Optical Properties, Electronic Structures and High Pressure Study of Nanostructured One Dimensional Titanium Dioxide by Synchrotron Radiation and Spectroscopy

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Graduate Program in Chemistry

A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science

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OPTICAL PROPERTIES, ELECTRONIC STRUCTURES AND HIGH PRESSURE
STUDY OF NANOSTRUCTURED ONE DIMENSIONAL TITANIUM DIOXIDE BY
SYNCHROTRON RADIATION AND SPECTROSCOPY

(Thesis Format: Integrated-Article)

By

Ankang Zhao

Graduate Program in Chemistry

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

The School of Graduate and Postdoctoral Studies
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Abstract
One dimensional (1D) titanium dioxide (TiO\textsubscript{2}) nanomaterials have been extensively studied in recent years due to their superior electrical, optical mechanical and chemical properties compared with their bulk counterparts. Two different kinds of 1D TiO\textsubscript{2} nanomaterials, TiO\textsubscript{2} nanowires (TiO\textsubscript{2} NW) and TiO\textsubscript{2} nanotubes (TiO\textsubscript{2} NT), are studied in this thesis by using various techniques.

In one study, TiO\textsubscript{2} NW synthesized by hydrothermal method and a series of calcinated TiO\textsubscript{2} NW were investigated by using absorption near edge structures (XANES), X-ray diffraction (XRD) and X-ray excited optical luminescence (XEOL). It is found that TiO\textsubscript{2} NW as synthesized undergo a phase transition under calcination: TiO\textsubscript{2}-B phase transformed to anatase phase and then to rutile phase. Moreover, a green photoluminescence (PL) started showing up at a wavelength of 470 nm at 650 °C, then shifts to 550 nm at 750 °C and finally at 1000 °C the green PL disappears and near infrared (IR) PL was observed. Also optical behaviours are consistent with the phase transformation sequence. The green PL at 550 nm and near IR PL at 830 nm is attributed to oxygen vacancies of anatase phase and the bulk defects of rutile phase respectively. However, a new phenomenon is observed, the green PL observed at 470 nm. Considering this green PL is consistent with the presence of the TiO\textsubscript{2}-B phase, it is proposed that the green PL at 470 is due to the TiO\textsubscript{2}-B phase.

In another study, the high-pressure behaviour of anatase TiO\textsubscript{2} NT is studied using Raman and synchrotron X-ray diffraction at increasing pressure up to 31.1 GPa. Upon compression, anatase phase directly transforms to baddeleyite phase at ~ 12.2 GPa. Besides, we found in the compression of anatase phase, (1) a higher compressibility along c-axis is observed compared to a-axis, which may be due to crystal structure and growth direction of TiO\textsubscript{2} NT, and (2) and the bulk modulus is 164 GPa which is much lower than that of other TiO\textsubscript{2} nanomaterials. Upon decompression, the α-PbO\textsubscript{2} phase is retrieved at ambient pressure and a compression-decompression cycle is finished. These results indicate that the 1D morphology of TiO\textsubscript{2} NT may be responsible for its high-pressure transition and bulk modulus.
Keywords

High pressure, diamond anvil cell, synchrotron X-ray diffraction, Raman, X-ray absorption near edge structure, X-ray excited optical luminescence, phase transition, bulk modulus, nanomaterials, nanowires, nanotubes, morphology effect.
The Co-Authorship Statement

I hereby declare that this thesis is written by Ankang Zhao. Dr. Yang Song and Dr. Tsun-Kong Sham played a major role in the editing and revision of the materials presented in all chapters.

TiO$_2$ nanowires in Chapter 3 were synthesized by Ankang Zhao in the Song laboratory. TiO$_2$ nanotubes in Chapter 4 were provided by Dr. Tsun-Kong Sham’s group in the University of Western Ontario. Besides, Ankang Zhao is responsible for all data collection and analysis.

I am aware of the University of Western Ontario Policy on Authorship and I certify that I have properly acknowledged the contribution of other researchers to my thesis.

I certify that, with the above qualifications, this thesis, and the research to which it refers, is the product of my own work.
To my loving family
Acknowledgements

First of all, I would like to express my great gratitude to both of my supervisors, Dr. Yang Song and Dr. Tsun-Kong Sham, for their exceptional supervision, encouragement, and unconditional support. It has been a great honor for having the opportunity to study and work under the guidance of such great supervisors. Your kindness, passion and enthusiasm always encourage me.

Next, I would like to thank my group members: Dr. Yun-Mui Yiu, Dr. Zhiqiang Wang, Dr. Haiyan Mao, Dr. Dongniu Wang, Ms. Olga Lobacheva, Mr. Xiaoxuan Guo, Mr. Yue Hu, Mr. Fuyan Zhao, Ms. Dong Zhao, Mr. Liang Zhou, Mr. Zhihao Yu and Mr. Jun Li for their helpful discussion constructive feedback on the ongoing research. And I really appreciate our former group members, Dr. Zhaohui Dong and Dr. Lijia Liu. You have been providing great help to me since the start of my graduate study.

I appreciate all the technical support by the following people: Dr. Robert Blyth, Mr. Tom Regier, Mr. David Chevrier from Canadian Light Source; Dr. Jesse Smith from Advanced Photon Source; Mr. Todd Simpson from Nanofabrication Laboratory. Their expertise and willingness to help made my experiments running more smoothly.

I would like to thank my friends (Jun Xu, Michael Linda Wu, Peng He, Xiaoxiao Wang, Renjie Hou, Yiyi Liu, Bo Fan). It is you who drive the loneliness away from me and leave me a colorful and joyful Canadian life.

Finally, I would like to give my special thanks to my parents for their love, unconditional supporting and understanding during my M.Sc. study.
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<table>
<thead>
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<th>0D</th>
<th>Zero dimension</th>
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<tbody>
<tr>
<td>1D</td>
<td>One dimension</td>
</tr>
<tr>
<td>2D</td>
<td>Two dimension</td>
</tr>
<tr>
<td>ANL</td>
<td>Argonne National Laboratory</td>
</tr>
<tr>
<td>APS</td>
<td>Advanced Photon Source</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>CLS</td>
<td>Canadian Light Source</td>
</tr>
<tr>
<td>DAC</td>
<td>Diamond anvil cell</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye-sensitized solar cell</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray fine structure</td>
</tr>
<tr>
<td>FLY</td>
<td>Fluorescence yield</td>
</tr>
<tr>
<td>ID</td>
<td>Insertion device</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LINAC</td>
<td>Linear accelerator</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PLY</td>
<td>Photoluminescence yield</td>
</tr>
<tr>
<td>PTM</td>
<td>Pressure transmitting medium</td>
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<tr>
<td>ROS</td>
<td>Reactive oxygen species</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>SGM</td>
<td>Spherical grating monochrometer</td>
</tr>
<tr>
<td>TEY</td>
<td>Total electron yield</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>TiO₂ NW</td>
<td>TiO₂ nanowires</td>
</tr>
<tr>
<td>TiO₂ NT</td>
<td>TiO₂ nanotubes</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>XAFS</td>
<td>X-ray absorption fine structure</td>
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<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
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<tr>
<td>XEOL</td>
<td>X-ray excited optical luminescence</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</tbody>
</table>
Chapter 1 Introduction

1.1 Titanium dioxide

1.1.1 Background

Among all transition-metal oxides, Titanium Dioxide (TiO$_2$) is one of the most investigated compounds in material science. The commercial application of TiO$_2$ started at the beginning of the 20$^{th}$ century and rapidly increased after the discovery of the sulphate process in 1916 by the Norwegian chemists Farup and Jebsen, and then of the chloride process which was introduced commercially by DuPont in 1958.\(^1\) Since then, TiO$_2$, which is non-toxic, environmentally friendly and corrosion-resistant, has been widely used as a pigment$^2$, paints$^3$, toothpaste$^4$, and etc.

In addition, TiO$_2$ is well known as a semiconductor with a band gap (gap between valence band and conduction band) energy $\sim$ 3 eV, which means that TiO$_2$ can absorb photons with wavelength in ultraviolet (UV) region and electrons in the valence band (VB) can be excited into conduction band (CB). Due to the unique electronic structures of TiO$_2$, TiO$_2$ also plays an important role other areas. Since the pioneer work of Fujishima and Honda$^5$, enormous efforts have been devoted to the research of TiO$_2$ material, which has led to many promising applications in areas ranging from photovoltaic and photocatalysis to photo-/electronchromics and sensors.$^6$-$^9$

1.1.2 Nanomaterials and TiO$_2$ nanomaterials

Nanomaterials are expected to be at the heart of the next technological revolution in solid-state electronics, to emerge as new structural materials, to serve as systems for controlled drug delivery and to have a considerable impact in particularly all domains of science. The unique functional properties of nanomaterials, such as chemical, optical, magnetic, mechanical, optoelectronic properties have been drastically influencing the direction of development of today’s science and technology.
Nanomaterials refer to materials with at least one dimension less than 100 nm. As shown in Figure 1-1, there are three kinds of nanomaterials based on the nanoscale on different dimensions. First one is the nanomaterials of which all three dimensions are in nanoscale, such as nanoparticles. Second one is the nanomaterials of which only two dimensions are in nanoscale, such as nanowires, nanorod and nanotubes etc.. The last one is the nanomaterials of which only one dimension is in nanoscale, such as nano film and nanomembrane. Materials of which all dimensions are larger than nanoscale is called bulk.

In nanomaterials, size is one of the most important factors, as properties of nanomaterials strongly depend on size. Nanomaterial is a kind of intermediate material between single atoms and bulk matter. Surface or interface phenomena become dominant and chemical and physical properties of nanomaterials are different from the bulk counterpart. By diminishing dimensions to nanoscale, surface area increases significantly, therefore much higher efficiency can be achieved. Moreover, as the size of the materials is reduced, the energy levels become discrete. And this is due to the quantum confinement effect. At nanoscale, confinement results in the reorganization of the electronic density of states. For example, Figure 1-2 shows a schematic illustration of quantum confinement for electronic states of a semiconductor. In the semiconducting particle, excitation from valence band to conduction band requires more energy, so-called “band gap widening”.

Figure 1-1 A schematic illustration of bulk material, nanofilm, nanowire and nanoparticle.
Figure 1-2 Schematic illustrations of density of states comparison (a) among bulk, nano and atom, and (b) among bulk and nanomaterials with specific dimensionality. CB: conduction band, VB: valence band

Due to the quantum confinement effect, TiO$_2$ nanomaterials exhibit a wider band gap than that of its bulk counterpart, which means that more energy is needed to excite the electrons from VB into CB. Moreover, high surface area brought about by small particles size is beneficial to many TiO$_2$-based devices, as it facilitates reaction/interaction between the devices and the interacting media, which mainly occurs on the surface or at the interface and strongly depends on the surface area of the material. As a result, TiO$_2$ nanomaterials lead to a higher potential of applications in solar cells, water splitting and so on.$^{6-9}$

Generally speaking, the functional properties of TiO$_2$ nanomaterials are influenced by a large number of factors.$^{12}$ Morphology is another important factor. Of all kinds of TiO$_2$ nanomaterials, 1D TiO$_2$ nanomaterials (nanowires and nanotubes) have two quantum confined directions, while still leaving one unconfined direction for electrical conduction. This allows nanowires to be used in applications where electrical conduction, rather than tunnelling transport, is required. Nanoparticulated electrodes are a commonly used architecture in solar cells and water splitting. In the electrode made of nanoparticles,
while these electrodes possess a high surface to volume ratio, the structural disorder at the contact between two crystalline particles leads to an enhanced scattering of free electron, thus reducing the electron mobility. However, TiO$_2$ NW and NT offer a large internal surface area without a concomitant decrease in geometric and structural order, which can provide direct channels for charge and mass transport to the back contact. Especially for highly ordered nanotubes arrays, it can eliminate randomization of the grain network and increases contact points for good electrical connection. Charge carrier recombination has been demonstrated to be significantly lower in dye-sensitized TiO$_2$ nanowires and nanotubes based solar cells. Besides, for highly ordered nanotubes arrays, the porosity of the ordered structure allows the incident photons to be more effectively absorbed than on a flat electrode, with anisotropic optical scattering occurring when the pore displacement period and the light wavelength have comparable values. This thesis only focuses on the TiO$_2$ NT and TiO$_2$ NW.

1.1.3 Applications

All the specific properties of nanomaterials have led to the exploitation of TiO$_2$ nanomaterials for a wide variety of applications in which TiO$_2$ nanomaterials is essentially preferred over conventional TiO$_2$ materials. Amongst the multiple uses of TiO$_2$ nanomaterials, two major applications can be highlighted, photocatalytic water splitting and solar cells.

Photocatalytic water splitting

Hydrogen has been identified as a potential energy carrier due to its high energy capacity and environmental friendliness. There are a lot of materials that can be the potential sources of hydrogen. However, CO$_2$ is produced or energy from an external resource is required in process of the hydrogen generation by using some of these hydrogen-containing materials. In the pursuit of a friendly way of hydrogen generation, TiO$_2$ came onto the stage and began to show its excellent advantages. In 1972, Fujishima and Honda achieved water splitting using TiO$_2$. In their pioneering work, when the surface of the TiO$_2$ electrode was irradiated by UV light, water was oxidized and oxygen appeared at the TiO$_2$ electrode, while the hydrogen at the platinum electrode. This is
attributed to the unique electronic properties of TiO$_2$: wide bandgap semiconductors with suitable band-edge positions and a good match of the redox potential of water. When TiO$_2$ absorbs a photon that has energy equal or higher than energy of its band gap, electron at cole level will be excited into CB, leaving a hole at the VB. The electrons (in CB) and holes (in VB) then migrate to the surface of the photocatalyst. The eletrons then act as reducing agent and the holes act as the oxidizing agent. For instance, considering the band gap energy of TiO$_2$ (~3.2 eV) is larger than the energy of water splitting (1.23 eV), water can be splitted into O$_2$ and H$_2$.

TiO$_2$ has two major problems in the way of continuing exploitation of its functional properties. The first problem is that electrons in the VB can not be excited into conduction band by a visible light photon and TiO$_2$ cannot take advantage of most of the sunlight spectrum on its own. In addition, once the electron-hole pairs are generated, there are several possibilities: 1) radiative recombination of electrons and holes on the surface or in the bulk of the semiconductor; 2) non-radiative recombination of the electrons and holes; 3) electrons and holes are separated and initiate photocatalysis. So the second problem is the efficiency of the usage of solar energy is very limited. Amongst them, luminescence (radiative recombination) is one of important properties of semiconductors, which associated with near-band-gap recombination and defets. So understanding of the mechanism of the luminescence of TiO$_2$ can help us to further improve the efficiency of the photocatalysis.

**Dye-sensitized solar cells (DSSC)**

DSSCs are based on dye-sensitization of a wide band gap semiconductor.$^{30}$ In TiO$_2$-based DSSC, TiO$_2$ nanomaterials are covered with an organo-metallic dye immersed in an electrolyte containing a redox couple. The anode is composed of semiconductor with a transparent conducting electrode. The cathode is generally made of platinum or carbon. In TiO$_2$-based DSSC, the light absorption and the charge separation functions are separated. When light is shined on the DSSC, the dye molecules interact with the photons and electrons are excited to a state that is energetically higher than the conduction band edge of the TiO$_2$. As a result, electron-hole paires are generated in the dye. Electrons are injected into the conduction band of semiconductor, while the holes left in the dye are
rapidly reduced by electrolyte, thus preventing recombination of the electrons and holes. Electrons travel through the semiconductor to the electrode, the external load and finally to the counter electrode where they reduce the electrolyte.\textsuperscript{31} The TiO\textsubscript{2} are important not only because of the large amount of dye that can be adsorbed on the very large surface but also for another two reasons: (a) they allow the semiconductor small particles to become almost totally depleted upon immersion in the electrolyte (allowing for large photovoltages) and (b) the proximity of the electrolyte to all particles makes screening of injected electrons, and thus their transport, possible.\textsuperscript{32}

1.1.4 Synthesis methods of TiO\textsubscript{2} NT and NW

The growth of 1D TiO\textsubscript{2} nanomaterials requires the arrangement of atoms in a controlled manner: e.g. composition, size growth direction and crystallinity. Various techniques have been developed to synthesize nanomaterials of desired morphologies and chemical compositions. Here, two different methods are introduced for synthesis of TiO\textsubscript{2} NT and TiO\textsubscript{2} NW, respectively.

Electrochemical anodization method

Highly ordered TiO\textsubscript{2} NT arrays in this work are synthesized by electrochemical anodization. Apart from electrochemical anodization, TiO\textsubscript{2} NT can be produced by a number of other methods. These methods include: using a template of nanoporous alumina\textsuperscript{33-36}, sol-gel transcription processes using organo-gelator\textsuperscript{37,38}, seeded growth mechanisms\textsuperscript{39}, and hydrothermal techniques\textsuperscript{40-42}. However, none of these methods can offer good control over the nanotube dimensions. TiO\textsubscript{2} NT obtained is either single tubes or loose agglomerates of the tubes or bundles that are dispersed in solution. The tube lengths are also in a wide distribution. In order to make use of the structures in electrically contacted devices, the nanotubes are usually compacted into layers and attached onto electrode surface. The electrochemical anodization method is a self-organization process: arrays of oxide nanotubes are formed by etching the metal substrate. As a result, nanotubes are aligned perpendicular to the metal surface with well-defined length. As the tubes are directly attached to the metal surface, tubes are also electrically connected with substrate and easy to handle. Electrochemical anodization method can
provide a dense and defined nanotube layer on any shape of titanium surfaces and is thus an extremely versatile parallel structuring process. The samples used in Chapter 4 are the TiO$_2$ NT peeled off the Ti substrate.

**Hydrothermal method**

TiO$_2$ NW investigated in this thesis is synthesized by hydrothermal method, which is one of the template-free methods. In the template-based methods, growth of nanowires is controlled by the template. Their growth depends on the boundary between the template and bulk liquid, which only occupies a small part of the total volume. However, the nanowire synthesis by using template-free methods, such as hydrothermal method, require stringent growth conditions since favourable conditions are needed to promote 1D growth in the entire bulk liquid.

Hydrothermal synthesis involves the crystallization and growth of a material in the high-temperature aqueous solution at high pressures. Hydrothermal synthesis is normally conducted in reactor chamber called autoclaves with or without Teflon liners, which can provide high temperature and high pressure inside. The temperature can be increased over the boiling point of water and reach the pressure of vapour saturation. Internal pressure produced is largely determined by the temperature and the amount of solution added to the autoclave.

The starting material composition and its homogeneity, purity, and quality must be carefully controlled in hydrothermal synthesis of nanowires. Reaction temperature, pH of the solution, and the type of oxidants used are the variables which affect the product. The disadvantage of hydrothermal method is the requirement of high temperatures and pressures and the expensive reactor chamber. The growth mechanism of 1D growth is not clearly understood yet. After the fundamental work of synthesis of TiO$_2$ NT by Kasuga et al$^{40, 43}$, the hydrothermal method is reported to be the most powerful technique because of its simplicity and the fact that the nanowires are synthesized in cost-effective and environmentally friendly way$^{44}$. Hydrothermal method has already been applied to prepare a wide range of TiO$_2$ NW. In my project, hydrothermal method is introduced to prepare the TiO$_2$ NW.
1.2 X-ray absorption and related spectroscopy

1.2.1 X-ray absorption near-edge structures (XANES)

When light interacts with matters, it can be totally or partially absorbed. However, depending on the nature and the thickness of the matter, light can be totally or partially absorbed. The amount of light transmitted can be related to the intensity of incident light according to Beer’s law:

\[ I = I_0 e^{-\mu t} \quad (1.1) \]

where \( I_0 \) and \( I \) are the intensity of the incident and transmitted light, respectively, \( t \) is the sample thickness, \( \mu \) is so-called absorption coefficient, as shown in Figure 1-3. For X-ray, as for all light, the X-ray intensity is proportional to the number of X-ray photons (~ 500 eV to 500 keV).

![Figure 1-3](image)

**Figure 1-3** Light absorption measurements: an incident beam of intensity \( I_0 \) passes through a sample of thickness \( t \), and the transmitted beam has intensity \( I \).

X-ray is absorbed by all matter through the photo-electric effect. When the X-ray has energy equal to the binding energy of a core electron (threshold), there is a sharp rise in absorption coefficient often referred to as an absorption edge, indicating the core electron has been excited to the lowest unoccupied electronic states (LUMO in molecules, states just above the Fermi level in metals, bottom of the conduction band in semiconductors, etc.). Since every element has its characteristic absorption edge, we can tell which element is present in a sample based on measuring the energy of the absorption edge. Figure 1-4 shows the atomic absorption cross section of platinum as a function of X-ray energy \( (E) \).\(^{45}\) As we can see in Figure 1-4, several absorption edges appear at energies...
which correspond to the core electrons at different levels being excited. The edges labeled with $K$, $L_1$, $L_2$ and $L_3$ refer to the excitations of the $1s$ core electrons, $2s$ core electrons, $2p_{1/2}$ electrons and $2p_{3/2}$ electrons, respectively. As the X-ray energy increases above the threshold, the excitation will probe the unoccupied electronic states with higher energy showing modulation in the absorption coefficient. The modulation is caused by the outgoing electron being scattered by a neighbouring atom, the feature of which is determined by the local environment (nearest neighbours and the local symmetry) of the absorbing atom.

![Log-log plot of the mass absorption coefficient of platinum as a function of X-ray photo energy.](image)

**Figure 1-4 Log-log plot of the mass absorption coefficient of platinum as a function of X-ray photo energy.**

X-ray absorption fine structure (XAFS) hence refers to the variation of $\mu$ as a function of X-ray energy ($E$) of an atom in a certain chemical environment. The XAFS is typically divided into two regimes: X-ray near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS). Although the two have the same physical origin, they represent different regions on the XAFS and can provide us different information. In this thesis the information we need for our analysis comes from the XANES. The first 50 eV
or so above the edge is often referred to as the XANES. Technically, by scanning the energy from a few eV below the absorption edge up to about 50 eV above the edge, XANES records the variation of absorption coefficient as a function of energy. XANES arises from bound-to-bound (e.g. $1s$ to LUMO of $p$ character), bound-to-quasibound (multiple-scattering state) and bound to continuum dipole transitions. XANES is sensitive to formal oxidation state and coordination environment and is often used to study local structure and bonding of the absorbing atom in a chemical environment.

1.2.2 X-ray excited optical luminescence (XEOL)

X-ray excited optical luminescence (XEOL) is an X-ray photon-in, optical photon-out spectroscopic technique that monitors light emission from matter in the optical region upon the absorption of X-ray. Figure 1-5 shows the absorption and luminescence process responsible for XEOL in a semiconductor.

![Figure 1-5 Schematic diagram of the electron-hole pair generation and recombination. (a) core electron excitation, (b) electron and hole thermalization, (c) examples of radiative recombination via (i) direct recombination, (ii) phononassisted indirect recombination, (iii) presence of traps](image)
The absorption of an X-ray photon creates a core hole followed by a cascade process of filling the hole with electrons from shallower levels via Auger electrons and X-ray fluorescence. In a semiconductor, the electrons and holes thermalize at the bottom of the CB and the top of VB, respectively. Then they can form an electron-hole pair (exciton) which recombines and the energy is released either radiatively (optical photon) or non-radiatively (phonon). The radiative recombination of electrons and holes will produce optical luminescence. And this process is called X-ray excited optical luminescence (XEOL). The XEOL process is shown in the Figure 1-5. The recombination can be a direct one, i.e. by the formation of an exciton. And the emitted light has energy equal to the energy difference between the band gap and the exciton binding energy. The recombination can also be an indirect one. This kind of luminescence is related to defects such as the trapped holes, trapped electrons and impurities and thus the energy of luminescence is lower than the band gap luminescence.

Researchers often study the photoluminescence of materials with a single energy excitation source, such as UV-visible source. So only the electronic transition from the valence electrons to the CB is excited. Considering in XEOL the luminescence is produced by using tuneable X-ray sources sufficient to excite the core-level electrons, the luminescence is related with the absorption process and also the intensity of the luminescence can be a function of the absorption coefficient of the core electrons. For instance, in multi-element or multi-component sample, if the energy tends to transfer to the optical channel associated with one element or one chemical environment, the variation of the XEOL intensity would be consist with the variation of the absorption coefficient of that element across the edge. On the contrary, if the X-ray excites the core-level of other elements, the XEOL would be less sensitive to the variation of the absorption coefficient.\textsuperscript{46,47} Being element, site, and excitation channels specific makes XEOL an advantageous technique for the study optical properties of nanomaterials, which can be achieved by tuning the excitation energy to a desired edge of a certain element and track its optical emission.
1.2.3 De-excitation processes following the X-ray absorption

Following an absorption event, the atom is said to be in an excited state, with one of the core electron levels left empty (a so-called core hole), and a photo-electron. The excited state will eventually decay typically within a few femtoseconds after the X-ray absorption. There are two main de-excitation processes occurring to fill the core-hole. The first of the de-excitation process is X-ray fluorescence (Figure 1-6).\textsuperscript{48} The fluorescence energies emitted are element-specific, and can be used to identify the elements in a system, and to quantify their concentrations. For example, an \textit{L} shell electron dropping into the \textit{K} level gives the \textit{K\alpha} fluorescence line. The second process for de-excitation of the core hole is the Auger Effect. In the Auger process, an electron at shallower level fills the core hole, and the energy released is transferred to excite another electron into continuum.

![Diagram of de-excitation processes](image)

\textbf{Figure 1-6} Decay of the excited state: x-ray fluorescence (left) and the Auger effect (right). In both cases, the probability of emission (x-ray or electron) is directly proportional to the absorption probability.\textsuperscript{48}
Both the Auger yield and fluorescence yield are proportional to the absorption coefficient $\mu$, because they are related to the probability of the presence of the core-hole created by X-ray absorption.

XAFS can be measured by transmission or fluorescence geometries. We can measure the energy dependence of the absorption coefficient $\mu(E)$ either in transmission as

$$\mu(E) = \log \left( \frac{I_0}{I} \right)$$ (1.2)

or in X-ray fluorescence (or Auger emission) as

$$\mu(E) \propto \frac{I_f}{I}$$ (1.3)

where $I_f$ is the monitored intensity of a fluorescence line associated with the absorption process.

1.3 High pressure phenomena

1.3.1 High-pressure study

Pressure is a thermodynamic parameter of paramount importance for chemical equilibrium and chemical kinetics. In universe, pressure spans over 60 orders of magnitude, from $10^{-32}$ Pa in the intergalactic space to $10^{32}$ Pa ($1 \text{ GPa} = 10^9 \text{ Pa}$) at the center of the neutron star. In such a large range of pressure, materials could have various structures with different properties. Pressure has been used to study the response of chemical systems in varying thermodynamic states in the laboratory. However, in the most of these researches, pressures applied only cover a small fraction, such as one atmosphere to a kilobar ($0.1 \text{ GPa}$) under which “high pressure” chemical reactions are carried out. It is obvious that these so-called “high pressures” are far from the magnitude of the high pressure in our nature, such as the pressure of the earth core (around 330-360 GPa).

High-pressure studies had a real development in the past few decades and became showing its potential in the fundamental chemical studies. Modern high pressure experiments started from pioneering work of P. W. Bridgman. And the later invention of the diamond anvil cell (DAC) established the foundation of static high-pressure study in
modern laboratories. The most popular high pressure device nowadays is the DAC which was designed by Lawson and Tang\textsuperscript{49} and developed by Jamieson et al.\textsuperscript{50} and Weir et al.\textsuperscript{51} This kind of DAC now enable physics and chemistry experiments to be carried out in the laboratory into multimegabar range (P > 100 GPa) and the highest pressure attained in the laboratory with a DAC is around 400 GPa.\textsuperscript{52}

Pressures now provided in laboratories can induce changes of free energy of materials\textsuperscript{53} that exceed the enthalpy of those strongest chemical bonds (>10 eV). This is because pressure (P) and energy (E) has a relationship given by,

\begin{equation}
P = -\frac{\partial E}{\partial V} \quad (1.4)
\end{equation}

In the equation above, E varies with the change of the volume (V). Under high pressure, interatomic distance is significantly shortened and the system becomes thermodynamically unstable. System will eventually retrieve a new free energy minimum and be stable again. Meanwhile, systems may go through different processes, such as phase transformation, ionization, polymerization, amorphization, dissociation and, even atomization and metallization. Thus high pressure can offer enhanced opportunities to discover new phases, trigger chemical reactions, forcing materials into new physical and chemical states. For example, under high pressure, oligomerization of butadiene can achieve polymerization without catalyst at 0.7 GPa\textsuperscript{54}. Under high pressure greater than 120 GPa and temperature of 2000 K, N\textsubscript{2} which contains the strongest homonuclear bond forms a polymer.\textsuperscript{53} Some materials can become metal under high pressure. Iodine becomes a monatomic metal by around 20 GPa. Si transforms into metallic polymorphs by 10-12 GPa.\textsuperscript{55} Once megabar pressures are attained, elements such as oxygen sulphur and xenon all become metals.\textsuperscript{56-58}

Investigation of pressure-induced phase transitions and structural changes, as well as characterization of new structures in materials represents a frontier area of materials research. In particular, extensive work on metal oxides has revealed rich information on new structures and properties that could potentially be adopted in novel functional materials, such as SnO\textsubscript{2},\textsuperscript{59} ZnO,\textsuperscript{60,61} TiO\textsubscript{2},\textsuperscript{6-9} etc. For example, TiO\textsubscript{2} is one of the
fundamental materials for lithium battery. However, among all the polymorphs of TiO$_2$, TiO$_2$-B phase exhibits a higher efficiency than the rutile phase and anatase phase.\textsuperscript{62} So searching the structures with properties which can satisfy the applications is of particular interest. One approach to obtain new structures is the application of high pressure.

![Figure 1-7 Phase transitions of wurtzite CdSe nanocrystals towards rocksalt structure as a function of the diameter of the crystal. The phase transition is taken at the midpoint of the hysteresis loop.\textsuperscript{65,66}](image)

1.3.2 High pressure effects on nanomaterials

The properties of nanomaterials largely depend on the synthetic methods. It has been demonstrated that high pressure can provide an additional force to modify the structures and morphologies of nanomaterials. For example, carbon nanotubes can transform into single crystal diamond at high pressure.\textsuperscript{63} Moreover, high-pressure behaviours of nanomaterials are much different from that of the corresponding bulk counterparts. For example, it is found that upon compression the bulk ZnS undergoes a phase transformation from wurtzite phase to sphalerite phase and then to rock salt phase. However, the high-pressure behaviours of the ZnS nanorods are totally different from their bulk counterpart. In the high-pressure study of ZnS nanorods, wurtzite phase
directly transforms into rock salt phase and the mediate phase of sphalerite phase is bypassed.\textsuperscript{64}

In addition, size of the nanomaterials is also an important factor which influences the high-pressure behaviours. For instance, CdSe nanomaterials undergo a phase transformation sequence upon compression: wurtzite phase to rocksalt phase. Interestingly, the phase transformation pressure shows a function of the size of the CdSe nanoparticles. As we can see in the Figure 1-8, with the increasing of the size of the CdSe nanoparticles, phase transformation pressure decreases. When the size of the nanocrystalline CdSe reaches 10 nm, the transition pressure is the same as that of the corresponding bulk materials. \textsuperscript{65,66}

Although many high-pressure studies have been carried out on nanomaterials, most of them are nanoparticles. High-pressure studies on 1D nanomaterials attract much attention in recent years, not only because of their superior properties and wide applications, but also because of the morphology-effects on high-pressure behaviours which is lack of understanding.

1.4 Motivations

The chemical and physical properties of TiO\textsubscript{2} have been widely studied since it has found to be an excellent candidate for DSSC and photocatalysis applications. Various researches have been conducted to achieve better DSSC and photocatalytic performance using TiO\textsubscript{2}-based devices\textsuperscript{6-9}. TiO\textsubscript{2} nanomaterials have a much higher surface to volume ratio, which maximizes the dye loading and light harvesting properties while maintaining its high electron transport ability. Among TiO\textsubscript{2} nanomaterials with different morphologies, such as nanowires, nanotubes, and nanoparticles, 1D nanomaterials show advanced properties in application.\textsuperscript{67-70} Anatase and rutile phases are two most commonly studied crystal phases of TiO\textsubscript{2} because of their high stabilities and natural abundance. Anatase and rutile have band gap energy of 3.2 eV, 3.0eV respectively, which correspond to the energy at UV region. In order to enhance the visible light harvest efficiency, band gap engineering such as metal and non-metal doping of TiO\textsubscript{2} has been performed by introduce new defect centers in the TiO\textsubscript{2} band gap.\textsuperscript{71-73} However, it is still crucial to
understand the basic properties of nanostructured TiO$_2$. Optical properties of non-doped TiO$_2$ in different crystal phases and morphologies even using different synthesis methods, which are closely related to the photocatalysis application, are not yet fully understood. Previous PL spectroscopy studies reveal that anatase TiO$_2$ nanoparticles and TiO$_2$ nanotubes emit visible green light and rutile TiO$_2$ exhibit a near IR.$^{74-76}$ However, considering TiO$_2$ nanowires is one of important 1D nanomaterials in industrial applications and their electronic structures and optical properties has never been fully studied before. So in my project, TiO$_2$ nanowires are studied by using XANES and XEOL in Chapter 3.

Compared to other nanostructure materials, one dimensional semiconducting nanomaterials have recently attracted considerable interest for their potential as the building blocks for fabricating various nanodevices.$^{67-70}$ Among these semiconducting nanomaterials, TiO$_2$ nanotubes synthesized using electrochemical anodization exhibit better electrical properties combined with much higher specific surface areas, thus TiO$_2$ nanotubes-based DSSC and water splitting system demonstrate far better properties.$^{16,17}$ Usually, these excellent properties originate from their unique nanotubes structures and crystal structures. Therefore, it is very important to explore the properties, stabilities, compressibilities of TiO$_2$ nanotubes under high pressure. A lot of high pressure studies of TiO$_2$ nanomaterials have been done in recent years.$^{77-82}$ Size- and morphology-effects on high-pressure behaviours of TiO$_2$ nanomaterials are found under high pressure. As no high-pressure study on TiO$_2$ nanotubes has been undertaken, many outstanding issues, such as, phase transition sequence, high pressure phases, compressibility, etc., still remain to be addressed. As a result, in-situ Raman spectroscopy and X-ray diffraction high-pressure study of TiO$_2$ nanotubes is done in Chapter 4.

1.5 References


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Chapter 2 Instrumentation

2.1 Synchrotron radiation

2.1.1 Principle of synchrotron radiation

Synchrotron radiation is produced by accelerating electrons approaching the speed of light. Controlled by a magnetic field, electromagnetic radiation is produced tangentially to the curved orbit of accelerated electrons. The power of the radiation by accelerated electrons is given by

$$P = \frac{2e^2 cE^4}{3(m_0c^2)^4 \rho^2}$$  \hspace{1cm} (2.1)

where $e$ is the electron charge, $c$ is the speed of light, $E$ is the energy of electron (in GeV), $m_0$ is the rest mass of the electron, and $\rho$ is the radius of the curvature.

Figure 2-1 Schematic layout of a synchrotron radiation facility.
Figure 2-1 shows a schematic layout of a synchrotron radiation facility. First the generated electrons are accelerated to a speed close to the speed of light with energy of hundreds of MeV in the linear accelerator (LINAC). Then the electrons are injected into the booster ring and further accelerated to reach the 99.9999985% of the speed of light. Finally electrons are injected into the storage ring and circulate for several hours. The storage ring consists of straight sections and curved sections. In the curved sections bending magnets are located, which bend the electron beam and make up a 360° bending in total. In the straight sections, the wigglers and undulators, known as “insertion devices” are placed.

Synchrotron radiation is emitted while the trajectory of the accelerated electrons is altered. This is achieved by the use of two kinds of magnets, the bending magnets, and the insertion devices (wigglers and undulators). The magnetic field in the vertical direction of bending magnets and insertion devices cause the oscillation of electrons in the horizontal plane. Each type of magnets provides radiation of different spatial distribution, which is determined by the opening angle \(1/\gamma\). \(\gamma\) is given by (Equation 1.8).

\[
\gamma = \frac{E}{m_0c^2} \quad (2.2)
\]

As shown in Figure 2-2, considering the electron beam bend along the orbit of curved section, a bending magnet produces sharp cone of radiation in the bending plane, shown in Figure 2-3. Because wigglers have high magnetic field, radiation beam generated in wigglers has a large open angle. However, undulators have a low magnetic field compared with wigglers, as a result the radiation beam has a smaller open angle, which leads to a narrower beam of higher brightness (number of photons per second per source area per unit angle). As seen in Figure 2-3, radiated energy is continuous for both bending magnet and wiggler, but it is a series of sharp peaks for undulators.\(^4\)
Overall, synchrotron radiation has many advantages comparing with traditional X-source: (1) the photon energy covers the energy range from IR ($10^{-3}$ eV) to hard X-ray ($10^5$ eV); (2) the flux (number of photon per second per milliradian of horizontal angle per 0.1% bandwidth integrated over all vertical angles) of synchrotron radiation is 12 orders of...
magnitude as that of the traditional X-ray; (3) the beam is highly collimated, which is able to provide a very small focal spot or highly spatial resolution.

Figure 2-4 Schematic layout of the CLS beamlines.  

2.1.2 Synchrotron facilities

Canadian Light Source (CLS)

Figure 2-4 shows the layout of the CLS. Canadian Light Source (CLS), a synchrotron source, is located in the University of Saskatchewan, Saskatoon, Canada. CLS includes 12 straight sections (9 of them are available for insertion devices), 24 bending magnets, and over 40 potential beamlines. So far, CLS has 14 beamlines in use and is capable to
provide photons from far IR to hard X-ray. The storage ring has a circumference of 171 m and is operated at an energy of 2.9 GeV and 500 mA.

Figure 2-5 Schematic layout of the APS beamlines

Advanced Photon Source (APS)

Figure 2-5 shows the layout of the APS. Advanced Photon Source (APS) is located at Argonne National Laboratory, Argonne, USA. It consists of 34 sectors, and each sector contains one or more beamlines for a variety of researches. The storage ring has a circumference of 1104 m and is operated at 7 GeV and current of 102 mA that runs in “top-up” mode, which means the beam is kept as a constant beam current by injection every 2 minutes.
2.1.3 Beamlines

**High resolution spherical grating monochromator (SGM) beamline-CLS: sector 11 insertion device-section 1 (11ID-1)**

The SGM beamline in CLS is used to conduct the X-ray absorption measurements in my project. SGM beamline (11ID-1) at CLS has the energy range from 250 eV to 2000 eV, which is ideal for studying $K$-edges of low-Z elements and $L$-edges of transition metals. SGM has three gratings available: low energy grating, medium energy grating and high energy grating, which correspond to different energy ranges, 250-700 eV, 450-1250eV and 740-2000 eV respectively. The resolution $E/\Delta E$ is $> 5000$ at energy below 1500 eV with focal spot of 1000 $\mu$m x 100 $\mu$m. Under 100 mA, SGM produce a flux (photons/s) is $> 10^{12}$ at 250 eV and $>10^{11}$ at 1900 eV.\(^9\)

**Beamline-APS: sector 16 insertion device-section B (16 ID-B)**

The 16ID-B beamline in APS is a dedicated high-pressure beamline for X-ray diffraction measurements. The source for 16ID-B is the dual undulator Type A, which provides X-ray in the energy region from 6 keV – 40 keV (normal) up to 60 keV – 70 keV. A Si double crystal was employed as monochromator. This beamline can provide a beam size of 4x5 $\mu$m$^2$ with the help of 200 mm KBr mirrors and produce a flux of $5 \times 10^{10}$ photons/s at the sample position. Such a small beam size and high energy at the sample position make it possible to conduct the XRD measurement on different sample spots in relatively short accumulation time. Besides, a MAR345 imaging plate detector is used to collect the diffraction patterns of the sample. In addition to the XRD technique, 16ID-B also provides many excellent technical supports such as the membrane and mechanical pressure control, online ruby and Raman system, and offline alignments and Ruby system.

2.2 High pressure techniques

2.2.1 Diamond anvil cells
High pressures are applied to materials in a controlled manner in our laboratory by using DAC. There are many kinds of DACs, such as membrane cell from Easylab, UK and P-type DAC from High Pressure Diamond Optics Inc. A symmetric type DAC manufactured by Princeton University is used in this project, which is shown in the Figure 2-6. The symmetric DAC has two parts: a piston and a cylinder. A pair of brilliant-cut diamonds with same size is mounted on the piston and the cylinder, one for each part. The schematic of the symmetric DAC is shown in Figure 2-7. In a closed DAC, the pair of identical diamond is placed between the two supporting seats. Between the two diamonds, there is a pre-indented metal gasket with hole drilled in the center. The hole is used as a sample chamber and it can be perfectly sealed by the two diamonds. Pressure is provided by the four screws. The force generated by the screws can be transmitted to the backup seats which further press the two diamonds, and yield a high pressure on the diamond tip and an even higher pressure in the gasket and sample.
There are two reasons to use the diamond as anvil. First, the diamond is the hardest material in nature. Therefore, diamond can sustained very high pressure on samples without breaking itself. Second, diamond is transparent to a wide range of electromagnetic radiation. As a result, the structure of the materials at high pressure can be characterized by multi techniques such as Raman and IR spectroscopy, XRD etc. There are two different types of diamonds used in DAC. Type I diamonds with higher impurity (e.g. nitrogen) are used for Raman and XRD measurement. Type II diamonds are used for IR measurements.

2.2.2 The ruby pressure gauge

For all high pressure experiments, reliable and accurate pressure gauge is very important. In our laboratory, a ruby gauge is adopted for the in situ high-pressure calibration in DAC, which is established by Mao. \(^{10}\) Ruby is Al\(_2\)O\(_3\) doped with Cr\(^{3+}\). It has two dominant luminescence peaks R\(_1\) and R\(_2\) excited under the radiations, which is associated with R\(_1\)
and R₂ transitions involving the Cr³⁺ ion. These two peaks are very sensitive to pressure and the peak positions shift to longer wavelength upon compression. As a result, the relationship between pressure and peak shift can be used to measure the pressure of the sample.

![Ruby fluorescence spectrum](image)

Figure 2-8 Ruby fluorescence measured at different pressures with the two luminescent peaks labeled (R₁ and R₂).²

The equation shown below is used to determine the pressure by measuring ruby fluorescence spectra.

\[
P = \frac{1904}{B} \left( \left( 1 + \frac{\Delta \lambda}{694.24} \right)^B - 1 \right)
\]

(2.3)

where \( P \) represents pressure in GPa, \( \Delta \lambda \) represents the shift of the R₁ peak. The parameter \( B \) is equal to 7.665 for quasi-hydrostatic conditions, and is equal to 5 for non-hydrostatic conditions. An example is shown in Figure 2-8. With the pressure increasing from 0.2 GPa to 0.8 GPa, there is a 0.25 red shift in R₁ peak.

2.2.3 Pressure transmitting medium
In high pressure range, homogeneity becomes a very serious problem. And the pressure across the sample chamber may not be uniform. So in order to improve the hydrostatic conditions, a pressure transmitting medium (PTM) is also loaded into the sample chamber. There several different kinds of PTM, which can maintain the hydrostatic condition up to different pressure. The first kind of PTM includes such as alcohol mixtures made of 4:1 methanol-ethanol and 16:3:1 methanol-ethanol-H$_2$O. This kind of PTM can maintain the hydrostatic condition to about 10.5 GPa.$^{11-13}$ The second kind of PTM can achieve higher pressure with keeping hydrostatic condition, such as silicon oil. Although silicon oil is much better than the alcohol mixtures, it cannot maintain the hydrostatic condition above 20 GPa.$^{14}$ This is because at about 20 GPa silicon oil undergoes a glass phase transition and lose its pressure transmitting ability. So if we want reach the pressure above 20 GPa or even higher pressure, the third PTM, noble gases, need to be introduced. Noble gases, such as Ne, Ar and He, are the best hydrostatic PTM known so far.$^{14}$ Ne, for example, can maintain the hydrostatic condition as high as 50 GPa. So the PTM used in the experiments varies as the highest pressure needed to be reached.

### 2.3 Raman spectroscopy

Due to diamond being transparent to a wide range of electromagnetic waves, different types of radiations can be used to characterize samples in DAC under high pressure. Raman spectroscopy is one of the techniques, which is widely used for high pressure measurements. Raman spectroscopy is used in physics and chemistry for the study of vibrational, rotational, and lattice modes of various materials.$^{15}$ The laser source for Raman scattering is monochromatic light, which covers visible, near IR, and near UV. When monochromatic light interacts with samples, electrons of the molecular system are excited into a virtual energy state. After relaxation, most of photons are elastically scattered. And this process is referred to Rayleigh scattering, whose energy equal to that of the incident beam. If some of the photons relax into a vibrational excited state from the virtual energy state, the energy of the scattered photon will be less than that of the incident beam. This process is called Stokes Raman scattering. In another case, if the molecule was already in an elevated vibrational energy state, energy of Raman scattering will be higher than that of the incident beam, which is called anti-Stokes Raman
scattering. However, only Stokes lines are measured in most instruments, because they are more intense than the anti-stokes lines. The energy difference between the incident and scattering photons is called Raman shifts, which can provide valuable spectroscopic information for the vibrational or rotational energy of the sample. Raman Scattering mechanism is shown in Figure 2-9.

![Figure 2-9](image)

**Figure 2-9 Three types of Raman scattering: Rayleigh Scattering, Stokes Raman Scattering and Anti-Stokes Raman Scattering.**

A user customized Raman system is used in our lab (Figure 2-10). An Argon ion laser is used as the excitation source (Coherent Innova 90C Series Ion Laser). Multiple discrete lines with different wavelengths are available covering a spectral range from 488 nm to 532 nm. In this project, 532 nm is used as the excitation wavelength. The microscope system containing 15× eyepieces and a 20× objective (Olympus Microscope) is used to focus the laser beam onto the samples. Raman spectrum is recorded by using a liquid nitrogen cooled CCD detector (Spec-10 system, Princeton Instrument). The Rayleigh scattering is removed by a pair of notch filters and an imaging spectrograph (SpectroPro-2500i, Acton Research Corporation) is used to analyze the Raman signals.
Besides, spectrometer is equipped with a triple grating (300 g/mm, 1200 g/mm, and 1800 g/mm) system with different resolutions. Standard neon lines are used to calibrate the system. With the calibration, the Raman system could achieve an uncertainty of ±1 cm⁻¹.

2.4 Other characterization techniques

2.4.1 Powder X-ray diffraction

The conventional powder X-ray diffraction facility in Department of Earth Science is also used to check the phase of the products at ambient condition. The X-ray diffraction facility is equipped with a Rigaku X-ray diffractometer and a Co K- radiation X-ray source.

2.4.2 Scanning electron microscope (SEM)

SEM images were collected by using the Leo-Zesis 1530 SEM from Western Nanofabrication Facility, the University of Western Ontario. The 1530 is equipped with a high resolution SEM for imaging. The spatial resolution of the images can focus down to 1 nm depending on the materials.
2.5. References


(2) Dong, Z., The University of Western Ontario, 2008.

(3) Walker, T. *Introduction to Synchrotron Radiation*; Canadian Light Source.


(7) Picture Courtesy of the Canadian Light Source.

(8) Picture Courtesy of the Advanced Photon Source.


Chapter 3 XANES and XEOL studies of TiO$_2$ nanowires

3.1 Introduction

Nanostructured TiO$_2$ is of great interest for possible application in photovoltaic cells, semiconductor photo-catalyst support, and gas and humidity sensor.$^{1-9}$ Insights gained from the electronic structure of TiO$_2$ NW will improve the understanding of this material, which will facilitate its engineering design. It is crucial to evaluate the structure and electronic properties of TiO$_2$ NW so that the optimal structures for specific applications can be realized and one can then increase the efficiencies for solar cells, electrolysis, and photocatalysis. XANES is a spectroscopic technique, which can probe the local symmetry and occupation of the states. The Ti $L_{3,2}$-edge of TiO$_2$ probes electron transition from Ti 2$p$ to the conduction band of Ti 3$d$ character, and the O K-edge probes the O 1$s$ to 2$p$ transition. The spectral features thus provide the information of the unoccupied density of states. Amorphous and crystalline TiO$_2$ differ in $d$-orbital splitting due to different degrees of distortion of the Ti-O octahedron and long-range order. So XANES, which measures the modulation of the X-ray absorption coefficient across an absorption threshold of the element of interest in a chemical environment, is a powerful tool in studying electronic structure.

Photoluminescence is a non-destructive and high-sensitivity technique widely used to investigate the photophysical and photochemical properties of solid semiconductors. The investigation of TiO$_2$ by PL can give us a better understanding about the optical properties of TiO$_2$. It is well known that the photoactivity of TiO$_2$ heavily depends on its crystal structure,$^{10,11}$ surface properties,$^{12,13}$ etc., which have essential correlation with the luminescence feature of TiO$_2$. Therefore, the investigation of TiO$_2$ by PL spectroscopy can provide information about the surface structure of TiO$_2$ and their contributions to the photoreaction performance of TiO$_2$.$^{14,15}$ Since most of the luminescence studies were carried out using a fixed excitation energy from a UV-visible source, the observed luminescence originates from the radiative recombination of excited valence electrons. In this experiment, we employ XEOL to investigate the correlation between luminescence and the electronic structure of TiO$_2$ nanowires of difference crystal phases. XEOL using excitation photons at a given edge is not only element but can also be site specific.
XANES and XEOL studies of 1D nanostructured TiO\textsubscript{2} in Dr. T. K. Sham’s group is started by Dr. Lijia Liu. The phase transformation process of TiO\textsubscript{2} NT induced by calcination was investigated.\textsuperscript{16} It has been found that TiO\textsubscript{2} nanotubes synthesized by anodization undergo amorphous-anatase-rutile phase transformation with the calcination temperature increasing. TiO\textsubscript{2} nanotubes show distinct optical properties at different crystal phases. Considering the electronic and optical properties of nanostructured TiO\textsubscript{2} could be highly dependent on the defect, surface state, purity, and morphology, it is very interesting and necessary to look into nanostructured TiO\textsubscript{2} of different morphologies synthesized by different methods and the corresponding electronic structures and optical properties. In this work, the TiO\textsubscript{2} nanowires were synthesized using hydrothermal method, and their electronic structure and optical properties were studied using XANES and XEOL.

3.2 Experimental section

3.2.1 Sample preparation

TiO\textsubscript{2} nanowires were prepared using the hydrothermal method.\textsuperscript{17,18} Anatase TiO\textsubscript{2} nanoparticles with average size of \textapprox 25 nm were purchased from “Nanostructured & Amorphous Material Inc.” and used without further purification. In a typical preparation procedure, 1 g of TiO\textsubscript{2} nanoparticle powders was placed into a Teflon-lined bottle with a capacity of 60 mL with 40 mL NaOH aqueous solution with the molarity of 10 M. Then the Teflon bottle was sealed into a stainless steel autoclave and maintained at a temperature of 200 °C for 24 h without shaking or stirring. After the autoclave was naturally cooled to room temperature, the sample obtained was sequentially washed with diluted HCl aqueous solution (1% wt), deionized (DI) water, and anhydrous ethanol alternatively until pH = \textapprox 7. The after-washed samples were dried at 70 °C for 6 h in air, at which step the product was white soft fibrous powder, as an indication of the formation of TiO\textsubscript{2} NW. The as-prepared TiO\textsubscript{2} NW was divided into 12 pieces, one of which was kept as a reference (as-prepared), and the rest were each calcinated at 120, 200, 300, 400, 500, 650, 700, 750, 800, 900, 1000 °C for 2 h, under ambient conditions, henceforth denoted as NW-ap, NW-120, NW-200, NW-300, NW-400, NW-500, NW-650, NW-700, NW-750, NW-800, NW-900 and NW-1000, respectively.
3.2.2 Characterization

Synchrotron radiation experiments were conducted at the High Resolution SGM beamline (Energy: 250-2000 eV, ΔE/E < 2×10^{-4}) at the CLS, University of Saskatchewan. XANES spectra were recorded in total electron yield (TEY), fluorescence yield (FLY) and photoluminescence yield (PLY, zero order). XEOL spectra, where applicable, were recorded with an optical spectrometer (Miniature Fiber Optic Spectrometer, USB65000, Ocean Optics). All spectra were normalized to the incident photon flux (I₀).

The powder X-ray diffraction facility in the Department of Earth Science was used to examine the crystallinity of the as-prepared products. The X-ray diffraction facility has a Rigaku X-ray diffractometer and uses the Co K-α radiation as the X-ray source.

The morphology of TiO₂ nanowires samples was characterized by Scanning Electron Microscopy (LEO 1530 SEM, LEO 1540 FIB/SEM) in the Nanofabrication Laboratory, the University of Western Ontario.

3.3 Results and discussion

3.3.1 Morphology

The SEM images of the as-prepared nanowires, and calcinated TiO₂ NW at 650, 700, 800, 900, 1000 °C are shown in Figure 3-1. It can be seen that the nanowires structure remains after calcinations at 700 °C, but broken nanowires are observed after calcinations at 800 °C. The broken nanowires begin to merge at 900 °C and the surfaces of nanowires become smooth. The nanowires calcinated at 1000 °C keep merging and become smoother.
Figure 3-1 SEM images of (a) as-prepared nanowires and TiO$_2$ NW calcinated for 2h (b) at 650 °C; (c) at 700 °C; (d) at 800 °C; (e) at 900 °C; (f) at 1000°C.
Figure 3-2 Ti $L_{3,2}$-edge XANES TEY of anatase phase of TiO$_2$ (red curve) and rutile phase of TiO$_2$ (blue curve)

3.3.2 XANES study of calcinated TiO$_2$ NW

Figure 3-2 shows the Ti $L_{3,2}$-edge XANES of commercial anatase and rutile. Figure 3-3 shows the Ti $L_{3,2}$-edge XANES of the as-prepared nanowires and the calcinated TiO$_2$ NW. The spectra shown in Figure 3-3 were recorded in TEY, which probe the sample surface of a few nanometers. Characteristic features of TiO$_2$ which is observed in Figure 3-2 correspond to transitions of Ti 2$p$ electrons to unoccupied 3$d$ electronic states. In Figure 3-2, peaks $a$, $b1$, and $b2$ is attributed to $L_3$-edge (transition of 2$p_{3/2}$-3$d$), and peaks $c1$ and $c2$ is attributed to $L_2$-edge (transition of 2$p_{1/2}$-3$d$). Due to the crystal field splitting of 3$d$ orbit distortion of Ti, both edges have two groups of peaks. By applying the molecular orbital in the case of 3$d$ transition metal,$^{19}$ $a$ and $c1$ is assigned to the transition 2$p$-t$_{2g}$ and $b1$, $b2$ and $c2$ is assigned to transition 2$p$-e$_g$.$^{20}$ However, we can still see that the peak corresponding to transition 2$p$-e$_g$ in $L_3$-edge split into $b1$ and $b2$. This splitting is due to the distorted octahedron TiO$_6$ basic unit and form local symmetries of $D_{2d}$ and $D_{2h}$ for
anatase and rutile, respectively. To assign these two peaks, first we need to compare the spectra of the two standard samples. First let’s take a look at the two standard samples in Figure 3-2: TiO$_2$ of anatase and rutile phases. It can be seen that the most significant differences is the intensity ratio of peak $b1$ and $b2$; i.e. $b1$ is more intense than $b2$ in anatase, but in rutile this is reversed. Due to $e_g$ state is more sensitive to the variation in symmetry, the relative ratio of $b1$ and $b2$ can be used to track the phase anatase and rutile. All features are broader due to lifetime broadening in both $L_2$-edge and $L_3$-edge. Although the splitting of peak $c2$ is no longer seen, we can still tell the difference between two crystal phases by the intervals between $c1$ and $c2$ that is larger in rutile than in anatase, which is correlated with the interval between the $t_{2g}$ and $e_g$ states in the two crystal phases.

![Figure 3-3 Ti $L_{3,2}$-edge XANES TEY of calcinated TiO$_2$ NW](image)

**Figure 3-3 Ti $L_{3,2}$-edge XANES TEY of calcinated TiO$_2$ NW**
Based on these established spectral features, we can track the crystal phase transformation under different calcination temperatures (Figure 3-3). And we will focus on the TEY spectra. After calcinations at 300°C, the spectrum shows well-resolved features. We can see the peak correspond to $2p_{3/2}$-$e_g$ is a broad asymmetric peak. There is no $e_g$ state splitting. This feature persists until 700 °C. Peak splitting shows up at 750 °C.
But peak $b_2$ becomes more obvious at 900 °C. Noticeable changes in the spectrum are observed for NW-1000, in which the ratio of peaks $b_1$ and $b_2$ are different from the ratios under 1000 °C. The intensity of $b_1$ is becoming lower and the intensity of $b_2$ is becoming higher. And peak $c_2$ shifts slightly to higher energy.

By comparing the experimental spectra with standard spectra, changes in the spectra indicate the phase transition from anatase to rutile upon heating to high temperature. From the spectra, we can see the anatase phase shows up at 750 °C and is best crystallized at 900 °C. Above 900 °C, a sudden transformation to the rutile phase takes place.

![Figure 3-5 FLY of Ti $L_{3,2}$-edge of as-prepared and calcinated TiO$_2$ NW](image)

In order to figure out the more precise phase transformation process, laboratory XRD was recorded. By comparing with the standard XRD patterns, we can see that anatase phase shows up at 650 °C and the anatase phase is best crystallized at 800 °C calcinations. At 1000 °C calcination, the sample shows a very good rutile phase. Besides, we can see the
TiO$_2$-B phase starts to show at 300 °C and did not disappear even at 900 °C. And this may be the reason why the peak splitting corresponding to $2p_{3/2}$-$e_g$ is not very obvious.

Now let us take a look at the FLY spectra of the TiO$_2$ NW, which are shown in Figure 3-5. All the features in FLY are similar to those of TEY. The broadening of the peaks in FLY is due to self-absorption. As in the TEY XANES, we can also see the gradually decreasing of the ratio of peaks $b1$ and $b2$ with the increasing of calcinations temperature. The temperature at which the spectra change from anatase-dominated to rutile-dominated is above 900 °C.

![Figure 3-6 O K-edge XANES TEY of as-prepared TiO$_2$ NW and TiO$_2$ NW at different calcinated temperatures](image)

**Figure 3-6** O K-edge XANES TEY of as-prepared TiO$_2$ NW and TiO$_2$ NW at different calcinated temperatures
The phase transformation from anatase to rutile can also be seen by looking at the O $K$-edge TEY. As we can see in Figure 3-6, there is a sharp peak at 533 eV energy and a very broad peak at 540 eV energy. After calcinations at 200°C, peaks $a1$ and $a2$ at 531 eV and 534 eV respectively appeared. A broad, weak peak $b1$ and broad peak $b2$ showed up at the first two sharp peaks are from the transition of the O 1$s$-to-2$p$ component in the TiO$_2$ 3$d$ band.$^{19}$ Because of the hybridization between O and Ti, it shows the similarity to the Ti $L_{3,2}$-edge for tracking different phases based on $t_{2g}$-$e_g$ splitting shown as a larger interval between peaks $a1$ and $a2$ in rutile. The peaks in the region of 535eV and 550eV are the O 2$p$ weight in the TiO$_2$ 3$a_{1g}$ and 4$t_{1u}$ environment mixed with Ti 4$s$ and 4$p$ states. The most obvious difference of the spectra between anatase and rutile phase in O TEY is that in anatase phase TiO$_2$ shows two peaks but rutile has three. As we can see in Figure 3-6, the NW-900 sample shows the anatase phase. And at 1000 °C calcinations, the sample has converted to rutile phase. The same trend can be also seen from the FLY of O $K$-edge in Figure 3-7. And this observation is totally accord with the Ti $L_{3,2}$-edge results.
By comparing with the previous work, it is found that no matter the TiO$_2$-B to anatase phase transformation or the anatase to rutile phase transformation, the both phase transformation points in my research are higher than those in literatures. Jaturong et al. observed that anatase phase showed up in the TiO$_2$ NW calcinated at 500 °C for 2 h and rutile phase showed up in the TiO$_2$ NW calcinated at 900 °C. And Ryuhei et al. found the similar results. These differences may be due to the removing of Na$^+$ by HCl solution, DI water and ethanol is not complete and some Na$^+$ still exist in the nanowires.

Figure 3-8 XEOL spectra collected with excitation photon energy at 550eV from NW-650, NW-700, NW-750, NW-800, NW-900, and NW-1000
Figure 3-9 PLY-XANES spectra (zero-order and wavelength-selected) at the Ti $L_{3,2}$-edge (left) and the O $K$-edge (right) of (a,b) NW-650, (c,d) NW-700, (e,f) NW-750
Figure 3-10 PLY-XANES spectra (zero-order and wavelength-selected) at the Ti $L_{3,2}$-edge (left) and the O K-edge (right) of (g,h) NW-800, (i,j) NW-900, (k,l) NW-1000
3.3.3 XEOL and PLY analysis of calcinated TiO$_2$ NW

From the XEOL study, we could not observe light emitting from the as-prepared nanowires, however the calcinated TiO$_2$ emits light and the wavelength of the light shows a significantly change with the variation of the calcination temperature. Figure 3-8 shows the XEOL spectra of NW-650, NW-700, NW-750, NW-800, NW-900, and NW-1000. The excitation photon energy is 550eV, which is above both the Ti $L_{3,2}$-edge and O K-edge. The 650 °C calcinated TiO$_2$ NW emits weak green PL, shown as a broad peak centered at 470 nm. The green PL shifts up to 550 nm after calcinations at 750 °C. At the calcination 1000 °C, the green PL becomes very weak, and a weak near IR PL is seen at 830 nm. The changes of spectra after calcination at 1000 °C correspond to the phase transformation from anatase to rutile. So the calcination of nanostructured TiO$_2$ NW results in a rutile phase with near IR PL. And this result is accorded with previous references. However, there are some phenomena, which have not been seen before. First, before the anatase phase transferring into rutile phase samples annealed at different temperatures show green PL, however, there are two different kinds of green PL. The samples TiO$_2$ NW-650 and TiO$_2$ NW-700 show the green PL centered at 470 nm, however, the samples TiO$_2$ NW-750, TiO$_2$ NW-800 and TiO$_2$ NW-900 shows the green PL centered at around 550 nm. Based on previous study, the green PL comes from the oxygen vacancy. However, they may come from different kinds of oxygen luminescence. Considering there are TiO$_2$-B phase existing in the samples annealed at temperatures below 750 °C, the green PL centered at 470 nm may be attributed to the existence of TiO$_2$-B phase. Besides, the phase transition is consisted with the green PL shift. As a result, we propose the green PL centered at 470 nm is due to the TiO$_2$-B phase.

From the XANES spectra above, we figure out the phase transformation from anatase to rutile as increasing of the calcination temperature. Next we will try to explain the phenomena of the light emitting of TiO$_2$ by using a combination of studies and analysis of wavelength-selected PLY and XANES at the Ti $L_{3,2}$- and O K-edges. Since the green PL in NW-1000 is too weak to be separated from the dominant luminescence, we will focus on the green PL in the anatase phase and near IR PL in the rutile phase in the following discussion.
A series of PLY spectra of TiO$_2$ NW at Ti $L_{3,2}$-edge and O $K$-edge for samples calcinated at temperatures of 650, 700, 750, 800, 900, 1000 °C are shown in Figure 3-9 and Figure 3-10. Except for the 1000 °C sample, all specimens are in anatase phase, and emit green PL. The green PL becomes very weak and near IR PL can be observed at 1000 °C. As we know at 1000 °C calcination temperature, anatase converts to rutile phase. However, at 1000 °C sample shows different intensities of near IR PL at TiO$_2$ $L_{3,2}$-edge and O $K$-edge. The near IR PL is more intense at Ti $L_{3,2}$-edge, and very weak at O $K$-edge. Besides, as we can see in the Figure 3-9 and 3-10, the intensity of luminescence varies as the excitation energy changing in both Ti $L$- and O $K$-edge. It is can be seen that the variations of the two luminescence bands are different, which indicate different luminescence mechanisms and origins.

From Figure 3-9 and Figure 3-10, we can notice some interesting things. First, samples calcinated at 650, 700, 750, 800, 900 °C emit the green PL. Considering the emission energy is well-below the band gap of TiO$_2$ three phases, so this kind of luminescence is due to self-trapped exciton but not the band edge emission. We attribute this green luminescence to surface states of anatase (electron traps), which is in agreement with previous observation. The green PL is intense, which means that energy transferring to this optical channel is effective, quenching the formation and decay of near band gap excitons. We attribute the disappearance of green PL to the phase transformation from anatase to rutile phase. Since the green PL disappeared at the same calcination temperature as the happening of the phase transformation. Second, it can be seen from Figure 3-9 and Figure 3-10 that the luminescence intensities vary as the excitation energy is scanned across both Ti and O edges. But the intensities of the PLYs at Ti and O edges show different edge jump. PLYs of green PL at Ti edge show the partial inversion to TEYs. However, the green PLYs at O edges show a totally positive edge jump. Compared with luminescence at Ti $L_{3,2}$-edge, the total luminescence intensity is less sensitive to the absorption coefficient of O 1$s$ electron. Third, the near IR PL shows up in NW-1000, which is attributed to the formation of rutile. As we can see the PLY in rutile TiO$_2$ NW, it shows a partial inversion at the Ti $L_{3,2}$-edge and a total inversion at the O $K$-edge. From the PLY spectra, we can see that upon excitation away from the edge (both
below and well above the edge) TiO$_2$ emits intense near IR emission, but just above the edge, the luminescence is partially quenched.

We attribute the PLYs inversion to TEY to the saturation effect when the luminescence is less likely surface-related. The inversion can be explained in details as follows. It is known that the secondary process ("reabsorption" of the Auger electrons and fluorescence X-rays) plays an important role in the energy transferring to the near IR channel. If the penetration depth of the incident photons is shallow, fluorescence X-rays and Auger electrons are generated at a shallow place of the material. So they can easily penetrate the thin layer of the material and escape out of the surface material without contributing to the secondary process. As a result, quantum yield of the near IR PL is decreased. In our case, the penetration depth of the X-rays photon is very short in these energy regions (e.g. ~900 nm below and 100 nm above the Ti $L_{3,2}$-edge), so the X-ray fluorescence and Auger electrons escape out of the surface directly and effective energy transfer reduce. The appearance of near IR PL along with quenching green luminescence by calcination of TiO$_2$-NW is due to the replacement of luminescence site from anatase by that from the rutile, which is caused by the phase transformation from anatase phase to rutile phase at 1000 °C.

The explanation can well fit the phenomenon of the near IR total inversion to TEY. As we can see that PLYs only show inversion at Ti $L_2$-edge from TiO$_2$ NW-650 to TiO$_2$ NW-900 and the PLYs at Ti $L_3$-edge do not have a very clear relation to the absorption coefficient until temperature reach 1000 °C. But the trend that with temperature increasing the inversion feature is becoming clearer and clearer can be seen.

### 3.4 Conclusions

XANES and XRD studies of TiO$_2$ nanowires indicate that phase transformation from TiO$_2$-B to anatase happens at temperatures between 500 and 650 °C, and that the phase transformation of anatase to rutile takes place at temperatures between 900 and 1000 °C. By comparing with previous work where the phase transformation from TiO$_2$-B to anatase occurs at 500 °C and phase transformation from anatase to rutile took place at 900 °C, TiO$_2$ nanowires in my research shows different phase transformation
temperatures, and they are a little bit higher. It is proposed that the higher transition temperature is due to the existence of Na\(^+\). In contrast to conventional TiO\(_2\) materials, these nanowires exhibit amazing optical properties. We have observed green PL from anatase TiO\(_2\) nanowires and near IR PL from rutile TiO\(_2\) nanowires. The green PL is attributed to oxygen vacancies of anatase phase. And the near IR PL is attributed to bulk defects at the center of the rutile phase, and it is a favourable channel in the mixed phase of anatase and rutile.

3.5 References


Chapter 4 Pressure-induced structural transformations of TiO$_2$ nanotubes by Raman spectroscopy and synchrotron X-ray diffraction

4.1 Introduction

It is well known that TiO$_2$ is a semiconductor material with a wide band gap. Outstanding properties of TiO$_2$ polymorphs have made it extremely useful in many applications that have appeared in the past 20 years. For instance, TiO$_2$ is extensively used in high efficiency solar cell$^{1,2}$, photocatalysis$^3$, and super-hard materials$^4$, etc. For many of above applications, it is crucial to maximize the specific surface area to achieve a maximum overall efficiency, and therefore TiO$_2$ nanomaterials are widely used. With the development of the nanotechnologies, TiO$_2$ nanomaterials with different morphologies (nanoparticles, nanowires, nanobelts, nanotubes) were produced.$^5$-$^{11}$ Compared to other nanostructured materials, 1D TiO$_2$ nanomaterials, such as nanotubes and nanowires, have attracted considerable interest due to their superior properties in different applications, especially in photocatalysis and solar cells.$^{12}$-$^{15}$

TiO$_2$ has rich structures, among which it has three major stable polymorphs at ambient condition, namely anatase (space group $I4_1$/amd), rutile (space group $P4_2$/nmn), and brookite (space group $Pbnc$). Specific to a particular application, the preferred structure is different. For example, anatase phase is more bioactive and robust for catalysis purposes, while rutile is one of the natural minerals and can be used for electronic devices due to its high dielectric constant and thermodynamic stability. So searching the structures with properties which can satisfy the applications is of particular interest.

One approach to obtain new structures is the application of high pressure. Among the various structures of TiO$_2$, anatase and rutile are the most promising phases in advanced technical applications. Therefore, most high-pressure studies are carried out on TiO$_2$ in either anatase or rutile phase. A number of experimental and theoretical studies indicate that TiO$_2$ has a series of high-pressure phases. It is known that TiO$_2$ at high pressure attains phases that are isostructures with columbite (orthorhombic $\alpha$-PbO$_2$)$^{16}$ and baddeleyite$^{17}$ (monoclinic ZrO$_2$), which are shown in the Figure 4-1. Previous work has shown that TiO$_2$ bulk materials in anatase phase follow the phase transition route: upon
compression anatase phase to $\alpha$-PbO$_2$ phase and then to baddeleyite; upon decompression $\alpha$-PbO$_2$ phase is retrieved at ambient pressure.$^{16,18-24}$ However, this phase transition routes is only applicable to bulk anatase TiO$_2$, but not anatase TiO$_2$ nanomaterials. For instance, the $\alpha$-PbO$_2$ phase was found to be bypassed during the compression process of TiO$_2$ nanoparticles, and anatase phase transformed into baddeleyite phase directly. However, the $\alpha$-PbO$_2$ phase was retrieved later upon decompression.$^{18,25,26}$

Figure 4-1 Crystal structures of TiO$_2$. a: anatase phase (space group I4$_1$/amd); b: $\alpha$-PbO$_2$ phase (space group Pbcn); c: baddeleyite phase (space group P2$_1$/c). The red and blue balls stand for the O atoms and Ti atoms, respectively.

And increasing research effort has been focused on nanostructured TiO$_2$, especially in exploring new structures and properties. In many high-pressure studies of the TiO$_2$ nanomaterials, it was also found that different high pressure behaviours are still found among different TiO$_2$ nanomaterials. For example, Wang and Saxena$^{27}$ found that nanocrystalline anatase (with crystallite size ranging from 7 to 11 nm) was stable up to 24 GPa, and then turned to an amorphous phase on further compression. The amorphous
phase was quenchable to ambient pressure. However, later work of Wang et al.\textsuperscript{28} showed a different high pressure phase transition in TiO\textsubscript{2} nanoparticles with size of 30 nm using XRD, in which anatase phase transformed into baddeleyite phase about 16.4 GPa. Such a large discrepancy was believed due to the variation in the grain size of nanoparticles. A lot of systematic studies have indicated that high pressure behaviours of TiO\textsubscript{2} nanomaterials largely depend on their particle size. Three different phase transition sequences were summarized: 1) when the size of the nanoparticles is less than 10 nm, crystalline transfers to amorphous phase at high pressure;\textsuperscript{18,29-32} 2) when the size of nanoparticle is between 12 and 50 nm, the anatase transform directly into baddeleyite phase;\textsuperscript{18,26,29} 3) when the size of the nanoparticle is larger than 50 nm, phase transition undergoes the sequence from anatase to $\alpha$-PbO\textsubscript{2} and then to baddeleyite phase.\textsuperscript{18,22-24,29,33} These unique high-pressure behaviours of TiO\textsubscript{2} nanoparticles indicate that high surface energy of the TiO\textsubscript{2} nanoparticles not only increase their phase transition pressure but also can change their high-pressure phase transition sequence.

However size-effects model on high-pressure behaviour of TiO\textsubscript{2} nanomaterials cannot provide a proper explanation for all kinds of TiO\textsubscript{2} nanomaterials. The high-pressure behaviours of 1D TiO\textsubscript{2} nanomaterials do not follow the size-effects model. For instance, the pressure-induced amorphization and polyamorphism were found in TiO\textsubscript{2}-B nanoribbons with widths in range of 50-200 nm and thickness of ~20 nm. Besides, in Dong’s high-pressure study of anatase TiO\textsubscript{2} nanowires with two different diameters, 50-100 nm and 150-200 nm, anatase transformed directly into the baddeleyite phase without going through the $\alpha$-PbO\textsubscript{2} phase. The same results were also observed in the high-pressure study of anatase TiO\textsubscript{2} nanowires by Li et al.\textsuperscript{34} These studies indicate that morphology also plays an important role in the high-pressure behaviours of the TiO\textsubscript{2} nanomaterials.

In contrast to the extensive high-pressure investigation of TiO\textsubscript{2} nanoparticles, 1D TiO\textsubscript{2} nanomaterials were sparsely investigated. In this work, as TiO\textsubscript{2} nanotubes have never been studied under high pressure before, a high pressure study was carried out on anatase TiO\textsubscript{2} NT using \textit{in-situ} Raman spectroscopy and synchrotron X-ray diffraction. Through
this study, we attempt to understand the morphology-effect on high-pressure behaviours of TiO$_2$ NT.

4.2 Experimental section

4.2.1 Sample preparation

TiO$_2$ NT was synthesized via electrochemical anodization. The experiment was carried in a home-made electrochemical cell of a two-electrode configuration. The Ti foil of 0.1 mm thick (Goodfellow Ltd.) was cut into 2 cm $\times$ 1 cm pieces and rinsed with acetone and ethanol to remove surface organic impurities prior to the anodization. Ethylene glycol containing 0.25% (wt.) NH$_4$F was used as electrolyte. The Ti foil was anodized with an applied potential of 50 V for 72 hours at room temperature. After anodization, the Ti foil was rinsed with ethanol and dried under a N$_2$ flow. After the experiment, the surface of the Ti foil turned yellow, and the thin TiO$_2$ NT membrane can be easily peeled off from the substrate. The as-prepared TiO$_2$ NT membrane was then calcinated at 550 °C. Calcination was carried out in a furnace under ambient condition with a heating rate of 18 °C/min to the desired temperature and held for two hours. The samples were then cooled naturally to room temperature.

4.2.2 Characterization

SEM

The morphologies of the TiO$_2$ NT were examined using scanning electron microscopy (SEM, LEO 1540) at the Nanofabrication Laboratory, University of Western Ontario (UWO).

DAC and sample loading

A symmetrical DAC with two type-II diamonds with 400 $\mu$m culets was used for the high-pressure Raman measurements and for the high-pressure XRD experiment. A hole with a diameter of 130 $\mu$m was drilled on a stainless steel gasket and used as the sample chamber. Silicone oil was used as the PTM for Raman measurements, whereas Neon gas
was loaded as the PTM for X-ray diffraction measurements. And a few ruby balls were inserted as pressure calibrant. Sample will be measured *in-situ*.

**Raman spectroscopy**

A customized Raman micro-spectroscopy system was used to collect the Raman spectra. A 532 nm wavelength laser was used as the excitation source. The scattered light was then dispersed using an imaging spectrograph equipped with a 1200 lines/mm grating achieving a 0.1 cm⁻¹ resolution. The system was calibrated by neon lines with an uncertainty of ± 1 cm⁻¹.

**Synchrotron X-ray diffraction**

The XRD experiments were carried out using the synchrotron facilities at beam-line 16ID-B at APS in Argonne National Laboratory (ANL). The wavelength used is 0.3738 Å. The monochromatic synchrotron X-ray beam is focused at the center of the sample. Diffraction patterns of the samples are collected as Debye-Scherrer rings by a 2D detector.

![Figure 4-2 SEM images of anatase TiO₂ NT in (a) bottom view, (b) side view, (c) top view and (d) view after-compression](image-url)
4.3 Results and discussion

4.3.1 Morphology

Figure 4-2 shows the SEM images of TiO$_2$ NT. The TiO$_2$ NT is closely packed, forming a TiO$_2$ NT of ~35 μm length (see Figure 4-2 b). The bottom view of the TiO$_2$ NT membrane shows that these nanotubes are close-ended and of ~100 nm in diameter (see Figure 4-2 c). SEM images reveal that the surface nanostructures are nanotubes.

![Figure 4-3](image-url)  
Figure 4-3 Selected Raman spectra for TiO$_2$ NT upon compression and decompression. The red and blue arrows indicate the compression and decompression sequence, respectively.
4.3.2 Raman results of TiO$_2$ NT upon compression and decompression

The anatase phase of TiO$_2$ has a space group of $D_{4h}^{19}$ ($I4_1/amd$, $Z=2$). According to factor group analysis, 15 optical modes with the following irreducible representation of normal vibrations were predicted: $1A_{1g} + 1A_{1u} + 2B_{1g} + 1B_{2u} + 3E_g + 2E_u$, among which six modes ($A_{1g}$+$2B_{1g}$+$3E_g$) are Raman-active and three modes ($A_{1u}$+$2E_u$) are infrared-active. Raman spectra for as synthesized TiO$_2$ NT, as seen in Figure 4-3, contained 5 Raman peaks, which are consistent with the anatase phase. The numbers labeled in the brackets of the subscripts are used for distinguishing peaks with the same Raman mode.

Selected Raman spectra of TiO$_2$ NT collected upon compression up to 17.7 GPa are shown in Figure 4-3. Upon compression all the Raman modes shifted to higher frequencies except for the $E_g(2)$ mode, which exhibited a red shift before its disappearance at about 3 GPa (see Figure 4-4). Compression resulted in the reduced intensity of all the Raman peaks associated with the anatase phase. Raman spectrum became very flat and Raman peaks of anatase phase were difficult to tell at 17.7 GPa.

The reversibility of pressure effect on crystal structures provides important information on transformation mechanism. Therefore, after sample compressed to 17.7 GPa, Raman measurements of TiO$_2$ NT were also conducted upon decompression. In general, the intensity of all the Raman peaks increased gradually as pressure decreased. Upon decompression all the Raman modes shifted to lower frequencies. After pressure was completely released, no Raman peaks of anatase phase were retrieved, indicating the phase transition was irreversible in TiO$_2$ NT. Considering there are no new peaks observed in the compression and decompression processes, this may indicate that during the compression, anatase phase is directly converted into amorphous.
Figure 4-4 Pressure dependence of the other Raman active mode frequencies of TiO$_2$ NT upon compression.

4.3.3 XRD results of TiO$_2$ NT upon compression and decompression

The pressure evolution of the XRD patterns for anatase TiO$_2$ NT is shown in Figure 4-5. In-situ high-pressure XRD measurements were performed on TiO$_2$ NT upon compression up to 31.1 GPa. Representative diffraction patterns are depicted in Figure 4-5. All reflections at the near ambient pressure can be indexed to the TiO$_2$ anatase phase. At the starting pressure, by using Rietveld refinement (see Figure 4-6 a), we obtained $a = b = 3.8068$ Å, $c = 9.5233$ Å, and $V = 138.01$ Å$^3$, close to the values observed for bulk anatase materials (JCPDS file 84-1286). As seen in Figure 4-5, all the reflections of anatase TiO$_2$ shifted to higher 2$\theta$ angle with increasing pressure, indicating a pressure-induced reduction of $d$-spacing or shrinkage of unit cells. When the pressure was increased to 12.2 GPa, two reflections appeared at 7.3198$^\circ$ and 8.0128$^\circ$ for baddeleyite phase, indicating
that anatase phase started transforming into baddeleyite phase. In Figure 4-6 b, Rietveld refinement indicates that the two reflections are indexed as (1 1 -1) and (1 1 1) for baddeleyite phase. As the pressure exceeded 14.8 GPa, the reflections corresponding to anatase weaken significantly. All the reflections of anatase phase disappeared at ~19 GPa, which means that anatase phase completely transforms into baddeleyite phase. At this pressure, all reflections can be indexed to baddeleyite phase by using Rietveld refinement. (see Figure 4-7 a) Upon further compression, the intensity of these reflections of baddeleyite increased. At the highest pressures of 31.1 GPa, the baddeleyite phase became the main phase as almost all the reflections were indexed with baddeleyite structure. Although the reflections for TiO₂ NT were broadened, the reflections of the baddeleyite phase can still be easily seen, suggesting the samples were still in a crystalline phase instead of an amorphous phase which was the result of Raman high-pressure study. At ~10.1 GPa, a new reflection appeared, which is marked with “*”. This reflection is neither from anatase phase nor from baddeleyite phase. This reflection is attributed to the impurity. Upon decompression, all the reflections of baddeleyite phase shifted to lower 2θ angle with decreasing pressure, indicating expending of the unit cells. As we can see in the Figure 4-5, when the pressure was decreased from 31.1 GPa down to ~ 5 GPa, a new reflection appeared at 7.5595°, which means that baddeleyite phase began to transform into a new phase at ~5 GPa. This new phase remained down to ambient pressure and baddeleyite phase disappeared completely. In Figure 4-7 b, Rietveld refinement indicates that all reflections can be indexed to the α-PbO₂ phase.
Figure 4-5 X-ray diffraction patterns for TiO$_2$ NT upon compression. The red and blue arrows indicate the compression and decompression sequence, respectively.
Figure 4-6 Rietveld refinement of XRD patterns at 0.91 GPa (a) and the XRD patterns at 12.2 GPa (b) upon compression. The red cross is experimental X-ray intensity, whereas the green solid line is the calculated diffraction pattern based on refinement with the black curve at the bottom showing the difference between the calculated and observed intensities. The vertical bars with different colors indicate the characteristic reflections of different phases labeled in the front.
Figure 4-7 Rietveld refinement of XRD patterns at 19.0 GPa upon compression (a) and the recovered phase (b). The red cross is experimental X-ray intensity, whereas the green solid line is the calculated diffraction pattern based on refinement with the black curve at the bottom showing the difference between the calculated and observed intensities. The vertical bars with different colors indicate the characteristic reflections of different phases labeled in the front.
4.3.4 Discussion

It is known that upon compression anatase bulk TiO\(_2\) undergoes a phase transition sequence of anatase phase to \(\alpha\)-PbO\(_2\) phase, and then to baddeleyite phase. However, in our study, anatase phase transformed directly into baddeleyite phase in TiO\(_2\) NT upon compression. The same phenomenon was also observed in high-pressure of anatase TiO\(_2\) nanoparticles. There were several attempts to explain why \(\alpha\)-PbO\(_2\) phase was hindered in anatase TiO\(_2\) nanoparticles. Swamy \textit{et al.}\(^{29}\) suggested a size-dependent phase selectivity of pressure-induced phase transition in anatase TiO\(_2\) nanoparticles. Just as mentioned before, anatase-baddeleyite phase transition occurs in the middle sized TiO\(_2\) nanoparticles (12-50 nm). Phase transition sequences of different size of nanoparticles are shown in the Table 4-1. The size-dependent selective phase transition for anatase TiO\(_2\) nanoparticles has been explained by critical diameter for nucleation and growth of baddeleyite phase and \(\alpha\)-PbO\(_2\) phase, which is determined by the high surface energy of nanoparticles. By experiments, these critical diameters are estimated to be \(\sim 12\) nm and \(\sim 50\) nm for baddeleyite phase and \(\alpha\)-PbO\(_2\) phase, respectively.\(^{29}\) This model indicates that, upon compression the phase transition from anatase to \(\alpha\)-PbO\(_2\) phase, then to baddeleyite would only appear in the nanoparticles larger than 50 nm, because this size is larger than the critical diameter for nucleation and growth of the \(\alpha\)-PbO\(_2\) phase. However, in our case, \(\alpha\)-PbO\(_2\) phase is still missed, although size of anatase TiO\(_2\) phase is larger than 50 nm, the critical diameter for \(\alpha\)-PbO\(_2\) phase. Anatase-baddeleyite phase transition also occurs in other type of 1D anatase TiO\(_2\) nanomaterials. For example, upon compression, the phase transition anatase-baddeleyite was observed in anatase TiO\(_2\) nanowires with diameters of 50-100 nm and 150-250 nm which were studied by Dong \textit{et al.}\(^{36}\) and nanowires with diameter of 50-200 nm studied by Li \textit{et al.}\(^{34}\) (see Table 4-1). These phenomena are obviously different from the expectation according to the critical diameter rule for the nanoparticles. High-pressure studies of these 1D anatase TiO\(_2\) nanomaterials (nanotubes and nanowires) indicate that morphology is also an important factor which affects the high-pressure behaviours of TiO\(_2\) nanomaterials. In this study, the missing of \(\alpha\)-PbO\(_2\) phase during the compression in anatase TiO\(_2\) NT suggests the TiO\(_2\) NT has higher surface energy, which prohibits the nucleation and growth of \(\alpha\)-PbO\(_2\) phase. And the
critical size for nucleation and growth of $\alpha$-PbO$_2$ phase in anatase TiO$_2$ NT is very different from that in the nanoparticles. High-pressure study of TiO$_2$ NT shows a morphology-dependent phase transition sequence.

![Graph showing the variation of relative lattice parameters $(a/a_0, c/c_0)$ of anatase TiO$_2$ NT and TiO$_2$ bulk materials.](image)

**Figure 4-8** Variation of relative lattice parameters $(a/a_0, c/c_0)$ of anatase TiO$_2$ NT and TiO$_2$ bulk materials

### Compressibility

Pressure-dependent variation of cell parameter shows the compressibility of unit cell along different axis. Figure 4-8 shows the pressure-dependent variations of the normalized unit cell lengths $(a/a_0, c/c_0)$ for the TiO$_2$ NT and for TiO$_2$ bulk materials as a comparison. We can see that $c$-axis length is found to be more compressible than the $a$-axis length, which is consistent with previous studies. The different compressibilities along $a$-axis and $c$-axis are due to the crystal structure of TiO$_2$ anatase phase. In anatase
phase, one Ti atom is coordinated by six O atoms. There are four occupied TiO$_6$ octahedra and 4 empty O$_6$ octahedra per unit cell. The existence of Ti atom inside the occupied octahedron (TiO$_6$) makes this polyhedron much more difficult to compress than the empty one (O$_6$). So the higher compressibility in the $c$-axis compared to $a$-axis for anatase has been interpreted in terms of the difference in the directional population of the hard occupied (TiO$_6$) and soft empty (O$_6$) oxygen octahedral. However when comparing with previous study, $c$-axis of TiO$_2$ NT show higher compressibility than those of the bulks and nanoparticles. As can be seen in Figure 4-8, the compressibility in $a$-axis for TiO$_2$ NT is very similar to that for TiO$_2$ bulk materials. However, $c$-axis length in TiO$_2$ NT is more compressible than that in bulk materials, which is also clearly shown in Figure 4-9.

![Graph showing the variation of normalized ratio $c/a$ of anatase TiO$_2$ NT and TiO$_2$ bulk materials](image-url)

**Figure 4-9** Variation of normalized ratio $c/a$ of anatase TiO$_2$ NT and TiO$_2$ bulk materials
Compressibility of materials is characterized by bulk modulus. The pressure volume data of the various phases have been fitted to Birch equation of state (equation 4.1)\textsuperscript{37}:

\[ \frac{P}{B_0} = \frac{3}{2}(x^{7/3} - x^{5/3}) \left[ 1 + \frac{3}{4}(B'_0 - 4)(x^{2/3} - 1) \right] \] (4.1)

Where \( x = V_0/V \), \( V \) being the volume at pressure \( P \) and \( V_0 \) is the zero-pressure volume. The constants \( B_0 \) and \( B'_0 \) are the isothermal bulk modulus and its pressure derivative, respectively. Both parameters are evaluated at zero pressure. They are calculated from the fit to the equation of state by a least-squares method.

The pressure-volume data of TiO\textsubscript{2} NT are shown in the Figure 4-10. By fitting the third-order Birch-Murnaghan equation of state, the bulk modulus (\( B_0 \)) of the anatase TiO\textsubscript{2} NT was determined to be 164 GPa, with the first derivative (\( B'_0 \)) being fixed at 4. Bulk modulus of TiO\textsubscript{2} bulk materials, TiO\textsubscript{2} nanoparticles and TiO\textsubscript{2} nanowires, are also shown in the Figure 4-10 as comparisons. As can be seen, bulk modulus of TiO\textsubscript{2} NT has the lowest value (164 GPa), which is similar to that of TiO\textsubscript{2} bulk materials (179 GPa). However, the other two TiO\textsubscript{2} nanomaterials, nanowires and nanoparticles, have much higher bulk modulus, 226 GPa and 240 GPa respectively. Size- and morphology-induced alteration of bulk modulus has been found in lots of high-pressure studies of nanomaterials. For example, CeO\textsubscript{2} and \( \gamma \)-Fe\textsubscript{2}O\textsubscript{3} nanoparticles exhibited an enhancement of the bulk modulus compared with the bulk materials,\textsuperscript{38,39} whereas no obvious difference in compressibility was observed for ZnS nanocrystals.\textsuperscript{40} In contrast, the compressibility PbS and \( \gamma \)-Al\textsubscript{2}O\textsubscript{3} was found to increase with decreasing nanoparticle size. Furthermore, a strongly contrasting compressibility was observed for nanoparticles; that is, the bulk modulus of rode-shape particles was reduced, whereas that of the rice-shape particles was enhanced by over 50\% relative to that of the corresponding bulk materials.\textsuperscript{41} In this work, TiO\textsubscript{2} NT has a much lower bulk modulus than other TiO\textsubscript{2} nanomaterials (nanowires and nanoparticles). Especially, both TiO\textsubscript{2} NT (diameter \( \sim \)100 nm) and TiO\textsubscript{2} NW (diameter 50-100 nm)\textsuperscript{36} have 1D nanostructure and similar diameters, but they have very different bulk modulus values, which show a morphology-induced alteration of bulk modulus.
Figure 4-10 Equation of state for anatase NT upon compression. The pink dashed line is the equation of state for anatase phase in bulk TiO$_2$ accepted from Ref. 16, the black dashed line is the equation of state for TiO$_2$ nanocrystals adapted from Ref. 24 and the blue dashed line is the equation of state for TiO$_2$ nanowires (50-100 nm) adapted from Ref. 36.

Multiple factors contribute to the mechanical properties of nanomaterials. Park et al.$^{41}$ suggested that bulk modulus may be influenced by the crystal growth directions of TiO$_2$ nanomaterials. In their study, they found the bulk modulus and compressibility along $c$-axis is accord with the crystal growth orientation. In their study, anatase TiO$_2$ nanorods (grown along the $a$-axis) showed lower modulus (243 GPa), but the anatase TiO$_2$ nanorice (grown along the $c$-axis) showed a higher modulus (319 GPa). Corresponding with the values of modulus, nanorods show a larger decrease in the $c$-axis length than nanorice. They suggested that the larger population of the “soft” empty O$_6$ oxygen octahedera in the $c$-axis contributs to the higher compressibility for the TiO$_2$ nanorods. Li
Table 4-1 Summary of the results of high-pressure studies of anatase TiO$_2$

<table>
<thead>
<tr>
<th>starting TiO$_2$ morphology</th>
<th>size (nm)</th>
<th>phase transitions pressure (GPa)</th>
<th>bulk modulus (GPa)</th>
<th>technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>&gt; 100 m</td>
<td>anatase to $\alpha$-PbO$_2$ type</td>
<td>4.3 – 4.6$^{14}$</td>
<td>Raman</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha$-PbO$_2$ type to baddeleyit</td>
<td>~ 5$^{42}$ 12 – 15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.4$^{43}$ ~ 10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.5 – 7$^{14}$ 13 – 17</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.5$^{14}$ ~ 13</td>
<td></td>
</tr>
<tr>
<td>Nano-particles</td>
<td>4$^{19}$</td>
<td>anatase to $\alpha$-PbO$_2$ type</td>
<td>&gt; 24</td>
<td>Raman</td>
</tr>
<tr>
<td></td>
<td>8$^{19}$</td>
<td></td>
<td>&gt; 21</td>
<td>Raman</td>
</tr>
<tr>
<td></td>
<td>7 – 11$^{44}$</td>
<td>anatase to $\alpha$-PbO$_2$ type</td>
<td>&gt; 24</td>
<td>Raman</td>
</tr>
<tr>
<td></td>
<td>12$^{42}$</td>
<td></td>
<td>&gt; 24</td>
<td>Raman</td>
</tr>
<tr>
<td></td>
<td>20$^{19}$</td>
<td></td>
<td>&gt; 24</td>
<td>Raman</td>
</tr>
<tr>
<td></td>
<td>32$^{19}$</td>
<td></td>
<td>&gt; 24</td>
<td>Raman</td>
</tr>
<tr>
<td></td>
<td>30 – 34$^{14}$</td>
<td>anatase to $\alpha$-PbO$_2$ type</td>
<td>&gt; 24</td>
<td>Raman &amp;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&gt; 24</td>
<td>XRD</td>
</tr>
<tr>
<td>Nanowire</td>
<td>50 – 100$^{36}$</td>
<td>$\alpha$-PbO$_2$ type to baddeleyit</td>
<td>~ 14</td>
<td>266.5</td>
</tr>
<tr>
<td></td>
<td>150 – 250$^{36}$</td>
<td>anatase to amorphous</td>
<td>~ 9</td>
<td>188.3</td>
</tr>
<tr>
<td></td>
<td>50 – 200$^{34}$</td>
<td>anatase to amorphous</td>
<td>~ 9</td>
<td>164</td>
</tr>
<tr>
<td>Nanotubes</td>
<td>~100*</td>
<td></td>
<td>~12</td>
<td>188.3</td>
</tr>
</tbody>
</table>

* This work
et al.\textsuperscript{34} obtained the similar results in the study of anatase TiO\textsubscript{2} nanowires. The anatase nanowires grown along $a$-axis showed a bulk modulus of 176 GPa, which is similar to that of the counterparts (180 GPa). In our case, we found that TiO\textsubscript{2} NT showed a higher compressibility along $c$-axis than the TiO\textsubscript{2} bulk materials (see Figure 4-9). So the low bulk modulus of the anatase TiO\textsubscript{2} NT might be due to the crystalline growth direction of TiO\textsubscript{2} NT. Because the matter of time, we did not check the fine crystal structure of TiO\textsubscript{2} NT and we are not sure crystal growth direction is the main reason. Besides, low bulk modulus might be due to the crystallo-chemical defects, such as oxygen vacancies\textsuperscript{45}, and their dependence on the size and shape.

4.4 Conclusions

In this work, anatase TiO\textsubscript{2} NT synthesized by electrochemical anodization method was investigated under high pressure using \textit{in-situ} Raman spectroscopy and synchrotron X-ray diffraction. The morphology-tuned structural phase transition under high pressure was found in the anatase TiO\textsubscript{2} nanotubes. Upon compression, TiO\textsubscript{2} NT underwent a phase transformation from anatase to baddeleyite phase without via the $\alpha$-PbO\textsubscript{2} phase. Upon decompression, the $\alpha$-PbO\textsubscript{2} phase missing from the compression was obtained and quenched to ambient condition. The inhibition of the $\alpha$-PbO\textsubscript{2} phase upon compression might be attributed to the high surface energy, which may prohibit the nucleation and growth of $\alpha$-PbO\textsubscript{2} phase in TiO\textsubscript{2} nanotubes. Moreover, compressibility of unit cell along different axis and overall volume compressibility were studied. TiO\textsubscript{2} NT shows a morphology-induced alteration of compressibility. We found higher compressibility in the $c$-axis compared to corresponding materials and the lower modulus of anatase TiO\textsubscript{2} NT than that of other TiO\textsubscript{2} nanomaterials (nanowires and nanoparticles). The morphology-induced alteration of compressibility might be due to the crystal growth direction or/and the crystallo-chemical defects, such as oxygen vacancies\textsuperscript{45}.

4.5 References


(36) Dong, Z., University of Western Ontario, 2012.


Chapter 5 Summary and future work

5.1 Summary

The chemical and physical properties of TiO$_2$ have been attracting world’s attention in recent years. Besides, 1D TiO$_2$ nanomaterials show unique electronic and optical properties comparing with other morphologies. As we know the properties are determined by the structures of the materials, TiO$_2$ is studied in two different levels in my project. First, we use XANES and XEOL to study the unique electronic and optical properties of TiO$_2$. Secondly, we use high pressure technique to investigate high-pressure phases of TiO$_2$ NT. The background and general methodology are provided in Chapter1 and Chapter 2.

In Chapter 3, XANES, XRD and XEOL techniques are applied to study the hydrothermal synthesized TiO$_2$ NW calcinated under elevated temperatures. Analysis of Ti $L_{3,2}$-edge, O $K$-edge and XRD pattern of the series of calcinated TiO$_2$ NW indicates that TiO$_2$ NW undergoes a phase transformation from TiO$_2$-B phase to anatase phase and then to rutile phase, which is consists with previous studies. However, we find that in our case phase transformation temperatures are a bit higher than that reported by other groups. We attributed the higher transformation temperatures to the existence of Na$^+$. XEOL study reveals that TiO$_2$ NW exhibits amazing properties comparing with conventional TiO$_2$. Green PL is observed from TiO$_2$-B phase, anatase phase, and near IR PL is observed from rutile phase. The green PL is attributed to oxygen vacancies of anatase phase. And the near IR PL is attributed to bulk defects of the rutile phase.

In Chapter 4, anatase TiO$_2$ NT synthesized by electrochemical anodization method was investigated under high pressure using in-situ Raman spectroscopy and synchrotron X-ray diffraction. Upon compression, TiO$_2$ NT underwent a phase transformation from anatase to baddeleyite phase without via the $\alpha$-PbO$_2$ phase. Upon decompression, the $\alpha$-PbO$_2$ phase missing from the compression was obtained and quenched to ambient condition. In the study, TiO$_2$ NT show some special high-pressure behaviors: (1) a phase transition sequence missing the $\alpha$-PbO$_2$ phase occurs in TiO$_2$ NT whose dimensions are larger than 50 nm; (2) a relatively low bulk modulus of TiO$_2$ NT is found compared with
other types of TiO$_2$ nanomaterials. All above-observed behavior may be attributed to the special 1D morphology of the anatase TiO$_2$ NT, which leads to morphology-tuned high-pressure behaviors.

5.2 Future work

By finishing this thesis, we have obtained many new exciting results about structural information under high pressure and optical, electronic structures of 1D TiO$_2$ nanomaterials. However, there is still much more work that needs to be done in the future.

For the study of Chapter 3, we have studied the electronic structure and optical properties of TiO$_2$ NW, which provide us more information about phase-dependent luminescence of 1D TiO$_2$ nanomaterials and enlarge our knowledge of factors affecting the efficiency of 1D TiO$_2$ nanomaterials as photocatalysts. As we know that, as fundamental materials used in photocatalysts or solar cells, pure TiO$_2$ is not a good choice due to its wide band gap and its bad electron-hole separation ability. Scientists and engineers have been working on the modification of TiO$_2$ to narrow its bandgap or improve the electron-hole separation efficiency. Different modification methods have been investigated and shown progress. For instance, in order to modifying the electronic band structure for visible light harvest, metal ion, such as V, Cr, Mn, Fe, Co, Ni etc., are doped into TiO$_2$.\textsuperscript{1,2} Besides, co-catalysts loading of noble metals, such as Pt, Pd, Au, etc., can help to achieve the efficient photogenerated charge separation.\textsuperscript{1,2} So these kinds of modified TiO$_2$ nanomaterials deserve more attentions. We can apply XANES and XEOL to study their electronic structures and optical properties in order to dig out more useful information about the mechanism of the photocatalysis.

For the study in Chapter 4, we have known that besides the size-effect of high-pressure behaviours, morphology is also an important factor which influences phase transformation pressure, phase transition sequence, bulk modulus, etc. However, a model system for understanding the morphology effects on high-pressure of TiO$_2$, just like the model for size effects on TiO$_2$ nanoparticles, has not been established yet. Furthermore, in most cases, size and morphology effects coexist. Which one plays the dominant roles in the phase transitions is also not clear and need further studies. On one hand, work need
to be done to search the origin for the morphology- or size- effects. For instance, we can do the high-pressure studies of 1D TiO$_2$ nanomaterials with different size and different crystal growth orientation and investigate its effects. On the other hand, we need to keep investigating the high-pressure behaviours of TiO$_2$ nanomaterials with other morphologies, such as nanoflowers.

5.3 References
Appendix I Data analysis methods

A1.1 FIT2D*

FIT2D is a general purpose and specialist for one and two dimensional data processing. It is widely used by lots of crystallography groups all over the world and on European Synchrotron Research Facility beam lines. FIT2D is used for both interactive and “batch” data processing, and is used by many different user communities for different purposes. In this project, this program is used to process the X-ray diffraction (XRD) data collected by MAR detector.

Firstly, the raw two dimensional XRD data are collected as Debye-Scherrer rings. Then, by using FIT2D, two dimensional images can be integrated into one dimensional profile with $2\theta$ or radial direction. Thus, this provides a number of different output configurations. For instance, we can obtain a number of different $2\theta$ scans, for different azimuth ranges, a one dimensional profile of intensity of a ring as a function of azimuth, or a polar transform of the data. Moreover, there are also different options of the output formats, which include GSAS formats, Cerius formats, as well as ASCII format. In the following, the GSAS format will be used in the Rietveld refinement analysis.

* Website: [http://www.esrf.eu/computing/scientific/FIT2D/](http://www.esrf.eu/computing/scientific/FIT2D/)
Figure A1 Raw 2D XRD image of TiO$_2$ nanotubes taken at ambient pressure.
Figure A2 Experimental parameters used for data analysis for TiO$_2$ nanotubes.
Figure A3 1D X-ray diffraction pattern converted from the original 2D image of TiO$_2$ nanotubes in Figure A1.
A1.2 Rietveld refinement method*

Rietveld refinement is a method developed by Hugo Rietveld for use in the characterization of crystalline materials. The height, width and position of peaks in neutron or X-ray diffraction can provide us lots of information of the materials structure, such as the unit cell parameters, positions of atoms, etc. The Rietveld refinement uses a least squares method to refine a calculated line profile and make it fits the observed profiles.

There are many programs that can be used to process Rietveld refinement, such as GSAS + EXPGUI, Fullprof and PowderCel, which can be freely downloaded from internet. Also, many commercial programs are available, such as MDI Jade and Bruker TOPAS. In this work, the program GSAS + EXPGUI is used to process all the refinements.

Appendix II Supporting materials for Chapter 4

Figure A4 Rietveld refinement of XRD pattern for TiO$_2$ nanotubes at 1.6 GPa upon compression. The observed data are depicted in crosses (obs), while green and black solid lines are the calculated (calc) profile and the difference (diff: I$_{obs}$ – I$_{calc}$) curve, respectively. The vertical bars indicate the reflection positions for crystal structures: magenta: anatase phase; blue: baddeleyite phase; orange: α-PbO$_2$ phase.
Figure A5 Rietveld refinement of XRD pattern for TiO$_2$ nanotubes at 10.1 GPa upon compression. See Figure A4 for figure caption.

Figure A6 Rietveld refinement of XRD pattern for TiO$_2$ nanotubes at 14.8 GPa upon compression. See Figure A4 for figure caption.
Figure A7 Rietveld refinement of XRD pattern for TiO$_2$ nanotubes at 31.1 GPa upon compression. See Figure A4 for figure caption.

Figure A8 Rietveld refinement of XRD pattern for TiO$_2$ nanotubes at 4.9 GPa upon decompression. See Figure A4 for figure caption.
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