. It prevents the etching process of TiO\textsubscript{2} under the presence of F\textsuperscript{-} and could lead to a break-down event; that is that the oxide layer will be detached from the metal substrate. If the voltage applied is too low (< 10 V) [30], the rate of field-assisted oxidation is lower than the rate of chemical dissolution of TiO\textsubscript{2}, preventing the formation of TiO\textsubscript{2} nanotube morphology.

Within the range of anodization voltage applied (35-65 V), the outer diameter and the thickness of the wall show an increasing trend as voltage increases. [9, 32] Basically, the higher the potential applied, the higher the electric field strength and thus the higher speed of migration of ions, leading to a higher rate of formation and the etching process. [9] More specifically, the high potential provides more force on the dissolution of TiO\textsubscript{2} by the effect of F\textsuperscript{-}, which contributes to the larger pore size and longer tube length. [30] However, the increasing potential at the higher range is not as efficient as the lower potential to increase the size of TiO\textsubscript{2} NTs. It can be considered that although the anodization voltage increases, the chemical dissolution of oxide by F\textsuperscript{-} in the etching
process is still low. In other words, the rate of chemical dissolution is lower than the rate of oxide formation with high potential applied, and the difference between them is increased as anodization potential increases. [30]

Figure 3-8 XRD pattern of #7 TiO$_2$ NTs samples: as-prepared NT samples (AP) and NTs annealed at 500 °C, 750 °C and 900 °C for 2 hours, respectively.

With annealing treatments, #7 TiO$_2$ NTs achieve phase transitions according to their XRD patterns (Figure 3-8). After annealing at 500 °C (for 2 hours), as-prepared TiO$_2$ NTs achieved their first phase transformation, from amorphous to anatase. When the annealing temperature was increased to 750 °C, the rutile phase appears while the tiny anatase phase still partly remain based on their XRD patterns. Therefore, they indicate a mixed-phase (anatase and rutile) structure of TiO$_2$ NTs was induced. These results agree with the results reported previously. [17]

To conduct a comprehensive study on the phase transition of the highly ordered voltage dependence of TiO$_2$ NTs on their morphology (size), electronic structure of mixed-phase samples is tracked by x-ray absorption near-edge structure (XANES) and x-ray excited optical luminescence (XEOL).
3.4.2 XANES spectra and XEOL analysis

Figure 3-9 Ti L_{3,2}-edge XANES of TiO$_2$ NTs samples (#7, #2 and #8) collected in total electron yield (TEY) mode (a) and in fluorescence yield (FLY) mode (b). O K-edge XANES collected in TEY mode (c) and in FLY mode (d). The standard anatase and rutile powder (Sigma-Aldrich) are also recorded for the reference in each spectroscopy.

Fine structure at the Ti L$_{3,2}$-edge XANES and the O K-edge XANES of TiO$_2$ NTs samples annealed at 750 °C as well as standard anatase and rutile were shown in Figure
3.9. **Figure 3-9 (a)** shows TEY at the Ti L₃,2-edge spectra of the TiO₂ NT samples with different sizes annealed at the same temperature (at 750 °C for 2 hours) as well as standard anatase and rutile spectra for reference. It is worth mentioning that there are different intensity ratios between features b and c which indicates different phase transition behaviour and dominant phase. Compared to the references, #7 TiO₂ NTs show a rutile-dominant structure from the surface perspective. The #2 NTs indicate a mixed-phase structure with the more rutile features (higher peak c). However, #8 TiO₂ NTs exhibit a mixed-phase structure with the more anatase character.

Based on their size information, it is evident that more and more anatase features and fewer and fewer rutile features as the size of NTs increasing. In other words, more anatase-to-rutile transitions occur in the smaller NTs compared to the larger NTs under the same annealing conditions.

The electronic structure in the bulk of TiO₂ NTs is investigated by FLY XANES spectra at the Ti-L₃,2-edge (**Figure 3-9 (b)**). Firstly, FLY spectra show damped and broader features compared with TEY spectra, which is due to the self-absorption. [7] It usually occurs in the soft X-ray region (photon energy range: 250 eV–1000 eV), especially for the thick sample. [21] In **Figure 3-9 (b)**, #7 TiO₂ NTs show a mixed-phase structure while #2 NTs indicate a structure with more anatase features (higher peak b). #8 TiO₂ NTs exhibit a mostly rutile structure. There are similar spectra for TEY and FLY at the Ti Ti-L₃,2-edge, which indicates that not only surface but also the bulk of TiO₂ NTs samples undergo phase transitions. The direction of phase transition from anatase to rutile can be explored by TEY together with FLY. In this case, #8 indicates a mixed-phase structure with more anatase features from the surface perspective while an almost entire anatase structure from the bulk perspective.

This observation indicates that the anatase-to-rutile phase transition probably occurs from surface to bulk. It is in good accordance with the previous study [33-35], which demonstrates that the surface nucleation dominates the anatase-to-rutile phase transition within the annealing temperature range of 700-800 °C. In that case, the phase growth of
rutile is highly dependent on the Gibbs free energy of the nanotube for anatase-to-rutile phase transitions ($\Delta G_{A\rightarrow R}$).

$$\Delta G_{A\rightarrow R} = \Delta G_{v,R}(T) - \Delta G_{v,A}(T) + (A_R \gamma_R - A_A \gamma_A) + (\Delta P_R V_R - \Delta P_A V_A)$$

$$= \Delta G_{v,R}(T) - \Delta G_{v,A}(T) + \left(\frac{3M \gamma_R}{\rho_R r_R} - \frac{3M \gamma_A}{\rho_A r_A}\right)$$

$$+ \left(\frac{2M f_R}{\rho_R r_R} - \frac{2M f_A}{\rho_A r_A}\right)$$

(3-3)

The total free energy is determined by volume energy $G_v$, surface energy $G_s$, and surface stress-induced energy, $G_f$. Subscripts A and R stand for anatase and rutile, respectively. A, V, M, r, and $\rho$ are surface area, molar volume, molecular weight, particle radius, and phase density. Subscript $\gamma$ is the surface free energy and $\Delta P$ is surface stress, $f$ is related excess pressure with a value of $(2f/r)$. As mentioned above, the anatase surface free energy contributes negative value to that free energy, which indicates that higher surface free energy will lead to a more negative impact on the total free energy and then more contribution to nonequilibrium transition from anatase to rutile. At the beginning of the transition, the rutile nucleation keeps consuming anatase structure from the surface until the total free energy becomes equal to or less than that of anatase. Thus, the smaller TiO$_2$ NTs with anatase structure can overcome the energy barrier easier to start the nucleation of a new phase (rutile in this case) compared to larger NTs, noting the smaller NTs have a larger free surface area. [35] In this way, there is more anatase features remain in the bigger NTs.

One the other side, TEY at the O K-edge provide valuable information to understand the electronic structures. Figure 3-9(c) shows the O K-edge TEY XANES spectra of 3 samples annealed at 750 °C (for 2 hours) as well as the standard anatase and rutile for the reference. At first glance, these 3 samples show different phase transition behaviours, with different splitting behaviour of peak D. #7 TiO$_2$ NTs show an entirely rutile-like structure with well-resolved D$_1$ and D$_2$ peaks. The #2 NTs indicates a rutile-like structure as well, in which peak D$_1$ and D$_2$ are not well resolved compared to #7 NTs and the standard rutile spectra. Furthermore, there is a redshift in the energy of peak E. They are responsible for that anatase feature also exists in #2 TiO$_2$ NTs and thus #2 has a mixed-
phase structure. It can be noted that an anatase-like structure of #8 TiO$_2$ NTs due to no obvious splitting of peak D. It is worth mentioning that a slightly broader peak D compared to standard anatase is observed, which suggests that a very small amount of rutile features remain in its structure. These results from the Ti L$_{3,2}$-edge TEY and the O K-edge XANES are corresponding to each other.

From the XANES perspective, the absorption behaviour of the element can be tracked, which is aimed to determine the element-specific local environment. Combining with XEOL technique, the relationship between luminescence and chemical environment can be built. In addition, it can provide valuable information especially for analyzing the structural defect luminescence [36] and determining the light-emitting component in the mixture of materials [37]. XEOL monitors the luminescence from the TiO$_2$ NTs under X-ray excitation. The luminescence intensity also depends on the size of the nanostructure, in which the thermalization path would be truncated due to the small size of nanostructures.

**Figure 3-10** shows XEOL spectra of #7 TiO$_2$ NTs with selected excitation energies at the Ti L$_{3,2}$-edge (a) and the O K-edge (b). The excitation energies are selected across the Ti L$_{3,2}$-edge and O K-edge, which are marked (with *) in **Figure 3-9 (a) and (c)**. In **Figure 3-10 (a)**, the visible emission peak at approximately 820 nm wavelength can be observed at all excitation energies. It is worth mentioning that 820 nm is consistent with 1.51 eV, which is less than band gap of the rutile phase (3.0 eV). Based on studies [21, 26], this emission is due to the radiation of defect in the rutile structure, which is an intrinsic defect where recombination happens between deep electron trap and holes. This emission band indicates the #7 TiO$_2$ NTs is rutile-dominant structure.
Figure 3-10 XEOL of #7 TiO$_2$ NTs annealed at 750 °C with selected excitation energies at the Ti L$_{3,2}$-edge (a) and the O K-edge (b). The x-axis is wavelength (in nm) of emission, the y-axis is excitation energy selected and the z-axis is the intensity of emission.
Figure 3-11 XEOL of #8 TiO$_2$ NTs annealed at 750 °C with selected excitation energies at the Ti L$_{3,2}$-edge (a) and the O K-edge (b). The x-axis is wavelength (in nm) of emission, the y-axis is excitation energy selected and the z-axis is the intensity of emission.
Furthermore, the intensity of luminescence is very sensitive to the excited edge, which indicates the elemental specificity of XEOL. More specifically, it is can be noted that there is an obvious decrease when the excitation energy above the edge (green curve in Figure 3-10 (a)). The luminescence intensity can be decreased when the energy transfer to a less efficient optical channel. In this case, the decreasing of sampling depth (increasing absorption) abruptly above the Ti L₃,₂-edge (458 eV) reduces the thermalization path, which is responsible for decreasing of luminescence intensity. In this process, the X-ray penetrate length decrease significantly due to the material absorbs a significant amount of the X-ray above its absorption edge. From this point, a significant fraction of electrons with high kinetic energy were created at or near the surface region, and these electrons do not fully participate in the thermalization. The decrease of luminescence also suggests that the defect is from the bulk region (deep level defect) of the rutile structure.

Figure 3-11 shows XEOL spectra of #8 TiO₂ NTs with selected excitation energies at the Ti L₃,₂-edge (a) and the O K-edge (b). It can be noted that two emission peaks display in Figure 3-11 (a), and visible emission (at 520 nm wavelength) indicates the defects from anatase structure while near-IR emission (at 820 nm wavelength) suggests the defects rutile phase, which can be used as the fingerprint to distinguish different crystalline structures. Thus, the #8 TiO₂ NTs indicates a mixed-phase structure while #7 indicates a rutile-dominant structure. Furthermore, it is worth mentioning that 520 nm is consistent with 2.38 eV, which is less than the band gap of the anatase phase (3.2 eV). The defect in anatase structure can be considered as an oxygen vacancy in the lattice. Following the theory discussing before, the intensity of luminescence above the Ti L₃,₂-edge (458 eV) can be noted (green curve) carefully. Interestingly, the visible emission peak shows a decrease while near-IR emission shows an increase when the exciting energy is above the edge. As illustrated above, the intensity will decrease when rutile defect has a bulk origin, which is in good agreement of discussion of #7 TiO₂ NTs. However, the increase of intensity of visible emission indicates that it is a surface-related defect of anatase origin. It can be considered that the X-ray penetrating length decrease significantly due to the material absorbs a significant amount of X-ray above its absorption edge. The increased intensity indicates more contributions to thermalization at the surface region.
The XEOL spectra at the O K-edge (Figure 3-10 (b) and Figure 3-11 (b)) provide valuable information to track their luminescence origin as well. At first glance, the XEOL spectra at the O K-edge indicate a similar emission band as XEOL spectra at the Ti L_{3,2}-edge, in which the #7 TiO\textsubscript{2} NTs indicates a rutile-dominant structure while the #8 TiO\textsubscript{2} NTs shows a mixed-phase structure. As illustrated above, the XEOL intensity is sensitive to the excited energy (edge of interest). In this case, the K-edge of O (531 eV) is higher in energy than the Ti L_{3,2}-edge (458 eV). When excitation energies were selected across the O K-edge (525-575 eV), these energies are above the Ti L_{3,2}-edge as well. It can be responsible for the higher intensity of the emission in the XEOL across the O K-edge than that of the Ti L_{3,2}-edge for both #7 and #8 TiO\textsubscript{2} NTs.

### 3.5 Conclusions

In this chapter, two series of TiO\textsubscript{2} NTs are synthesized by a two-step electrochemical anodization method; they are anodization time-dependent and anodization voltage-dependent highly ordered amorphous TiO\textsubscript{2} NTs. Thermal treatments were applied to achieve their desired phase, by phase transition from amorphous to anatase and then to rutile. The morphology features including size were tracked by SEM and phases are determined by XRD experiments, which shows a good control of size (length, diameter and thickness of the wall) and desirable phase of TiO\textsubscript{2} NTs. It is worth mentioning that the anodization time has a significant impact on the length of TiO\textsubscript{2} NTs while the anodization voltage mainly influences their diameter and thickness.

More importantly, the local environment and electronic structure of mixed-phase (anatase and rutile) TiO\textsubscript{2} NTs were tracked by XANES. The splitting behaviour of Ti 3d-t_{2g} state indicates their phase structure and it varies with different size TiO\textsubscript{2} NTs. It can be noted that there are more anatase features and fewer rutile features in the sample as anodization voltage increase based on their sizes, which indicates that more anatase-to-rutile transition occurred in smaller NTs compared to larger NTs under the same annealing conditions. The phase growth of rutile highly depends on the Gibbs free energy of the nanotube for anatase-to-rutile phase transitions. The smaller anatase NTs with higher surface free energy contributes to a more negative impact on the total free energy and then more contribution to nonequilibrium transition from anatase to rutile. The smaller
TiO$_2$ NTs in each series with anatase structure is easier to overcome the energy barrier to start the nucleation of a new phase (rutile in this case) compared to larger NTs. There are similar spectra between TEY and FLY at the Ti-L$_{3,2}$-edge, which indicates that not only surface but also the bulk of TiO$_2$ NTs samples undergoes phase transitions. As mentioned above, combining the surface-sensitive TEY and bulk sensitive FLY can determine the direction of phase transition. It is evident that the anatase-to-rutile phase transition occurs from surface to bulk at 750 °C annealing, which agreed with the previous studies [33-35]. They demonstrated that the surface nucleation dominates anatase-to-rutile phase transition occurs within in annealing temperature range of 700-800 °C.

XEOL is the product of the recombination of electrons and holes near the bandgap via transition or energy transfer to defect states associated with the thermalization process. Visible emission (at 520 nm wavelength) originates from defects in anatase structure while near-IR rutile emission (at 820 nm wavelength) results from the rutile phase, which can be used as a finger-print to distinguish its crystalline structure. The intensity of luminescence can decrease due to less efficient energy transfer (to the optical channel). In this case, the visible emission peak shows a decrease while near-IR emission shows an increase when the exciting energy is above the Ti L$_{3,2}$-edge of #8 TiO$_2$ NTs annealed at 750 °C. The results indicated that anatase emission and rutile emission are from the different regions of the specimen. More specifically, that rutile structure is related to the defects from bulk while the luminescent center is from anatase structure in the surface and near-surface region. Furthermore, the intensity of XEOL is very sensitive to the excited edge of interest, which indicates the elemental specificity of XEOL. Dominant characters of different phases from XEOL were in line with XANES results.

### 3.6 References


Chapter 4

4 Temperature-induced phase transitions of TiO$_2$ nanotubes by synchrotron based in-situ XRD

4.1 Introduction

The one-dimensional (1D) TiO$_2$ nanotubes (NTs) and their derivatives have been extensively developed due to their potential use in water-splitting, solar cell, and lithium-ion batteries. [1] For most applications, crystalline structures showed better performance than amorphous TiO$_2$. However, different phases, such as anatase and rutile, have different structures and properties, which lead to different performances in applications. Rather, anatase is preferred in photo-electrochemistry while rutile showed better performance in photocatalytic like degradation of methyl orange. [2] Furthermore, it is supposed that the anatase nanocrystal exhibits better photocatalytic properties than other phases of TiO$_2$. [3] Normally, the phase transitions, from amorphous to anatase and then to rutile, are induced by annealing treatments. Here, knowing the temperatures of annealing for a given morphology leading to phase transitions are highly valuable for their applications. Many factors are influencing this temperature, such as impurities, morphology and annealing conditions. [2] In these years, the phase transition of TiO$_2$ are investigated by X-ray diffraction [4-7], X-ray absorption spectroscopy [8, 9] and also X-ray excited optical luminescence [10]. However, there are fewer studies on synchrotron based in-situ high-temperature XRD on TiO$_2$ nanotubes, which can provide valuable information for real-time thermal treatment to induce phase transitions.

In this chapter, the characterization of the highly-ordered TiO$_2$ NTs arrays with different sizes (length, diameter and thickness) using in-situ synchrotron-based XRD will reveal the temperatures when phase transitions occur and show the difference of the phase transition process between NTs with different sizes, leading to a better understanding of the phase transition of TiO$_2$ in nanoscale and a precise control of composition in mixed-phases TiO$_2$ for better performance.
4.2 Experimental section

4.2.1 TiO$_2$ nanotubes synthesis

Highly ordered TiO$_2$ nanotubes arrays are prepared via a two-step electrochemical anodization method. In the experiments, the Ti foil (Goodfellow, 0.1 mm thick, ~1 cm × 2.5 cm) is used as the anode and the Pt wire is used as the cathode. A fluoride-containing solution (0.5 wt.% NH$_4$F, 2 vol% water and ethylene glycol) is used as the electrolyte. In the first-step of anodization, the Ti foil is anodized at the potential of 50 V for samples henceforth labelled #11 and #13 TiO$_2$ NTs, respectively and 35 V for #12 TiO$_2$ NTs (Hewlett-Packard 6209B DC power supply) for 240 min at room temperature (21 °C). After that, TiO$_2$ NTs formed on the Ti foil is peeled off by the ultrasonic rinse in 1 M HCl solution. Before the next step, the TiO$_2$ NTs are rinsed by DI water and ethanol several times. In the second-step of anodization, the cleaned Ti foil is anodized again to produce highly ordered TiO$_2$ nanotubes with different anodization time. The anodization time is 30 min, 240 min and 240 min for #13, #12 and #11 TiO$_2$ NTs, respectively. After that, the TiO$_2$ NTs are rinsed by DI water and ethanol several times to clean the electrolyte on the surface of TiO$_2$ NTs samples.

4.2.2 Characterization

Scanning electron microscopy (SEM, LEO 1540XB and 1530XB) is used to provide morphology information especially size information of different TiO$_2$ NTs and X-ray diffraction (XRD, Rigaku Ru200BVH, Co K$\alpha$ radiation with $\lambda$=1.7892 Å) is used to determine the phase of TiO$_2$ NTs. The XANES experiments data was collected at CLS (Saskatoon, SK, Canada). The X-ray absorption near edge structure (XANES) on the Ti L$_{3,2}$-edge is aimed to track the local and electronic structures. The XANES spectra were collected at the Spherical Grating Monochromator (SGM) beamline (resolving power E/ΔE > 5000). [11] Before the measurement, TiO$_2$ NTs standing on the Ti metal substrate was mounted on a sample holder, which has a normal angle of the incident beam. In the measurement, the data of the energy range of the Ti L$_{3,2}$-edge XANES e is collected at 453–478 eV. Furthermore, the total electron yield (TEY) and fluorescence yield (FLY) modes are applied and specimen current and fluorescence are recorded at the same time.
Figure 4-1 Schematic layout of the sample mounting into a quartz capillary sticker on a sample holder (a) and illustration plot of increasing temperature condition (b).

The diameter of a quartz capillary is 0.3 mm, the length of the powder sample packed is around 5 mm and the beam size in the experiments is around 2 mm. In the capillary, there are also SiO$_2$ powder and clay for sealing it.

All XANES spectra in this study are normalized to the incident photon flux, $I_0$. The in-situ XRD experiments were conducted at 09A beamline at Taiwan Photon Source (TPS) in Hsinchu, Taiwan. HFM (horizontal focusing mirror) with coating materials Pt is used, and the X-ray energy is 15 KeV ($\lambda=0.83\text{Å}$). The powder diffraction patterns were recorded by a position-sensitive detector covering a 2θ range of 120°. Before the experiments, the temperature of the heating blower was calibrated by the thermocouple.
The amorphous TiO$_2$ powder sample was loaded into the 0.3 mm quartz capillaries to obtain radiant and heating directly. The sample holder (Figure 4-1 (a)) is designed to fit a capillary and it was rotating during the data collection to absorb heating and radiation uniformly. Figure 4-1 (b) shows the experimental condition of increasing temperature for sample #11 TiO$_2$ NTs. The rate of increasing temperature is ~10 °C per minute and collecting data at each temperature takes 3 min. In the in-situ XRD experiments, the temperature was increased from 150 °C to 200 °C with an interval 50 °C, from 200 °C to 300 °C with the intervals 20 °C (for sample #11 TiO$_2$ NTs) or the intervals 10 °C (for sample #12 and #13 TiO$_2$ NTs), and from 300 °C to 500 °C with an interval 20 °C.

4.3 Results and discussions

4.3.1 Morphology

The SEM images (Figure 4-2) show the side view of as-prepared TiO$_2$ NTs samples synthesized under various conditions. The #11 and #12 NTs were grown at 50 V and 35 V for 240 min, respectively. The #13 TiO$_2$ NTs was anodized at 50 V for 30 min. It can be noted that there are different size TiO$_2$ with nanotube morphology. These three samples show highly-ordered nanotube arrays and their size information, as well as fabrication conditions, are summarized in Table 4-1.

Based on their size information, the main difference of their size is length of NTs, the #11 indicates a longest NT while the #13 shows a shortest NT morphology. Compared to #13 NTs (30 min), the #11 TiO$_2$ NTs were grown for longer anodization time (240 min) at the same anodization potential (50 V). The length of the TiO$_2$ NTs shows the obvious increase with increasing anodization time. More specifically, the #11 TiO$_2$ displays 10.78-μm-long nanotubes while the length for #13 NT is 2.75 μm, which indicates the octuple anodization time is corresponded to the approximately triple length of nanotubes. Furthermore, there is a different story for the thickness of the nanotubes’ wall. According to previous results (Chapter 3), the thickness and outer diameter show slight decreases with increasing reaction time. In this case, there is a smaller inner diameter (43 nm) and a bigger thickness (29 nm) for the longer nanotube (#11). This could be a consequence of that the slower chemical dissolution of TiO$_2$ by F, noting its 10.78-micrometer-long.
During the long-time anodization, the $\text{F}^-$ in the electrolyte has an extremely long path to migrate towards the oxide/metal interface and thus there is a lower dissolution rate and slightly bigger thickness in #11 TiO$_2$ NTs. [12]

![Figure 4-2 SEM images of as-prepared TiO$_2$ NTs samples (#11, #12 and #13) anodized at various conditions.](image)

**Table 4-1 Size information of the as-prepared (amorphous) TiO$_2$ NTs anodized at different conditions.**

<table>
<thead>
<tr>
<th>NTs</th>
<th>Voltage (V)</th>
<th>1$^{\text{st}}$ time (min)</th>
<th>2$^{\text{nd}}$ time (min)</th>
<th>Electrolyte</th>
<th>Length (μm)</th>
<th>Outer diameter (nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>50</td>
<td>240</td>
<td>240</td>
<td>0.5%NH$_4$F+EG</td>
<td>10.78±0.1</td>
<td>101±15</td>
<td>29±4</td>
</tr>
<tr>
<td>12</td>
<td>35</td>
<td>240</td>
<td>240</td>
<td>0.5%NH$_4$F+EG</td>
<td>4.89±0.1</td>
<td>92±7</td>
<td>26±3</td>
</tr>
<tr>
<td>13</td>
<td>50</td>
<td>240</td>
<td>30</td>
<td>0.5%NH$_4$F+EG</td>
<td>2.75±0.1</td>
<td>110±12</td>
<td>25±5</td>
</tr>
</tbody>
</table>

Comparing to #11 NTs (50 V), the #12 NTs was grown at lower anodization potential (35 V) for the same reaction time (240 min). The #12 NTs achieve a well-aligned nanotube with a length of approximately 4.59 μm, a diameter of approximately 92 nm and a
thickness of 34 nm. It is evident that shorter TiO$_2$ NTs with smaller thickness and diameter can be obtained at lower anodization voltage. These results are in good agreement with the observations in Chapter 3. As illustrated above, the anodization potential determines the rate of ions’ migration, by governing the electric field strength across the oxide. The higher the potential applied, the bigger the diameter of nanotubes achieved. [1]

Figure 4-3 Ex-situ XRD patterns of #13 TiO$_2$ NTs on the titanium metal substrate with (500 °C, 750 °C and 900 °C for 2 hours) and without annealing (AP). The patterns were measured using Co K$_\alpha$ radiation with $\lambda=1.79$ Å.

Figure 4-3 shows the laboratory ex-situ XRD results of #13 TiO$_2$ NTs samples with the different annealing treatments. At first glance, these three temperatures have good control on the phase in #13 NTs. The 500 °C and 900 °C annealing for 2 hours lead to the anatase and rutile structure, respectively. Furthermore, the 750 °C annealing induces a mixed-phase structure efficiently. Also, there are three peaks (101), (102) and (110) in the as-prepared NTs (AP) are assigned to titanium metal, which results from the metal substrate.
To locate the temperatures range when the phase transitions occur, especially the
temperature region amorphous to anatase phase change occurs, which was not explored
in detail before, more detailed experiments were conducted. The phase transitions of TiO\(_2\)
NTs are tracked by XANES of post-annealed samples.

4.3.2 XANES analysis

Figure 4-4 Ti L\(_{3,2}\)-edge XANES of TiO\(_2\) NTs samples (#13) with increased annealing
temperatures collected in total electron yield (TEY) mode (a) and in fluoresce yield
(FLY) mode (b). The standard anatase and rutile powder (Sigma-Aldrich) are also
recorded for the reference in each spectroscopy.

The evolution of fine structure at the Ti L\(_{3,2}\)-edge XANES of TiO\(_2\) NTs samples as
annealing temperature increases as well as standard anatase and rutile are shown in
Figure 4-4. As mentioned above, there are two detection modes for XANES
measurement: surface-sensitive-TEY (Figure 4-4 (a)) and bulk-sensitive-FLY (Figure 4-
In Figure 4-4, the As-prepared (AP) TiO$_2$ NTs show broad features due to their amorphous structure. As illustrated above, peaks b and c suggest the unique characteristics of anatase (D$_{2d}$) and rutile (D$_{2h}$), respectively. The further splitting of 3d-$e_g$ starts to exhibit when the annealing temperature is above 350 °C, noting that the intensity of peak b is higher than the peak c. It indicates that the amorphous-to-anatase phase transition occurs and anatase structure forms at this temperature. Compared to standard anatase spectra, TiO$_2$ NTs show an anatase-dominant structure with an annealing temperature below 700 °C. These results are in good agreement with the literature results.[13] With the increased calcination temperatures, the splitting behaviour remains with different ratios between peaks b and c. At 700 °C, the TEY spectra show a mixed-phase (anatase and rutile) structure with 1:1 intensity ratio of peaks b and c. The results thus imply that the anatase-to-rutile phase transition occurs, and the rutile phase shows up. After that, the higher temperatures induce a mixed-phase structure with a higher rutile proportion (higher peak c) at 750 °C. Besides, TiO$_2$ NTs annealed at 900 °C shows the entire rutile structure compared with the standard rutile spectrum. These spectra at 500 °C, 750 °C and 900 °C are in good accordance with their XRD analysis.

On the other side, FLY spectra at the Ti L$_{3,2}$-edge also provide valuable information as TEY, which demonstrates phase transition behaviour as temperatures increased from the bulk perspective. It is worth mentioning that the TiO$_2$ NTs annealed at 700 °C show a mixed-phase structure with approximately 1:1 anatase and rutile from its TEY spectra while the FLY spectra indicate a mixed-phase structure with a higher anatase proportion. Furthermore, the post-annealed (750 °C) at TiO$_2$ NTs shows a rutile-dominant structure from TEY spectra while it exhibits more anatase character from the perspective of FLY. As mentioned above, the TiO$_2$ NTs undergo the phase transition from amorphous to anatase and then to rutile. It is evident that the anatase-rutile transition is dominated by surface nucleation. It is in good accordance with the previous studies [14-16], which demonstrate that the surface nucleation dominates anatase-to-rutile phase transition within annealing temperature range of 700-800 °C.

To find the exact annealing temperature to induce the phase transitions, in-situ high-temperature XRD experiments were also performed on these three TiO$_2$ NTs samples.
4.3.3 In-situ XRD results with increasing temperatures

Figure 4.5 In-situ synchrotron-based XRD patterns of #11 TiO$_2$ NTs annealed at increased temperatures. The powder sample was calcinated at each temperature for at least 5 min to reach the constant temperature. The patterns were measured with $\lambda=0.83$ Å. The spectra of standard anatase, rutile and titanium metal are provided for the reference.
Figure 4-6 In-situ synchrotron-based XRD patterns of #12 TiO$_2$ NTs annealed at increased temperatures. The powder sample was calcinated at each temperature for at least 5 min to reach the constant temperature. The patterns were measured with $\lambda=0.83$ Å. The spectra of standard anatase, rutile and titanium metal are provided for the reference.
Figure 4-7 In-situ synchrotron-based XRD patterns of #13 TiO₂ NTs annealed at increased temperatures. The powder sample was calcinated at each temperature for at least 5 min to reach the constant temperature. The patterns were measured with λ=0.83 Å. The spectra of standard anatase, rutile and titanium metal are provided for the reference.
Table 4-2 Summary of size information of TiO$_2$ NTs samples and temperatures to induce phase transition (from amorphous to anatase) in each sample.

<table>
<thead>
<tr>
<th>NTs</th>
<th>Length (μm)</th>
<th>Outer diameter (Å)</th>
<th>Thickness (nm)</th>
<th>Temperatures (°C) to induce phase transition to anatase</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>10.78±0.1</td>
<td>101±15</td>
<td>29±4</td>
<td>240</td>
</tr>
<tr>
<td>12</td>
<td>4.89±0.1</td>
<td>92±7</td>
<td>26±3</td>
<td>220</td>
</tr>
<tr>
<td>13</td>
<td>2.75±0.1</td>
<td>110±12</td>
<td>25±5</td>
<td>210</td>
</tr>
</tbody>
</table>

Figure 4-5, Figure 4-6 and Figure 4-7 show in-situ synchrotron-based XRD patterns of #11, #12 and #13 TiO$_2$ NTs powder samples annealed at increased temperatures, respectively. For the #11 TiO$_2$ NT, there is no obvious peak below 240 °C due to its amorphous form. It is can be noted that the anatase phase shows up with an obvious (101) peak when the annealing temperature is 240 °C. With the annealing temperatures increasing, the anatase structure grows, noting the anatase peaks are more intense. There is no other phase showed until the annealing temperature is 500 °C. Based on the results of #12 TiO$_2$ NTs, the (101) peak of anatase exhibited with low intensity at 220 °C. Furthermore, other peaks show up as well, which indicates that anatase structure forms. However, the #13 TiO$_2$ NTs phase transition occurs at the lowest temperature; the peak assigned to anatase appeared when the annealing temperature was approaching 210 °C. These annealing temperatures of phase transition (amorphous to anatase) occurring are summarized in Table 4-2 as well as their size information.

Comparing to XRD results collected in the laboratory, it is worth mentioning that the advantages of in-situ XRD measured in the synchrotron radiation facility (TPS). At first glance, synchrotron-based XRD patterns have more diffraction peaks assigned to the anatase phase, which is due to better spatial precision of the incident or diffracted X-ray beams. The peak width (full width at half maximum) in the synchrotron-based XRD is significantly smaller than that in lab XRD, which contributes to a sharper peak and better resolved the pattern due to higher energy resolution of synchrotron X-ray with crystal monochromators. This better resolution is desired for reducing or even avoiding overlap of neighbouring diffraction peaks. Furthermore, there are more intense peaks resulting from the greater beam intensity, which leads to the lower noises and better signals. In addition, it is more efficient to obtain the XRD pattern than measurements in the
laboratory. In this case, each pattern takes 10 min for measurements in the lab while 3 min in synchrotron-based experiments with higher quality. Moreover, it is worth mentioning that the tunable wavelength also can avoid fluorescence from the background.

Figure 4-8 Shift in the XRD peak position of anatase (101) peak with increasing annealing temperature for #11 TiO$_2$ NTs powder sample. The x-axis is 2 theta (in degree) that indicates peak position, the y-axis is temperature annealing and the z-axis is the intensity of anatase (101) peak. The black dashed line indicates the position of peak center.
Figure 4-9 Shift in the XRD peak position of anatase (101) peak with increasing annealing temperature for #12 TiO$_2$ NTs powder sample. The x-axis is 2 theta (in degree) that indicates peak position, the y-axis is temperature annealing and the z-axis is the intensity of anatase (101) peak. The black dashed line indicates the position of peak center.
Figure 4-10 Shift in the XRD peak position of anatase (101) peak with increasing annealing temperature for #13 TiO$_2$ NTs powder sample. The x-axis is 2 theta (in degree) that indicates peak position, the y-axis is temperature annealing and the z-axis is the intensity of anatase (101) peak. The black dashed line indicates the position of peak center.
Table 4-3 Summary of shifts in the XRD peak positions of anatase (101) and change of calculated d-spacing of anatase (101) for #11, #12 and #13 TiO$_2$ NTs powder samples. Theta-a is the position of anatase (101) peak firstly appears and theta-c is the position of anatase (101) peak with highest shifts (to higher degree) The values of d-spacing-a and d-spacing-c represent the anatase (101) d-spacing corresponding to these two peak positions, respectively.

<table>
<thead>
<tr>
<th>NTs</th>
<th>Temperatures (°C)</th>
<th>theta-a (degree)</th>
<th>theta-c (degree)</th>
<th>d-spacing-a (Å)</th>
<th>d-spacing-c (Å)</th>
<th>Change of d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>240</td>
<td>13.434</td>
<td>13.444</td>
<td>3.534</td>
<td>3.531</td>
<td>0.003</td>
</tr>
<tr>
<td>12</td>
<td>220</td>
<td>13.428</td>
<td>13.441</td>
<td>3.535</td>
<td>3.532</td>
<td>0.003</td>
</tr>
<tr>
<td>13</td>
<td>210</td>
<td>13.398</td>
<td>13.425</td>
<td>3.543</td>
<td>3.536</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Figure 4-8, Figure 4-9 and Figure 4-10 show the intensity of anatase (101) peak in #11, #12 and #13 TiO$_2$ NTs powder samples with increasing annealing temperatures. It can be noted that a very broad peak begins to appear, which indicates that its amorphous form of the sample from the very beginning of the phase transition. After that, the intensity of anatase (101) peak increases gradually, indicating the growth of an ordered crystalline structure. The intensity keeps increasing until it reaches its highest value, indicating that the amorphous sample finishes converting to anatase phase. For #11, #12 TiO$_2$ NTs, the intensities do not increase any further after arriving at approximately 360 °C. However, #13 TiO$_2$ NTs shows its saturated value of anatase (101) peak intensity at around 260 °C, noting the amorphous to anatase phase transition starts at 210 °C. It indicates a faster speed of crystallization in this small nanostructure than that of the other two larger samples.

Furthermore, it is evident that the anatase (101) peak position exhibits a temperature-dependence shift in all TiO$_2$ NTs samples. Interestingly, there is a trend for each sample that the (101) peak shifts to a higher angle (2θ) and then shifts back to a lower angle with increasing temperatures. According to Bragg’s Law, this trend for angle indicates the d-spacing of anatase (101) peak decreases and then increases within the temperature range. More importantly, shift behaviours varies with different samples. The #13 TiO$_2$ NTs sample shows a largest shift among these three samples. The peak shifts and changes of
d-spacing of anatase (101) are summarized in Table 4-3. The d-spacing of anatase is calculated by Bragg’s Law (Equation 4-1).

\[
d = \frac{n\lambda}{2\sin\theta}
\]  

(4-1)

In this equation, the \( \lambda \) is the wavelength of X-ray (0.083 nm in this case) and angle \( \theta \) is the peak position of anatase (101). In the table, the theta-a is the peak position when anatase comes into sight and theta-c is the peak position which occurs with the highest angle and changes its shift direction in the following. The values of d-spacing-a and d-spacing-c represent the anatase (101) d-spacing corresponding to these two peak positions, respectively.

Noted that the standard d-spacing for anatase (101) is 3.52 Å based on the previous study [17] and the d-spacing results calculated for all three samples are slightly larger than the literature value. Also, the change of d-spacing of #13 TiO\(_2\) (0.007 Å) is larger than that of #11 TiO\(_2\) (0.003 Å) and #12 TiO\(_2\) (0.003 Å). Combining with their size information, the smaller TiO\(_2\) NTs (#13) shows the largest shifts to high angles as temperature increases. Based on previous studies [3, 18], it is probably connected to tensile stresses existing in the crystallization process. The anatase structure has elastic anisotropy properties, which make it possible. The tensile stresses are formed at the beginning of crystallization from the amorphous state due to the reduction of specific volume. These stresses decrease in post-annealed TiO\(_2\) samples, which leads to a decrease of lattice spacing after the initial annealing. [3, 18] In addition, the tensile residual stresses release (decrease) significantly with a decrease of thickness in the annealing progress. It indicates that there is the most decrease in tensile residual stresses in the thinnest TiO\(_2\) sample. It can be taken into account that there is the most obvious change of d-spacing of anatase (101) during the annealing process among these three TiO\(_2\) samples. In this stage, the tensile residual stresses dominate the d-spacing of the lattice, which overcompensates the thermal expansion. After that, the anatase (101) peak position shifts to a lower angle, indicating the d-spacing of lattice increases. The consideration of this sequence can be that the lattice expands in the annealing process. In this stage, the increasing temperature is the
dominant-character of lattice spacing while the tensile residual stresses can no longer be observed.

As discussing above, the peak position (2θ) is corresponding to a certain d-spacing Bragg’s equation. [19] Another peak feature should be noted is full width at half maximum intensity (FWHM), which can be used to determine the crystal size. The relationship between the broadening of the peak and crystal size can be expressed by the Scherrer equation. [20]

\[ \beta_{hkl} = \frac{K \lambda}{L_{hkl} \cos \theta_{hkl}} \]  

(4-2)

where the \( \beta_{hkl} \) is FWHM of the peak for a certain phase (hkl), the Scherrer constant K is 0.94 in this case, \( \lambda \) is the wavelength of incident X-ray (0.083 nm), the \( \theta_{hkl} \) is the angle of the peak position and \( L_{hkl} \) is crystalline length. The crystal size L of sample #11, #12 and #13 TiO\(_2\) NTs are determined using the width and peak position of anatase (101) and the results are presented in Table 4-4. There are two crystal sizes calculated based on two anatase (101) peak widths calculated of each sample; one is at the highest intensity (peak-1) and the other peak-2 at the highest annealing temperature (500 °C).

**Table 4-4** The calculated crystallite size based on their width of peak anatase (101). Two anatase (101) peaks were used to calculate the crystal size: one is the anatase (101) with the highest intensity (peak-I) among all spectra and the annealing temperatures various with samples; the other (peak-T) is anatase (101) when annealing samples at the highest temperature (500 °C).

<table>
<thead>
<tr>
<th>NTs</th>
<th>Temperatures (°C)</th>
<th>Peak-I position</th>
<th>FWHM-I (degree)</th>
<th>L-I (nm)</th>
<th>Temperatures (°C)</th>
<th>Peak-T position</th>
<th>FWHM-T (degree)</th>
<th>L-T (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>380</td>
<td>13.448</td>
<td>0.115</td>
<td>38.88</td>
<td>500</td>
<td>13.440</td>
<td>0.116</td>
<td>38.7</td>
</tr>
<tr>
<td>12</td>
<td>380</td>
<td>13.440</td>
<td>0.074</td>
<td>60.44</td>
<td>500</td>
<td>13.440</td>
<td>0.076</td>
<td>59.1</td>
</tr>
<tr>
<td>13</td>
<td>270</td>
<td>13.404</td>
<td>0.116</td>
<td>38.66</td>
<td>500</td>
<td>13.433</td>
<td>0.118</td>
<td>37.9</td>
</tr>
</tbody>
</table>

Based on the results, the crystallite sizes calculated for sample #11 TiO\(_2\) NTs are 38.88 nm and 38.74 nm annealed at 380 °C and 500 °C, respectively. Furthermore, the crystallite sizes of sample #13 NTs (38.66 nm at 270 °C and 37.95 nm at 500 °C) are
close to that of #11 NTs. However, sample #12 NTs shows 60.44 nm (at 380 °C) and 59.16 nm (at 500 °C) of crystallite sizes. It is evident that no significant difference between calculated crystallite sizes (L) at two temperatures in each sample, which indicates that annealing temperatures have little impact on the crystallite size once the anatase (101) peak reaches its highest intensity.

Table 4-5 The calculated crystallite sizes of TiO₂ NTs samples (#11, #12 and #13) annealed at 500 °C together with their experimental condition and size information.

<table>
<thead>
<tr>
<th>NTs</th>
<th>Voltage (V)</th>
<th>2nd time (min)</th>
<th>Length (μm)</th>
<th>Outer diameter (nm)</th>
<th>Thickness (degree)</th>
<th>Width-T (nm)</th>
<th>L-T (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>50</td>
<td>240</td>
<td>10.78±0.1</td>
<td>101±15</td>
<td>29±4</td>
<td>0.116</td>
<td>38.7</td>
</tr>
<tr>
<td>12</td>
<td>35</td>
<td>240</td>
<td>4.89±0.1</td>
<td>92±7</td>
<td>26±3</td>
<td>0.076</td>
<td>59.1</td>
</tr>
<tr>
<td>13</td>
<td>50</td>
<td>30</td>
<td>2.75±0.1</td>
<td>110±12</td>
<td>25±5</td>
<td>0.118</td>
<td>37.9</td>
</tr>
</tbody>
</table>

Noted that sample #12 presents the narrowest peak width and then the highest crystallite size. Combining their synthesis condition and size information (Table 4-5), the crystallite sizes of samples are not appreciably affected by the variation of their size. Another consideration is that the crystallite size is probably related to their synthesizing conditions, such as pH and voltage in the anodization. [21, 22]

Figure 4-11 shows the comparison of ex-situ and in-situ synchrotron-based XRD patterns of #11 TiO₂ NTs. As illustrated above, the phase transition (from amorphous to anatase) in this sample shows up when the calcination temperature reaches 240 °C. The anatase peaks are obvious and more intense at 260 °C, which indicates that the amount of anatase crystal is increased significantly. The ex-situ experiments were performed at TPS at room temperatures after annealing #11 TiO₂ powder sample in the furnace at specific temperatures. The #11 TiO₂ NTs was annealed at 250 °C for 2 hours in the furnace, and the XRD experiment of the powder sample was performed. In Figure 4-5, the XRD pattern of ex-situ 250 °C shows anatase features. The intensities of anatase peaks are higher than that of in-situ 240 °C and slightly lower than in-situ 260 °C. These results can be interpreted to that the phase transition undergoes within the temperature range of 240-260 °C. Besides, this temperature obtained during the in-situ experiments are in good
accordance with temperature recorded by the furnace, noting their (in-situ 260 °C and ex-situ 250 °C) close intensities.

Figure 4-11 Ex-situ and in-situ synchrotron-based XRD patterns of #11 TiO₂ NTs powder with certain annealing temperatures. The sample powder was calcinated at each temperature (240 °C and 260 °C) for 5 min during the in-situ experiments. It was calcinated at 250 °C by a furnace for 2 h in the ex-situ experiment. The pattern of standard anatase is provided for reference.

4.4 Conclusions

In this chapter, it shows a synchrotron-based in-situ study to reveal the temperatures of annealing treatments when amorphous to anatase phase transitions of a given morphology of TiO₂ NTs occur, and the process of phase transformations as a function of tube morphology. The highly-ordered TiO₂ NTs synthesized by the electrochemical method, which allows to precisely control the size (length, diameter and thickness) of NTs. Ex-situ XRD experiments are performed in the laboratory, indicating the phase structure of post-annealed #13 TiO₂ NTs samples. Furthermore, the phase transition of #13 TiO₂ NTs is determined by the TEY and FLY XANES spectra at the Ti L-edge. It is evident that the
phase transition from amorphous to anatase starts within the annealing temperature range of 300-350 °C and then it converts to rutile at approximately 700 °C. Combining surface-sensitive TEY and bulk sensitive FLY, it is worth noting that the anatase-rutile transition is dominated by surface nucleation within in annealing temperature range of 700-800 °C. The in-situ temperature-dependent XRD experiments are performed on three TiO$_2$ NTs. It indicates that the TiO$_2$ NTs with a larger diameter, thickness and longer length (#11) requires a higher temperature (240 °C) to start phase transition from amorphous to anatase, while #13 NTs with smaller diameter, thickness and shorter length undergoes amorphous to anatase at approximately 210 °C. Furthermore, anatase (101) peak shows shifts to higher angles first and then shifts to lower angles as temperature increases. The amount of higher-angle-shift varies with different samples and the #13 NTs shows the highest shifts among these three samples. The consideration of this consequence can be that the tensile residual stresses are released faster in the smaller NTs, which leads to a decrease of lattice space (higher angle). Also, these results imply that there is a faster growth of anatase crystallization in #13 NTs that of the other two samples.

4.5 References


Chapter 5

5 Summary and future work

5.1 Summary

This thesis has focused on tracking the electronic and structural properties of two series of highly-ordered TiO₂ NTs arrays prepared as a function of voltage control and time control upon the size-dependence solid-state phase transitions. The XANES, XEOL and in-situ synchrotron-based XRD were applied as powerful tools to study these associated phenomena with both element and chemical site specificities. The cores of the studies are presented in Chapter 3 and Chapter 4.

In Chapter 3, I present a study of the phase transition of two series TiO₂ NTs (anodization time-dependent and anodization voltage-dependent) by XANES and XEOL. Two series of highly-ordered amorphous TiO₂ NTs are synthesized by a two-step electrochemical anodization method. Thermal treatments were applied to achieve their desired phase. The morphology features including sizes were tracked by SEM, which shows a good control of size (length, diameter and thickness of the wall). The influences of these two factors (anodization time and voltage) on the growth of TiO₂ NTs are discussed; the anodization time has a significant impact on the length of TiO₂ NTs while the anodization voltage mainly influences its diameter and thickness. The laboratory XRD is used to determine the phase structure of TiO₂ NTs. More importantly, XANES is used to track the local environment and electronic structure of mixed-phase (anatase and rutile) TiO₂ NTs. The splitting behaviours of Ti 3d-t⁴ state are various with the different sizes of TiO₂ NTs, which indicates more anatase features and fewer rutile features in the sample as anodization voltage or time increase. It can be considered that the faster anatase-to-rutile transition occurred in smaller NTs compared to larger NTs under the same the annealing treatment. The smaller TiO₂ NTs in each series with anatase structure is easier to overcome the energy barrier to start the nucleation of a new phase (rutile in this case), which is due to the fact that higher surface free energy of smaller NTs have more negative impact on Gibbs free energy of the nanotube for anatase-to-rutile phase...
transitions and the more contribution to nonequilibrium transition from anatase to rutile. FLY spectra also provide valuable information to track the electronic properties of TiO$_2$ NTs. Combining the surface-sensitive TEY and bulk sensitive FLY, we can determine the direction of phase transition within the NT. It is evident that the anatase-to-rutile phase transition occurs from surface to bulk at 750 °C annealing, which is in good accordance with the previous study [1-3] that demonstrated the surface nucleation dominates anatase-to-rutile phase transition within an annealing temperature range of 700-800 °C. The relationship between observed luminescence and the elemental and chemical environment was discussed as well. Visible emission (at 520 nm) from defects in anatase structure that was considered as oxygen vacancy while near-IR emission (at 820 nm) results from intrinsic defects in the rutile phase, which can be used as fingerprint to distinguish the crystalline structures. In this case, it is evident that rutile structure is related to the defects from bulk while the luminescent center from anatase structure is in the surface and near-surface region. Furthermore, the intensity of XEOL is very sensitive to the excited edge of interest, which indicates its elemental specificity. Dominant characters of different phases from XEOL were in line with XANES results. The most significant of this work is that we can now establish a calibration curve based on which we can synthesize any composition of TiO$_2$ NTs anatase-rutile composite.

In Chapter 4, I show a synchrotron-based in-situ XRD study to reveal the temperatures of annealing treatments when phase transitions (from amorphous to anatase) of a given morphology of TiO$_2$ NTs occur, and the process of phase transformations as a function of tube morphology. Three highly-ordered TiO$_2$ NTs arrays samples (#11, #12 and #13 TiO$_2$ NTs) are synthesized with various sizes (length, diameter and thickness) by the electrochemical method. Laboratory ex-situ XRD results determined the phase structure of post-annealed #13 TiO$_2$ NTs samples. The phase transition of #13 TiO$_2$ NTs was tracked by the TEY and FLY XANES spectra at the Ti L-edge, which shows that the phase transition from amorphous to anatase starts within the annealing temperature range of 300-350 °C and then the NTs convert to the rutile at approximately 700 °C. It can be noted that the anatase-rutile transition is dominated by surface nucleation. Additionally, the results of in-situ high-temperature XRD experiments were displayed. They showed that the amorphous TiO$_2$ NTs with a larger diameter, thickness and longer length (#11)
require higher temperature (240 °C) to start phase transition (from amorphous to anatase) while #13 NTs (with smaller diameter, thickness and shorter length) undergoes amorphous to anatase transition at approximately 210 °C. Furthermore, anatase (101) peak shows shifts to higher angles first and then shifts back to lower angles as temperature increases within temperature range 150-500 °C. The amount of higher-angle-shift varies with different samples and the #13 NTs shows the largest shifts among these three samples. The consideration of this consequence can be that the tensile residual stresses are released faster in the shortes NTs, which leads to a decrease of lattice space (higher angle). Also, these results imply there is a faster growth of anatase crystallization in #13 NTs than that of the other two samples. This work also demonstrates the power of synchrotron XRD in both intensity and energy resolution, which allows to further resolve peaks unresolvable with laboratory XRD.

5.2 Future work

The TiO$_2$ NTs and their derivatives have been extensively developed due to their potential use in water-splitting, solar cells, and lithium-ion batteries. However, anatase (3.2 eV) and rutile (3.0 eV) are large band gap semiconductors [4, 5], which limits the photo-absorption efficiency and solar energy conversion. The rapid combination rate of photo-generated electrons in the CB and associated holes in the VB of TiO$_2$ is another obstacle to superior photoactivity [6-8]. As TiO$_2$ is an important building block of photovoltaics, the solution to optimize their morphology for higher photocatalytic efficiency has been sought for some time. The key solution to narrow the band gap is to introduce a secondary species (non-metal or transition metal) to the TiO$_2$ lattice (doping). Another strategy is to extend the electron-hole pair lifetime by morphology engineering, phase control and noble-metal sensitizing.

This thesis focuses on the morphology engineering and phase control by constructing the mixed-phase (anatase and rutile) TiO$_2$ NTs structure with various sizes. Based on the current study, mixed-phase structure with various ratios (amorphous and anatase or anatase and rutile) can be fabricated by annealing treatments (various temperatures for various times). A further photo-performance test regarding photoconversion as well as photocatalytic efficiency needs to be conducted to optimize this type of structure with
their sizes and ratios of mixed-phase to seek higher absorption efficiency. Following the theory above, there are two possible research directions to seek for higher photoabsorption efficiency of TiO₂ NTs in the future; doped TiO₂ NTs with non-metal or transition metal elements and another is noble-metal sensitizing.

Introduction of non-metal species (such as N, C, F, and S) and transition metal species (such as Cr, Fe, and Ni) to TiO₂ can shift the absorption range to visible and even infrared regions by reducing the band gap via raising the energy level of VB [6, 9, 10] and adjusting the CB [11, 12], respectively. For example, it is reported that the TiO₂ NTs doped with N can achieve the heterostructure of anatase-amorphous core-shell. [13] Interestingly, it shows dramatic photoabsorption at the UV-NIR region. [13]. These studies indicate that doping has a significant impact on enhancing the photoabsorption of TiO₂ NTs.

Another possible future work is to introduce noble-metal (such as Ag, Au, Pd, and Pt) sensitizing to TiO₂ [6, 14]. In this case, the noble metal can stick on nanostructure to act as an electron sink or holder to forbid the recombination of electrons and holes [7, 8, 14]. Additionally, it is reported that the heterostructure of TiO₂ NTs and other alloys grown on TiO₂ showed a higher catalytic efficiency. In this method, morphology engineering and phase control can be combined to obtain higher efficiency. Furthermore, in-situ XAFS analysis of the metal (alloy)/TiO₂ system during the photocatalytic reaction will provide further details on dynamic electronic interactions.

### 5.3 References


Curriculum Vitae

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Conference Presentation:
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