SYNTHESIS OF METAL OXIDE NANOTUBES AND NANOWIRES
BY LIQUID PHASE DEPOSITION

A Thesis

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By

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ABSTRACT

A novel method for synthesizing titanium oxide nanotubes and nanowires from liquid phase deposition in an aqueous solution at near-ambient conditions has been developed. The as-synthesized nanotubes and nanowires have been analyzed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). This synthesis method has also been expanded to include other metal oxides: tin oxide, zirconium oxide, and iron oxyhydroxide. This approach offers simplified nanocapabilities which could open a wider field of applications for low cost ceramic nanotubes and nanowires.

Titanium dioxide nanotubes and nanowires composed of densely packed nanometer sized grains have been successfully deposited inside an anodic aluminum oxide template at near-room temperature (45 °C) from an aqueous solution using a simple, inexpensive, reproducible, and an environmentally friendly method. The aqueous solution was obtained by dissolving ammonium hexafluorotitante in a boric acid solution. The average length of the TiO$_2$ nanotubes and nanowires is 2 μm with diameters from 60 – 250 nm depending on the template pore size.
The nanotubes and nanowires were uniform, homogeneous, and without visible defects. Ions were hydrolyzed in an aqueous solution to produce metal oxides which adhered to the inner pores of the substrate. The growth rate and crystallinity can be controlled by careful manipulation of solution parameters and the surface functionality of the substrate.
This thesis is dedicated to my Mom, whose unimaginable strength and selfless love are examples not only to me but to all of those with whom she comes in contact.
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Go Bucks!!
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LIST OF ACRONYMS AND SYMBOLS

\( n_e \) - density of electrons
\((\text{NH}_4)_2\text{SnF}_6\) - ammonium hexafluorostannate
\((\text{NH}_4)_2\text{TiF}_6\) - ammonium hexafluorotitanate
\( \Delta G \) - free energy
0D - zero dimensional
1D - one-dimensional
AAO - anodic aluminum oxide
A - surface area of the particle
CO - carbon monoxide
CVD - chemical vapor deposition
DLVO - Derjaguin, Landau, Verwey, and Overbeek theory on surface forces
ESEM - environmental scanning electron microscopy
FeOOH - Iron Oxyhydroxide
FIB - focused ion beam
HRTEM - high resolution transmission electron microscopy
IEP - isoelectric point
K - Boltzmann's constant
l - liquid
LPD - liquid phase deposition
Na\(_2\)SiF\(_6\) - sodium hexafluorosilicate
Na\(_3\)FeF\(_6\) - sodium hexfluoroferrate
N - number of nuclei
OTS - octadecyl-trichlorosilane
PL - photoluminescence
PMT - photomultiplier tube
P - particle
PVD - physical vapor deposition
\( q_e \) - charge on an electron
R - gas constant
SAEDP - selected area electron diffraction pattern
SEM - scanning electron microscopy
SiO\(_2\) - silicon oxide
SnO\(_2\) - tin oxide
s - substrate
S - supersaturation
\( T_e \) and \( T_i \) - temperatures of electrons and ions, respectively
TEM - transmission electron microscopy
TiO\(_2\) - titanium oxide
T - temperature
\( V_a \) - van der Waals interaction
\( V_e \) - electrical double-layer interaction
VLS - vapor-liquid-solid
$V_{tot}$ - DLVO theory representing total interaction

XEDS - x-ray energy dispersive spectroscopy

XPS - x-ray photoelectron spectroscopy

XRD - x-ray diffraction

ZrO$_2$ - zirconium oxide

$\varepsilon_0$ - permittivity of free space

$\lambda_D$ - Debye length

$\sigma_{pl}$ - interfacial energy

$\Omega$ - cm-ohm-centimeter
CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 BACKGROUND

1.1.1 ONE-DIMENSIONAL NANOSTRUCTURES

Dimensionality is a crucial factor in determining the properties of a nanomaterial. The ability to control the size and shape of materials is of great interest. One-dimensional (1D) nanostructured materials such as nanotubes and nanowires have attracted extensive attention over the past decade due to their unique physical properties and their potential applications in constructing nanoscaled electronic and optoelectronic devices[1].

The essence of one-dimensional nanostructure formation relates to crystallization[2], a process that has already been investigated for hundreds of years. The evolution of a structure from a vapor, liquid, or solid phase involves two fundamental steps: nucleation and growth. As the concentration of the building units (atoms, ions, or molecules) of a solid becomes sufficiently high, they aggregate into small nuclei or clusters through homogeneous nucleation.
In 1959 Richard Feynman, the physics Nobel Laureate, suggested in his famous lecture, entitled "There's Plenty of Room at the Bottom"[3] a variety of tests that could be achieved at very small scales. Feynman’s vision opened a new field of nanostructures classified as having dimensions from 10 to 1000 Å (i.e. 1-100 nm), a size that is small by engineering standards, common to biological standards, and large to physicists. Feynman believed that there was the possibility for direct manipulation of individual atoms to be incorporated into a powerful form of synthetic chemistry.

1.1.2. MECHANICAL AND THERMAL STABILITY

The small sizes and high surface-to-volume ratios of one-dimensional nanostructures give them a variety of interesting and useful mechanical properties. Their high rigidity and strength lend them to nanoscale applications including composites, actuators, sensors, and electronic devices. One-dimensional nanostructures also showcase unique stability effects driven by the dominance of their external and internal surfaces.

One of the most familiar mechanical phenomenon involving size dependency is the Hall-Petch effect characteristic of polycrystalline solids. Two classic papers on the relationship between grain boundaries and strength were developed independently by Hall[4] and Petch[5] around 1950. Hall and Petch studied different
behaviors but arrived at essentially the same conclusion; that the grain size
dependence of yield strength can be described by the Hall-Petch equation:

\[
\sigma_y = \sigma_0 + \frac{K}{\sqrt{d}}
\]  

(1.1)

where \( K \) is a constant and \( d \) is the mean grain size.

The yield strength and hardness of a microstructured material typically
increases with decreasing grain size yielding to the progressively more effective
disruption of dislocation motion by grain boundaries. As the scale of materials
reduces to nanometers, the tendency of surfaces to minimize their free energy drives
structural changes that propagate into the bulk. Nanotube and nanowire synthesis
techniques can yield single-crystalline structures with a much lower density of line
defects than typically found in bulk materials. As a result, one-dimensional
nanostructures often feature mechanical strength, stiffness, and toughness
approaching the theoretical limits of perfect crystals. The small sizes and high
surface-to-volume ratios of one-dimensional nanostructures endow them with a
variety of interesting and useful mechanical properties.

There are a large number of obtainable opportunities from incorporating and
making new types of nanostructures, or by downsizing currently existing structures
into the nanoscale regime. Nanocrystalline ceramics can have higher electrical
conductivity, enhanced ductility, toughness, and formability than their counterparts
with larger grain sizes, as well as increased luminescent efficiency when used in
semiconductor applications. The thermal stability of nanostructures is critically
important for their implantation as building blocks in nanoscale electronic and photonic devices.

The melting point of solid materials will be greatly reduced when they are processed as nanostructures\textsuperscript{[1]}. This results from the important role of the surface as the size of the structures decreases. As the size of the nanostructures decreases, an increased proportion of atoms occupy the surface or interfacial sites. These atoms are more loosely bound than bulk atoms, which facilitates the melting of the nanostructures\textsuperscript{[6]}. Realizing the potential of nanotechnology has required the evolution of both science and the supporting technology base. Nanotechnology is increasingly viewed as a key enabler for the growing economy. There is an unprecedented ability and capability to achieve properties using nanosized materials.

1.1.3 SYNTHESIS OF ONE-DIMENSIONAL NANOSTRUCTURES

One of the crucial factors in nanotube and nanowire synthesis is the control of composition, size, and crystallinity. One-dimensional nanostructure synthesis can be categorized into two major approaches based on the reaction media during the preparation: solution phase process and gas phase process. Compared to some of the physical methods, such as patterning techniques, chemical methods are more versatile for the synthesis of nanowires. Several synthetic strategies have been developed for one-dimensional nanowires with different levels of control over the growth parameters. They include: (i) use of the anisotropic crystallographic
structure of the solid to facilitate one-dimensional nanowire growth (Figure 1(A)); (ii) introduction of a solid-liquid interface and confined by a catalyst (Figure 1(B)); (iii) use of one-dimensional templates to direct formation of the nanotubes and nanowires (Figure 1(C)); (iv) use of capping agents to kinetically control the growth rates (Figure 1(D)); (v) self-assembly of zero-dimensional (0D) nanostructures (Figure 1(E)); and (vi) anisotropic size reduction (Figure 1(F))\(^7\). In order to have a successful and reproducible synthetic method for developing nanostructures there should be understanding and control over dimensions, morphology, and uniformity.

![Diagram](https://via.placeholder.com/612x792)

**Figure 1.** Schematic illustrations of six different strategies for achieving one-dimensional growth: (A) crystallographic anisotropy, (B) confinement by catalyst (usually vapor phase), (C) confinement by a template, (D) growth kinetics controlled by anisotropic capping, (E) self-assembly of 0D nanomaterials, and (F) anisotropic size reduction\(^7\).
1.2 CURRENT GROWTH METHODS OF NANOTUBES AND NANOWIRES

Many methodologies\textsuperscript{[8, 9]} have been developed to synthesize one dimensional structures using gas phase and solution phase growth. Nanoscale materials and devices can be fabricated using either “bottom up” or “top down” fabrication approaches. The “bottom-up” approach ingeniously controls the building of nanoscale structures. This approach shapes the vital functional structures by building atom by atom and molecule by molecule. The “bottom up” is an approach where nanomaterials or structures are fabricated from the mechanism of self-assembly. Self-assembly is the creation of functional units by the buildup of atoms and molecules growing into crystals and creating nanotubes and nanowires.

“Top down” is an approach that downsizes things from large-scale structures into nanometer-scale structures. Minimizing fabrication from millimeter size to micrometer size is defined as microtechnology. The “top-down” approach is an extension of microtechnology. It is believed that the “bottom-up” approach to nanoelectronics has the potential to go beyond the limits of the traditional “top-down” manufacturing techniques. One of the appeals of the “bottom-up” approach is the size of the diameter of the nanowire building blocks can be readily tuned to 100 nm and smaller.

There has been a growing interest in the “bottom up” approach to building nanoelectronic devices, where nanoscale building blocks have been synthesized using a variety of methods including chemical vapor deposition\textsuperscript{[7, 10]}, physical vapor deposition\textsuperscript{[11, 12]}, hydrothermal synthesis\textsuperscript{[13-15]}, template-directed synthesis\textsuperscript{[16-18]},
electrodeposition of sols\textsuperscript{19, 20}, electrochemical deposition\textsuperscript{21-23}, and electroless deposition\textsuperscript{11}. Most of these one-dimensional nanostructures were synthesized by methods needing high temperature firing.

The mechanism for growth of nanowires via a gas phase reaction involving vapor-liquid-solid (VLS) was proposed by Wagner\textsuperscript{2} in the 1960s. He studied the growth of mm-sized Si whiskers in the presence of Au particles. According to this mechanism, the anisotropic crystal growth is promoted by the presence of a liquid alloy or solid interface. The diameter of the nanowires is determined by the diameter of the catalyst particles, making this method an efficient means of obtaining uniform-sized nanowires. A solution synthetic strategy utilizes anisotropic growth dictated by the crystallographic structure of the solid material, confined and directed by templates, kinetically controlled by supersaturation\textsuperscript{24}.

1.2.1 CHEMICAL VAPOR DEPOSITION

Chemical vapor deposition (CVD) has been widely used for the formation of solid thin films by the decomposition or reaction of reactant gases on a substrate at an elevated temperature\textsuperscript{10}. Recently, CVD has been applied to synthesizing one dimensional nanostructures of various materials\textsuperscript{7}. The formation of CVD nanotubes and nanowires usually require metal catalysts (e.g. Ni). Vapor-liquid-solid growth is believed to be the mechanism for the nanotube and nanowire growth on the metal catalysts.
1.2.2 PHYSICAL VAPOR DEPOSITION

Physical vapor deposition (PVD) also known as “sputtering” is a process where ions of an inert gas such as argon are electrically accelerated in a high vacuum toward a metal target\textsuperscript{[11]}. The basic process of PVD is sublimating the source materials in a powder form at high temperatures followed by a subsequent deposition of the vapor in a certain temperature region to form desired nanostructures.

1.2.3 HYDROTHERMAL SYNTHESIS

Hydrothermal processing is an approach utilizing the reaction of solid materials with high temperature and high pressure aqueous solutions, vapors, or fluids\textsuperscript{[14]}. Kasuga et al.\textsuperscript{[13]} produced high quality TiO\textsubscript{2} nanotubes with uniform diameters of around 10 nm by a hydrothermal treatment of crystalline TiO\textsubscript{2}–SiO\textsubscript{2} particles using NaOH aqueous solutions.

1.2.4 TEMPLATE-DIRECTED SYNTHESIS

Template-directed synthesis is a convenient, versatile method for generating one-dimensional nanostructures\textsuperscript{[16, 17]}. The template substrate serves as a scaffold for other materials with similar morphologies to be synthesized. The \textit{in situ} generated material is shaped into a nanostructure with morphology complementary to that of the template. Templates could be nanoscale channels within mesoporous materials, porous alumina, or track-etched polycarbonate membranes. The nanoscale channels
are filled using the solution, sol-gel, or the electrochemical method. The nanotubes and nanowires are released from the templates by removing the host matrix.

A significant challenge in the chemical synthesis of nanowires is how to rationally control the nanostructure assemblies so that their size, dimensionality and interfaces are predictable. Many physical and thermodynamic properties are diameter dependent. Of the most common nanoporous templates, two candidates stand out as the most versatile: track-etched polymer membranes and nanoporous anodic aluminum oxide (AAO)[17]. The superior properties of nanoporous alumina templates provide controllable pore depth, width, and orientation, making it a more favorable choice over the track-etched polymer membrane.

In the track-etched membrane, a nanoporous substrate prepared by bombarding a non-porous sheet of the desired material (standard thickness 6-20 mm) with nuclear fission fragments to create damage tracks in the material, and then chemically etching these tracks into pores. The resulting membranes contain randomly distributed cylindrical pores of uniform diameter[17]. Unlike polymer membranes fabricated by track etching, the porous AAO membranes contain hexagonally packed two-dimensional arrays of cylindrical pores of uniform size prepared using a method of anodizing aluminum foil in an acidic medium[25].

The template directed synthesis route has the following desirable characteristics: relative ease of template production, potentially high production once commercially scaled, and also allows the complex topology present on the surface of the template to be duplicated in a single synthetic step. Using a template,
four general deposition methods can be utilized: (i) using a porous template for deposition on the pore walls; (ii) using a template to protect against topological features on top of solid substrates; (iii) using a template as a barrier against self-assembled molecular structures produced by surfactants; and (iv) implanting a template with existing nanostructures potentially forming conformal, coaxial layers[11].

Of these four template-directed methods, using a porous substrate for deposition along the channel walls (i) was identified as having the greatest degree of flexibility in both manipulating the characteristics of the template and resulting nanostructures, as well as the largest applicability to a wide variety of materials[16]. This list includes metals, semiconductors, ceramics, and organic polymers. The methods prevalently used for template synthesis to date are vapor-phase sputtering, liquid phase injection, or solution-phase chemical or electrochemical deposition.

The AAO template directed synthesis has been the most commonly used method for the fabrication of nanostructures for its interesting and useful features. Compared with lithographic polymer or carbon nanotubule templates, AAO is much cheaper and has a higher pore density. At the same time, the pore diameter and the aspect ratio in an AAO template are controllable and can be adjusted by varying the anodization conditions. Using alumina as a template for fabricating nanostructures, the pores are filled with semiconducting or metallic materials during the deposition process.
1.2.5 DEPOSITION OF SOLS

Sol-gel chemistry typically involves hydrolysis of a solution of a precursor molecule to obtain first a suspension of colloidal particles (the sol) and a gel composed of aggregated sol particles[19, 20]. The gel is then thermally treated to yield the desired product. Lakshmi et al.\textsuperscript{[15]} used a precursor molecule for the sol-gel formation of TiO\textsubscript{2} nanowires. The nanowires were formed by dipping a template in the sol solutions and then heating at 400 °C to solidify the nanowires.

1.2.6 ELECTROCHEMICAL DEPOSITION

Electrochemical deposition of a material within the pores is accomplished by coating one face of the template with a metal film (usually either by ion sputtering or thermal evaporation) and using this metal film as a cathode for electroplating\textsuperscript{[21-23]}. This method has been used to prepare a variety of metal nanowires including copper, platinum, gold, silver, and nickel[11]. The lengths of these nanowires can be controlled by varying the amount of metal deposited. By depositing a small amount of metal, short wires can be obtained; depositing large quantities of metal increases the wire length. Non-conductive materials cannot typically be deposited by electrochemical means because of the requirement of participating in the charge-transfer reaction occurring at the electrode-solution interface.

The backing electrode metal is usually hundreds of nm thick and serves as the working electrode to either reduce metal ions in the solution (electroplating) or to move charged particles (sols, electrophoresis) and fill the template. It has also
been demonstrated that immersion in different solutions will form a layered one-dimensional structure. As the materials were driven by the electric field, the pores are filled from the backing as shown in Figure 2.

![Diagram of Electrochemical Deposition](image)

**Figure 2.** Electrochemical deposition for the formation of nanowires using template synthesis.

Tresback *et al.*\(^{[26]}\) demonstrated a procedure for preparing metal-oxide-metal heterojunction nanowires. Au-Sn-Au and Au-Ni-Au nanowires were prepared with electroplating and were then selectively oxidized to Au-SnO\(_2\)-Au and Au-NiO-Au nanowires, respectively.
1.2.7 ELECTROLESS DEPOSITION

The key feature in the electroless deposition process is that metal deposition in the pores originates at the pore wall. After short deposition times, a hollow metal tube forms in each pore of the substrate while longer deposition times result in solid metal nanowires. Unlike the electrochemical deposition method where the length of the metal nanowires can be controlled, electroless deposition yields structures that are dependent on the thickness of the substrate. Using electroless deposition, the inside diameter of the nanotubes can be controlled by varying the deposition time. The outside diameter is determined by the diameter of the pores in the substrate. This method diverges from electrochemical deposition because the surface being coated does not need to be electronically conductive[^1].

1.3 APPLICATIONS AND STRUCTURE OF TITANIUM OXIDE (TiO₂)

1.3.1 APPLICATIONS OF TiO₂

Metal oxides and multicomponent oxides have attracted interest as inorganic functional materials in the fields of electrical and optical applications. They possess various kinds of interesting electrical and optical applications, because they can contain elements in more than a single valence state, and there is an electronic transition from a low valence state to a higher valence state. Such multifunctional materials are being increasingly used in research of nanostructures including nanotubes, nanowires, nanobelts, and nanoparticles.
TiO$_2$ was chosen as the prototypical material for deposition in a porous template because of its rich literature base linking a variety of synthetic routes to microstructure, electrical, and optical properties. The engineering application for this work is directed towards devices, sensors, photocatalysis, and photovoltaics. There has been an increased interest in pursuing research of TiO$_2$ nanostructures (i.e. structures with at least one dimension in the range of 1-100 nm), due to their enhanced properties compared to thin films or bulk materials.

TiO$_2$ has been used as a photocatalyst$^{[27, 28]}$, as an electrode in photovoltaic cells for the production of hydrogen and electric energy$^{[29]}$, as a gas sensor$^{[30]}$, as white pigment (e.g. in paints and cosmetic products)$^{[31, 32]}$, as a corrosion-protective coating$^{[33, 34]}$, as an optical coating$^{[34]}$ and in electric devices$^{[35, 36]}$. The ability to fashion transparent-conducting and gas sensing nanocrystalline anatase TiO$_2$ into nanotubes and nanowires at near-ambient conditions is likely to have a broad impact. This could open a wider field of high-profile and topical applications for TiO$_2$, including nanoelectronics, chemical sensing, solar cells, "smart" windows and mirrors, touch-screen displays, and invisible security circuits$^{[14]}$. Another apparent advantage of TiO$_2$ over currently used transparent-conductors (Sn-doped In$_2$O$_3$) and gas-sensor oxides (SnO$_2$) is its relative lower cost of processing.
1.3.2 STRUCTURE OF TiO$_2$

The phase content and grain size of TiO$_2$ often have a strong influence on properties for a variety of applications. In many cases, it would be desirable to produce the stable rutile phase with an ultra-fine particle size (< 10 nm), but most low temperature synthesis routes produce predominantly the metastable anatase phase. The anatase-rutile transformation of TiO$_2$ is known to be affected by dopant type and concentration, as well as the titanium precursor used in solution chemical synthesis. Metal oxide systems have mixed ionic and covalent bonding so the surface structure has an even stronger influence on local surface chemistry as compared to metals or elemental semiconductors\(^{[37]}\).

From the thermodynamics point of view, the large dielectric constant of TiO$_2$ reduces electrostatic interactions between point defects. Ideal mass action laws can therefore be used for comparably large defect concentrations\(^{[38]}\). Atomic defects are designated as the dislocation of the positive (\textit{i.e.} cation) and negative (\textit{i.e.} anion) ions. The intrinsic disorder of TiO$_2$ is reputedly of the cationic Frenkel type (\textit{i.e.} cation vacancy and cation interstitial pair), although alternative models are based on Schottky disorder (\textit{i.e.} cation vacancy-anion vacancy pair)\(^{[38]}\).
TiO$_2$ is generally an oxygen-deficient oxide exhibiting n-type conduction. The oxygen deficiency has been attributed to both oxygen vacancies and titanium interstitials.

Frenkel defects: $\text{Ti}_i' \leftrightarrow \text{Ti}_i''\rightarrow +V_{i''\rightarrow}$

Schottky defects: $\text{nil} \leftrightarrow V_{i''\rightarrow} +2V_{O''\rightarrow}$

The corresponding equilibrium constant is:

$$[\text{Ti}_i''\rightarrow][V_{i''\rightarrow}] = \exp(-\Delta_fG^\circ/R\Delta)$$

where $-\Delta_fG^\circ$ is the standard Gibbs free energy of the Frenkel reaction. The square brackets represent molar fractions. Cation interstitials may be formed on empty octahedral sites (one site per formula unit)$^{[38]}$.

A dopant introduces a defect into the TiO$_2$ crystal that leaves voids, creating oxygen vacancies. An electron acceptor doped TiO$_2$ increases the interstitial defects and increases the overall conductivity of the TiO$_2$. For an electron donor doped TiO$_2$, the Ti vacancies and O$_2$ interstitials increase along with the overall conductivity of the TiO$_2$.

TiO$_2$ has three distinct polymorph crystal structures: brookite, rutile, and anatase. Brookite is the orthorhombic structure of TiO$_2$ and is relatively rare and not usually observed in TiO$_2$. Each unit cell of rutile consists of two TiO$_2$ molecules while anatase has four TiO$_2$ molecules. Figure 3 shows the crystal structures of rutile and anatase. The common features for these structures: Ti atom is positioned at the center of the six O atoms, forming a deformed Ti-O octahedron. The shared octahedral top points and a rhombic side join together and construct a crystal. The
differences between them are three shared sides for brookite, four for anatase, and two for rutile. Rutile and anatase have the same symmetry, tetragonal $4/m 2/m 2/m$, despite having different structures as shown in Figure 3. In both structures, the basic building block consists of a titanium atom surrounded by six oxygen atoms in an octahedral configuration.

![Rutile and Anatase Structures](image)

**Figure 3.** Crystallographic structures of rutile and anatase TiO$_2$.$^{[39]}$
TiO$_2$ is a wide-band gap semiconductor (e.g. 3.0 eV for rutile phase and 3.2 eV for anatase phase$^{[40]}$), and in pure, bulk form it has a very high electrical resistivity at room temperature (10$^{13}$ Ω·cm)$^{[36]}$. It has been shown that the resistivity of TiO$_2$ can be decreased dramatically by making it nanostructured$^{[41]}$ and by doping$^{[42]}$. Highly conducting nanostructures of TiO$_2$ would enhance present applications and develop new sets of applications for TiO$_2$.

1.4 PROBLEMS OF CURRENT NANOTECHNOLOGY

Widespread utilization of nanostructured TiO$_2$ is often hindered by the conflicting demands for i) precise control of fine, well-ordered surface features and ii) low-cost, rapid mass production. Most wet chemical processes like template-direct synthesis of nanostructures requires many chemical steps which increase production costs. In addition, all variables such as temperature and pH should be controlled during synthesis. The expensive equipment and extensive training that are often needed to produce nanoscale structures limit their practical viability in industrial and commercial applications. It is therefore necessary to develop a novel technology that allows for rapid, low cost production of high surface area ordered nanostructures.

Control over crystal structure, size, and shape of nanostructured TiO$_2$ is important in both fundamental and applied research. Nanostructured TiO$_2$ needs to possess high crystallinity for most applications as well. TiO$_2$ nanotubes and
nanowires produced by anodization and electrospinning are amorphous after synthesis. For photocatalytic applications, crystallinity is very important factor to increase catalytic ability since the amorphous state provides trap sites at which photo-generated charge carriers recombine. Amorphous TiO₂ nanomaterials would require additional heat treatment for a crystalline structure, which may collapse the nanostructure due to sintering or grain growth. Therefore, a novel nanotechnology which ensures a low cost and ordered structure is desirable for further improvement of the chemical and electrical properties of TiO₂.

1.5 DIRECT PREPARATION OF TiO₂ IN POROUS AAO TEMPLATES

Hollow nanotubes of TiO₂ have been directly prepared using a porous AAO template by a deposition technique using an aqueous solution system of titanium tetrafluoride (TiF₄)⁴³,⁴⁴. The pH of the aqueous solution was adjusted to 2.0 and set to a temperature of 60 °C. The hydrolysis of TiF₄ in solution produces TiO₂ by the following steps:

\[ \text{TiF}_4 \rightarrow \text{Ti(OH)}_{4-x}\text{F}_x \rightarrow \text{TiO}_2 \]

The formation of polycrystalline anatase TiO₂ nanotubes has been attributed to heterogeneous nucleation on the pore walls of the AAO template. The nanotubes grow in bundles and form perpendicular to the surface of the template. The inner diameters of the TiO₂ nanotubes are ~2.5-5.5 nm, and the outer diameter is ~20-40 nm with lengths up to a few hundred nanometers⁴⁴.
1.6 LIQUID PHASE DEPOSITION

Liquid phase deposition (LPD) of oxide thin films was first accomplished by Nagayama et al.\textsuperscript{[45]}, who used this technique to prepare silica (SiO\textsubscript{2}) coatings on silicon substrates. This process has since been extended to the formation of other oxides, including those of Ti, Zr, V, Fe, Ni, and Sn\textsuperscript{[46]}. This method involves immersion of a substrate into an aqueous solution containing a precursor species (commonly a fluoro-anion) which hydrolyzes and forms metal oxide particles on the template as shown in the schematic diagram in Figure 4. Metal oxides have attracted interest as inorganic functional materials in the fields of electrical and optical applications. By using this method, it is possible to form metal oxide nanotubes and nanowires homogeneously on AAO templates immersed in acidic aqueous solutions of the reactant. In this research, a study has been performed on the growth of metal oxide nanotubes and nanowires using the LPD technique.

![Diagram of the experimental set-up for the LPD method.](image)

\textbf{Figure 4.} Diagram of the experimental set-up for the LPD method.
The key technique in LPD is to prepare thin films by means of the ligand-exchange (hydrolysis) equilibrium reaction of metal-fluoro complex species. The LPD method may enable individual components to be mixed on a molecular level and offers strict control over stoichiometry. The addition of water directly forces precipitation of the oxide. Boric acid or aluminum act as fluoride scavengers, destabilizing the fluoro-complex and promoting precipitation of the oxide. The distinguishable characteristic of LPD is the use of a solution of metal-fluoride complexes whose hydrolysis in water is modulated by adding boric acid (H₃BO₃)[⁴⁶]. The LPD technique is in principle suitable for the deposition of metal oxides that form stable fluoride complexes.

The equipment for liquid-based techniques is simple and less costly than using vacuum systems and glove boxes. Aqueous solutions also have readily available reagents, reducing the reliance on expensive or sensitive organometallic precursors. The potential exists for reduced environmental impact in comparison with many other chemical routes.

The LPD technique is based on the overall equilibrium reaction:

(a) \[ \text{H}_(n-m)\text{MF}_n + m/2\text{H}_2\text{O} \rightleftharpoons \text{MO}_{m/2} + n\text{HF} \]

where \( m \) is the charge of the metal cation. According to this reaction, the equilibrium will be shifted towards the oxide if the concentration of water is increased or if the hydrogen fluoride concentration is decreased by adding fluorine scavengers such as boric acid as shown in reaction (b)⁴⁵.

(b) \[ \text{BO}_3^{3-} + 4\text{F}^- + 6\text{H}^+ \rightleftharpoons \text{BF}_4^- + 3\text{H}_2\text{O} \]
Boric acid functions not only as a fluorine scavenger, but it also helps to shift the reaction (a) to the right by producing water\textsuperscript{46}. Homogeneous nucleation and colloid formation occur if the oxide’s solubility limit is reached. Nanoparticles adhere to the inside of the substrate by attachment of the colloidal particles. In the LPD process, any compound that can react with F\textsuperscript{-} or any form of hydrolysis product of [MF\textsubscript{n}]\textsuperscript{m-n} can shift the reaction equilibrium toward the oxide deposition. The TiF\textsubscript{6}\textsuperscript{2-} ion is stable in water\textsuperscript{47} but still a hydrolysis reaction occurs. For TiF\textsubscript{6}\textsuperscript{2-} to hydrolyze in water, an acid solution is required, because the formation of a hydrogen bond to fluorine weakens the Ti-F bond\textsuperscript{48}.

The first use of ammonia with a precursor solution for LPD of silicon dioxide was by Ming-Kwei Lee et al.\textsuperscript{49}. Aqueous ammonia provided more OH\textsuperscript{-} ions, so the concentration of SiF\textsubscript{m}(OH)\textsubscript{4-m} was enhanced in the solution. Higher concentrations of SiF\textsubscript{m}(OH)\textsubscript{4-m} resulted in higher deposition rates. The OH\textsuperscript{-} bonds to the substrate surface dominating the LPD SiO\textsubscript{2} deposition\textsuperscript{50}. The objective of this research was to make metal oxide nanotubes and nanowires using the LPD method.

Preparing crystalline metal oxides in the nanopores of the substrates of uniform diameter is difficult using conventional methods. Hoyer\textsuperscript{51} electrochemically prepared TiO\textsubscript{2} nanotubes in a negative structured porous substrate requiring a complicated process including metal evaporation, polymer formation, dissolution of alumina, electrodeposition, and dissolution of polymers. A direct deposition technique is desirable for the preparation of clearly shaped nanotubes consisting of crystalline metal oxides.
CHAPTER 2

LPD DEPOSITION OF TITANIUM OXIDE

2.1 SYNTHESIS METHODS

A process has been developed of using a dilute hexafluorotitanate precursor and then immersing a porous anodic aluminum oxide (AAO) template for the infiltration of TiO$_2$ nanotubes and nanowires by surface nucleation on the inner walls of the template. The template-based LPD method for synthesizing nanotubes (Figure 5A) and nanowires (Figure 5B) of nanocrystalline anatase TiO$_2$ at near-ambient conditions has been researched. This new method differs from previous methods because of the following attributes: (i) synthesis of nanocrystalline anatase TiO$_2$ occurs at 45 °C under ambient atmosphere, (ii) no external electric field is applied, and (iii) no heat-treatment is required.
Figure 5. Schematic diagram showing the two types of anatase TiO$_2$ structures synthesized: (A) nanotubes and (B) nanowires.

2.2 ANODIZED ALUMINUM OXIDE TEMPLATES

For nanomaterial synthesis, anodization has been considered to be a technique to prepare AAO substrates for one-dimensional nanostructures. Since the diameter of the cylindrical pores can be varied between 10 and 400 nm by altering the preparation conditions, the direct-template synthesis method has a number of useful and interesting features for the production of microscopically tailored materials. Solid or hollow microcylinders of desired materials such as polymers$^{[9, 52, 53]}$, metals$^{[9, 53]}$, carbons$^{[54]}$, and semiconductors$^{[17, 51]}$ have been obtained within cylindrical pores of uniform diameter within the substrates.

Masuda et al.$^{[55]}$ have reported a remarkable strategy for producing highly ordered templates using a two-step anodization process, which leads to a densely packed hexagonal pore array under appropriate chemical and electrochemical
conditions. Highly ordered templates are beneficial because their constituent pores are more uniform than in anodic films produced in a single, short synthesis step. These membranes contain cylindrical pores of uniform diameter arranged in a hexagonal array.

The templates used were commercially available AAO membranes (Whatman®, Anodisc 25) with a pore diameter of ~200 nm and a depth of 60 μm. Porous AAO membrane in-house templates were also prepared electrochemically from aluminum metal to achieve substrates with pore sizes of ~60 nm controlled by the anodizing voltage and time. The commercial and in-house prepared templates pore sizes are shown in Figure 6.

![Figure 6. AAO commercial template from Whatman® with pore sizes of 200 nm (a) and an in-house prepared AAO template with pore sizes of 60 nm (b)](image_url)
2.2.1 ANODIZATION OF NANO-SCALE POROUS TEMPLATES

The two-step anodization procedure used for creating nanoscale pores for the deposition of metal oxides was employed in this research. High purity Aluminum foil (Alfa Aesar, Ward Hill, MA) of 100 μm thickness acts as the anode in a 0.3 M oxalic acid solution with a constant potential of 40 V DC bias at 20 °C for 0.5 to 1 hour. Alumina (Al₂O₃) was removed by wet chemical etching in a mixture of 0.2 M chromic acid and 0.4 M phosphoric acid at 60 °C for the same amount of time as the initial anodization. The concaved patterned aluminum was re-anodized in the oxalic acid for 0.5 to 12 hours depending on the desired pore length. An anodization time of one hour yields an approximate pore length of 60 μm.

Increasing the anodization voltage will increase the pore channel diameter as graphed in Figure 7. There is also a slight variation between anodizing under different acid conditions. Figure 7 compares the pore channel diameter after anodizing with phosphoric acid, sulfuric acid, or oxalic acid. The pore diameter increases linearly with voltage represented by the relation between the pore diameter, \( d \) and the anodic voltage, \( U_a \) where

\[
d = -1.7 + 2.81U_a^{[25]}.
\] (2.1)
Figure 7. Graphical depiction of the effect of anodizing voltage and acid on the template pore diameter[25].

The anodized aluminum template was dissolved by placing it in a saturated HgCl$_2$ solution for approximately an hour. There was still a trace of the barrier oxide layer at the bottom of the pores. The substrate was then immersed in a 5 weight percent phosphoric acid solution for one hour to remove the barrier layer and the final pore widening. A schematic diagram of the porous AAO template is depicted in Figure 8. The AAO templates used have the following features: (i) highly ordered pores; (ii) long range anodization; and (iii) moderate temperatures (0-20 °C) leading to constant conditions (e.g. stable current) during the anodization process.
Figure 8. Diagram representing an anodized aluminum oxide porous template.

2.3 DEPOSITION OF TITANIUM OXIDE

The starting materials for the TiO$_2$ nanowires and nanotubes were ammonium hexafluorotitanate ((NH$_4$)$_2$TiF$_6$) (Acros Organics, New Jersey), boric acid (H$_3$BO$_3$), and hydrochloric acid (HCl). All reagents were used in the as-received form without further purification. The aqueous solution consisted of 100 mL of distilled water which had been boiled and cooled to purge any gases. The 30 mM of H$_3$BO$_3$ and concentrations of (NH$_4$)$_2$TiF$_6$ from 1-20 mM were dissolved in the aqueous solution. The pH of the solution was adjusted to approximately 2.5 using HCl. The deposition of the TiO$_2$ solid phase was conducted by immersing an AAO template into the solution at a constant temperature of 40-50 °C. The aqueous LPD solution was slowly stirred in a mineral oil bath for 1-24 hours as illustrated in Figure 9. The
deposition of TiO$_2$ proceeds by the following mechanisms:

(a) \[ \text{TiF}_6^{2-} + 2\text{H}_2\text{O} \rightleftharpoons \text{TiO}_2 + 4\text{H}^+ + 6\text{F}^- \]

(b) \[ \text{BO}_3^{3-} + 4\text{F}^- + 6\text{H}^+ \rightleftharpoons \text{BF}_4^- + 3\text{H}_2\text{O} \]

![Diagram of TiO$_2$ deposition process]

**Figure 9.** Schematic diagram for growth of TiO$_2$ in a porous template in TiF$_6^{2-}$ aqueous solution.

After deposition, the template was rinsed carefully in distilled water and ethyl alcohol before air-drying. The nanotubes and nanowires can be released by dissolving the template in a strong base. The template was dissolved by immersing it in 10 mL of 1 M NaOH with ultrasonication. In order to decrease the time for the AAO to dissipate, the template was broken into small pieces to increase the surface area. The template was washed numerous times in NaOH to fully dissolve the AAO and the nanotubes and nanowires were collected using a centrifuge (Eppendorf Centrifuge Minispin Plus, Brinkman Instruments, Westburg, NY) set at 14,400 RPM.
for 3 minutes. Once the AAO was dissolved, the nanotubes and nanowires were cleaned with multiple washings in water to remove the NaOH and then dispersed in ethyl alcohol. An approximation of the number of nanotubes and nanowires in a drop of solution is calculated in Appendix A.

2.4 CHARACTERIZATION OF TITANIUM OXIDE NANOTUBES AND NANOWIRES

A scanning electron microscope (SEM, Philips XL30-FEG ESEM) was used to observe the TiO$_2$ deposition and wire length in the template. Figure 10 shows the nanotubes and nanowires as deposited in the AAO template. The chemical composition of the nanotubes and nanowires were analyzed by X-ray Energy Dispersive Spectroscopy (XEDS). The morphology and microstructure of the prepared nanotubes and nanowires were further investigated with transmission electron microscopy (TEM, Philips CM 200) and high-resolution transmission microscopy (HRTEM, FEI Tecnai F20) operated at 200 kV. A drop of dispersed nanotubes and nanowires in ethyl alcohol solution was placed on 3-mm TEM grids with continuous amorphous carbon (Electron Microscopy Science, 200 mesh copper, Hatfield, PA). Typical TEM images show that the TiO$_2$ nanotubes and nanowires were straight with uniform diameters. Single crystal fine filaments can be found along the walls of the wire or tube.
Figure 10. TiO$_2$ nanotubes and nanowires as deposited in the Whatman® AAO template with conditions of 10 mM TiO$_2$ precursor solution for 24 hours.

Uniformly sized nanotubes and nanowires of approximately 45-100 nm in diameter and 5-15 μm in length can be grown over large areas with near unidirectional alignment in the homemade template. A TiO$_2$ nanowire is shown in Figure 11(A) from the commercial AAO template with a diameter of ~250 nm, and a length of ~2.2 μm; a TiO$_2$ nanotube is shown in Figure 11(B) from the commercial AAO template with a diameter of ~250 nm, and a length ~2.3 μm; and Figure 11(C) shows a nanowire synthesized inside a in-house prepared AAO template with a diameter of 60 nm, and a length of ~1.1 μm.
Figure 11(D) shows a high resolution TEM image and a selected area electron diffraction pattern (SAEDP) of the TiO$_2$ nanowire. The SAEDP has diffuse rings indicating an extremely small grain size (~5 nm) and amorphous regions between the grains. The SAEDP was indexed to confirm that the nanotubes and nanowires were anatase phase. An XEDS of the TiO$_2$ nanowire shows the presence of Ti, O, F and Al (Cu and C observed in the spectrum were from the TEM grid). Trace amounts of fluorine were present from the precursor and aluminum from the AAO template.
Figure 11. TEM images of TiO$_2$ nanotubes and nanowires. (A) nanowire in commercial AAO template; (B) nanotube in commercial AAO template; (C) nanowire in-house prepared AAO template. (D) HRTEM image and indexed SAEDP (inset) of the nanowire in (A). (E) XEDS spectrum from nanowire in (A), (C and Cu are from the supporting grid).
The precursor solutions were supersaturated with Ti\textsuperscript{4+} ions to produce crystal nuclei of anatase. Since Ti-F bonds are relatively stable, rapid hydrolysis and polymerization of the precursor molecules does not occur and such moderate reaction conditions led to the deposition of stable crystalline particles in the substrate through surface nucleation. As a consequence, crystalline anatase nanotubes and nanowires were directly obtained at a low temperature. Since no high-temperature annealing was required for crystallization, the infiltration and nanotube and nanowire morphology are controlled by this technique.

2.5 HINDERING DEPOSITION WITH OTS

The surface walls of the template can be modified by using octadecyltrichlorosilane (OTS) (Aldrich, Milwaukee, WI) to slow down the TiO\textsubscript{2} deposition kinetics, resulting in better control of the formation of nanotubes and nanowires. The AAO template was placed in 10 mL of BiCycloHexyl (BCH) (Acros Organics, New Jersey) and 0.1 mL OTS is added. The solution was slow stirred for approximately 24 hours. The AAO template was then removed and rinsed with chloroform (CHCl\textsubscript{3}) (Mallinckrodt Chemicals, New Jersey) and allowed to air dry. The deposition procedure was then followed on the OTS protected AAO template as outlined in section 2.1.
OTS forms a temporary hydrophobic layer on the surface of the template as shown in Figure 12(b). OTS allowed for slower growth rates which made the formation of nanotubes shown in Figure 13 more prevalent. After a period of time, the OTS becomes ineffective and deposition becomes uninhibited\textsuperscript{[56]}. After immersing the OTS modified AAO template in a blank pH 2.5 solution, the change in wetting behavior indicated that the OTS layer was damaged.

In Figure 14 and Figure 15 the x-ray photoelectron spectroscopy (XPS) (PHI Model 5600, MultiTechnique System) peak comparison between an untreated AAO surface and an AAO surface modified by OTS shows that after OTS deposition, Si was observed. This system is equipped with a conventional dual anode x-ray source, hemispherical electron energy analyzer, x-ray source with a monochromator, and an inert-gas sputtering source (ion gun). XPS was reported in units of binding energy \textit{(i.e. eV)}. The Si:Al ratio is notably lower than the untreated AAO surface than the AAO template protected by OTS. A comparison was also made with a hydrolyzed OTS coated AAO template in Figure 15. This result hypothesizes that the OTS coating may not be uniform on the surface of the AAO template and the OTS can become ineffective.
Figure 12. In-house prepared AAO template without OTS, with water drop (a). In-house prepared substrate protected by OTS with water drop.

Figure 13. LPD deposition at conditions of 10 mM TiO₂ precursor solution for 24 hours forming (a) nanowire without OTS protected template and (b) nanotube formed by using OTS to slow down the deposition kinetics.
Figure 14. AAO surface (A) and OTS modified AAO (B). After OTS deposition, the Si peak is observed.
Figure 15. XPS comparison of AAO template, AAO template protected by OTS, and a hydrolyzed AAO template.

2.6 ACCELERATING DEPOSITION WITH CONTINUOUS CONVECTION

The deposition process can be accelerated by a continuous ultrasonic treatment (Sonifer Cell Disruptor, SLPe, Danbury, CT) as shown in Figure 16. The continuous convection at an output power of approximately 20% during deposition increased the overall length of the nanotubes and nanowires. Templates that were treated with continuous convection consisted of mostly nanowires with an average length of ~5.6 \( \mu \text{m} \) compared to the average length of ~2.2 \( \mu \text{m} \) without convection. A temperature rise of approximately 5 °C was induced by the ultrasonic treatment.
Figure 16. The set-up used for continuous convection during LPD.

2.7 EFFECT OF HEAT TREATMENT

Heat treatment was performed to improve the mechanical stability of the wires to help minimize fracturing upon dispersion. Two heat treatment conditions were performed at 250 °C and 550 °C before dissolving the AAO template. After heat treating at 250 °C, there was no noticeable difference between the un-heat treated and heat treated nanotubes and nanowires observed in the TEM. After heat treating at 550 °C, the nanotubes and nanowires were still characterized as being the anatase phase without any evidence of the rutile phase indicated by the diffraction pattern in Figure 17. There was an increase in grain size after the 550 °C heat treatment. The temperature did not exceed 600 °C to avoid the conversion of TiO₂ from the anatase phase to the rutile phase.
Figure 17. Diffraction pattern indicating that the TiO$_2$ nanotubes and nanowires were still anatase phase after a heat treatment of 550 °C.

2.8 PHOTOLUMINESCENCE SPECTRA OF TiO$_2$

Photoluminescence (PL) is the emission of light from a material under optical excitation. In a typical PL experiment, light (laser, monochromatic, or filtered) with energy greater than the bandgap energy of the material excites a non-equilibrium population of electrons from the filled valence band into the conduction band, creating electron-hole pairs. The electron and hole can annihilate or recombine in two ways: (i) radiatively, by emitting photons or (ii) non-radiatively, by emitting phonons or by transferring energy to another particle. PL refers to the light emitted in radiative recombination processes, and photoluminescence spectroscopy to the collection and analysis of this light emission.$^{[57]}$ A luminescent meter can be used in cathode ray tubes, fluorescence lamps, vacuum fluorescent display devices, color plasma display panels, and electroluminescent flat-panel displays.$^{[58]}$
The PL of the nanotubes and nanowires was measured using a visible ultraviolet spectrofluorometer with two monochrometers (SPEX Fluorology-2, Model FL 112) with a Xe lamp as the excitation light source at room temperature shown in the schematic diagram in Figure 18. Figure 19 presents the PL spectra of nanotubes and nanowires which were dispersed in water. The emission spectra was fixed at 370 nm to measure absorption in the conduction band. The excitation spectrum was fixed at 250 nm to measure absorption in the valence band. The smaller peaks (i.e. between 350-475 nm) are due to vibrational states. The PL spectra for TiO$_2$ shows a strong scattering especially at lower wavelengths. Due to the strong scattering, it is hard to make conclusive results from the data other than the absorption band is ~250 nm.

The emission spectrum of the TiO$_2$ nanotubes and nanowires fixed at 250 nm excitation is similar to that of LPD TiO$_2$ thin films heat treated at 500, 700, and 900 °C$^{[59]}$ and shown in Figure 20. The shoulder below 350 nm could be caused by scattering. The PL has been found to decrease with heat treatment of TiO$_2$ thin films$^{[59]}$ but since heat treatment was not done on the nanotubes and nanowires in this research this won’t be a factor. The broad peaks are not evident in the PL of the nanotubes and nanowires dispersed in ethanol which indicates that the broad peaks are a result of the solvent effect. The excitation spectrum shows the excitation of the fluorescence of a range of wavelengths of the incident light. The shapes of the emission and excitation spectrum are mirror images to each other which is often observed in PL because the vibration state is a mirror image between the conduction
and valence bands\textsuperscript{[60]}. The peak position is similar to reported results from LPD TiO\textsubscript{2} thin films\textsuperscript{[59]}.

**Figure 18.** Schematic diagram of the photoluminescence spectrofluorimeter\textsuperscript{[61]}. 
Figure 19. Photoluminescence results of TiO$_2$ nanotubes and nanowires dispersed in water.

Figure 20. Photoluminescence results of LPD TiO$_2$ thin films after three different heat treatments at a-500 °C, b-700 °C and c-900 °C$^{[62]}$. 
CHAPTER 3

LPD DEPOSITION OF OTHER METAL OXIDES

3.1 DEPOSITION OF ZIRCONIUM OXIDE (ZrO\textsubscript{2})

3.1.1 EXPERIMENTAL PROCEDURES FOR ZrO\textsubscript{2}

Zirconium oxide (ZrO\textsubscript{2}) has many applications involving structural ceramics\textsuperscript{[63]}, catalyst\textsuperscript{[64]}, oxygen sensors\textsuperscript{[65, 66]}, fuel cells\textsuperscript{[67]}, and electronic devices\textsuperscript{[35, 36]}. Synthesis of zirconium oxide thin films from an aqueous solution has been demonstrated by Yao et al.\textsuperscript{[68]}. Similar to the properties of TiO\textsubscript{2} semiconductor nanotubes and nanowires, the high aspect ratio and small size of ZrO\textsubscript{2} nanotubes and nanowires is expected to improve the sensitivity of chemical sensors and reinforce the material's thermal stability and toughness. Pure ZrO\textsubscript{2} can exist in three polymorphs at atmospheric pressure: monoclinic, tetragonal, and cubic.

ZrO\textsubscript{2} was deposited in a similar LPD method with an AAO template procedure as TiO\textsubscript{2} using sodium hexafluorozirconate (Na\textsubscript{2}ZrF\textsubscript{6}) (Aldrich, Milwaukee, WI) at pH 2.5 held between 40-50 ℃. Various concentrations of Na\textsubscript{2}ZrF\textsubscript{6} from 1-20 mM and solution times from 1 to 24 hours were observed. The supersaturation rate for ZrO\textsubscript{2} was slower than TiO\textsubscript{2}, which minimized the deposition
on the surface of the substrate. The wall thickness and lengths of the ZrO$_2$ nanotubes and nanowires ($\sim$7.7 $\mu$m) were much thicker and longer than that of TiO$_2$ nanotubes and nanowires ($\sim$4.5 $\mu$m) under the same deposition conditions of 10 mM concentration for 24 hours. ZrO$_2$ nanotubes and nanowires formed in the commercial AAO template with a length of $\sim$7.7 $\mu$m are shown in Figure 21 (a) and (b). ZrO$_2$ nanotubes and nanowires formed in an in-house AAO template with a length of $\sim$6.5 $\mu$m are shown in Figure 21 (c) and (d).

The chemical equilibrium between the hexafluorozirconate ion and ZrO$_2$ is as depicted in these reactions:

\[(a) \text{ZrF}_6^{2-} + 2\text{H}_2\text{O} \rightleftharpoons \text{ZrO}_2 + 4\text{H}^+ + 6\text{F}^-\]

When the boric acid is added, the fluoride ions produced in (a) are consumed in reaction (b):

\[(b) \text{BO}_3^{3-} + 4\text{F}^- + 6\text{H}^+ \rightleftharpoons \text{BF}_4^- + 3\text{H}_2\text{O}\]

3.1.2 CHARACTERIZATION OF ZrO$_2$ NANOSTRUCTURES

An XEDS of the ZrO$_2$ nanotubes and nanowires show the presence of Zr, O, F and Al (Cu and C observed in the spectrum are from the TEM grid) as shown in Figure 22(a). Trace amounts are also present of fluorine from the precursor and aluminum from the AAO template. The Energy Filtered Transmission Electron Microscope (EFTEM) using Zr-M line shows that the observed nanotubes and nanowires are composed of ZrO$_2$ as shown in Figure 22 (b) and (c). In the EFTEM images the nanotube and nanowire walls shows a stronger intensity compared to the
center regions because there is more Zr atoms per pixel at the wall creating a thickness contrast. The EFTEM image was slightly defocused because fine focusing can only be done with the Zero Loss Peak (ZLP). The electron diffraction pattern results showed diffuse rings and matched up with tetragonal ZrO$_2$ (JCPDS 88-1007) as shown in Figure 22(d).

Figure 21. TEM images of ZrO$_2$ nanotubes and nanowires formed in commercial template (a) and (b) with an average length of 7.7 µm and ZrO$_2$ nanotubes and nanowires formed in an in-house template (c) and (d) with an average length of 6.5 µm.
Figure 22. Confirmation of ZrO$_2$ nanowires (a) and nanotubes by EFTEM (b) XEDS (c) and diffraction pattern (d) indicates the tetragonal phase.

The HRTEM shows the grain size about ~6 nm as shown in Figure 23 (a). The crystallinity is stronger than that of TiO$_2$ and the amorphous region is not as pronounced. The stronger crystallinity could explain why the length of the ZrO$_2$ nanotubes and nanowires were longer than that of TiO$_2$ because there was less
damage and breakage during dispersion. It was not possible to get a sharp
diffraction pattern due to the diffuse rings of the amorphous phase. The HRTEM in
Figure 23 (b) and (c) shows "doubling" or alternating bright and dark spots while
defocusing. The doubling effect can only be observed in tetragonal phase materials.
Therefore, it was concluded to be tetragonal ZrO$_2$ even though nanocrystalline cubic
ZrO$_2$ will produce the same diffraction pattern.
Figure 23. HRTEM image of ZrO$_2$ showing grain sizes of ~6 nm and a crystalline phase (a). Higher magnification (b) and (c) also shows the doubling effect which disappears after adjusting the focus indicating the tetragonal phase.
3.1.3 PHOTOLUMINESCENCE SPECTRA OF ZrO$_2$

In order to further confirm the phase of the ZrO$_2$ nanotubes and nanowires, PL spectra were collected and shown in Figure 24 with the nanotubes and nanowires dispersed in water. The PL is an indication of the vibrational state, which is directly related to its symmetry and crystalline phase. The PL spectra for ZrO$_2$ shows strong scattering at lower wavelengths and the absorption band is ~250 nm. The PL results obtained in this research were compared to results found in literature$^{[58]}$ as indicated in Figure 25. The results in Figure 25 show the ideal mirrored symmetry between the emission and excitation spectra. The ZrO$_2$ nanotubes in Figure 25 were excited at different wavelengths and the emission peaks are centered around 470 nm. These published results could have different values than what was obtained in this research due to the thicker walled ZrO$_2$ nanotubes used for the PL measurements. The PL peaks and position change under different excitation wavelengths. The pH could also have an effect on the different outcomes of the PL spectrum.

The similarity of the PL presented here and the PL of the TiO$_2$ anatase nanowire shown in Figure 24 suggests a similar symmetry between the ZrO$_2$ nanowires and anatase. Combining the PL results and the doubling effect observed in the HRTEM, it can be concluded that the ZrO$_2$ nanotubes and nanowires are the tetragonal phase.
Figure 24. Photoluminescence results of ZrO$_2$ nanotubes and nanowires dispersed in water.
Figure 25. Photoluminescence spectra of single-crystal ZrO$_2$ nanotubes found in literature\textsuperscript{[58]}. 
Figure 26. Comparison between ZrO$_2$ and TiO$_2$ PL spectra showing that the two patterns are very similar indicating that they are both tetragonal phase.

3.2 DEPOSITION OF TIN OXIDE (SnO$_2$)

3.2.1 EXPERIMENTAL PROCEDURES FOR SnO$_2$

A LPD solution with the chemical reagent ammonium hexafluorostannate ((NH$_4$)$_2$SnF$_6$) (Aldrich, Milwaukee, WI) was used for the deposition of tin oxide (SnO$_2$). The solution conditions used were 10 mM of (NH$_4$)$_2$SnF$_6$ for 24 hours in the commercial AAO template at pH 2.5 between 40-50 °C with the same experimental
set-up used for TiO₂. After 24 hours the aqueous solution was still completely clear showing no signs of bulk-precipitation.

3.2.2 CHARACTERIZATION OF SnO₂ NANOSTRUCTURES

The growth of the SnO₂ wires within the AAO was observed in the SEM as shown in Figure 27. The dispersed SnO₂ nanotubes and nanowires were observed in the TEM and shown in Figure 28. SnO₂ nanotubes and nanowires formed in commercial template with an average length of 1 μm, a wall thickness of 20 nm, and a diameter of 120 nm. The diameter of the nanotubes and nanowires was much smaller than the pore diameter of the commercial AAO (i.e. 200 nm). The SEM observations showed that the SnO₂ had the same diameter as the AAO pore channel while in the template. Therefore, it can be surmised that while dissolving the AAO template in a strong base, the SnO₂ is also being slightly dissolved. SnO₂ dissolves at high pH but it appears that there is also some redeposition back onto the surface leaving the smooth nanotube and nanowire pore walls.
Figure 27. \( \text{SnO}_2 \) nanotubes and nanowires as deposited in the AAO template using 10 mM \( \text{SnO}_2 \) precursor solution for 24 hours.
Figure 28. SnO$_2$ nanotubes and nanowires formed in commercial template with an average length of 1 µm, a wall thickness of 20 nm, and a diameter of 120 nm.

A TEM-XEDS of the SnO$_2$ nanotubes and nanowires shows the presence of Sn, O, F, Na, N, and Al as shown in Figure 29(a) (Cu and C observed from the TEM grid). The electron diffraction pattern results showed diffuse rings and matched up with tetragonal SnO$_2$ (JCPDS 88-0287, cassiterite) as shown in Figure 29 (b). HRTEM images showed that the nanotube and nanowire grain size is ~5-7 nm as seen in Figure 28 (c). The ring pattern and HRTEM indicate that the SnO$_2$ is amorphous with some crystallinity.
Figure 29. The XEDS (a) showing the nanostructures were composed of Sn and O. There are trace amounts of Na and F from the precursor solution and Al from the template. The HRTEM (b) shows the amorphous grains of ~5-7 nm in size and diffraction pattern (c) for a SnO₂ nanowire indicating the tetragonal phase.
3.3 DEPOSITION OF IRON OXYHYDROXIDE (FeOOH)

3.3.1 EXPERIMENTAL PROCEDURES FOR FeOOH

Sodium hexfluoroferrate (Na$_3$FeF$_6$) was used for the LPD of iron oxyhydroxide (FeOOH) (Aldrich, Milwaukee, WI). The solution conditions were 10mM Na$_3$FeF$_6$ at pH 2.5 at 40-50 °C for 24 hours with a commercial AAO template. The solution was not homogeneous during deposition; a thick layer of orange powder settled at the bottom of the beaker over the template and was not suspended in the solution.

3.3.2 CHARACTERIZATION OF FeOOH NANOSTRUCTURES

The nanotube and nanowire growth inside the AAO template was observed in the SEM as shown in Figure 30. There seemed to be large FeOOH particles on top of the template but growth of the nanotubes and nanowires still occurred within the template. TEM images of the dispersed nanotubes and nanowires showed that the nanowires and nanotubes had an average length of 2 μm, an average wall thickness of 50 nm, and a diameter of ~260-300 nm as shown in Figure 31.
Figure 30. SEM image showing the growth of FeOOH nanotubes and nanowires within the commercial AAO template. Large particles of FeOOH deposition are evident on top of the AAO template.

Figure 31. FeOOH nanotube (a) and nanowire (b) with ~50 nm wall thickness, 2 µm length, and 260-300 nm in diameter.

A TEM-XEDS of the FeOOH nanotubes and nanowires show the presence of Fe, O, Na, and Al as shown in Figure 32(a) (Cu and C observed from the TEM grid). The electron diffraction pattern results showed diffuse rings and matched up most accurately with hexagonal FeOOH (JCPDS 77-0247) as shown in Figure 32(b). The
match with FeOOH was much more accurate than Fe₂O₃. There was no observable peak for fluorine (F) since the peak overlaps with the Fe. The grain size of the FeOOH nanotubes and nanowires were ~2-3 nm as shown by the HRTEM in Figure 32 (c) and (d).
Figure 32. XEDS showing FeOOH nanotubes and nanowires were composed of Fe and O (a) and the diffraction pattern indicating the hexagonal phase(b). HRTEM indicated a grain size of 2-3 nm (c) and (d).
3.4 DEPOSITION OF SILICON OXIDE (SiO₂)

3.4.1 EXPERIMENTAL PROCEDURES FOR SiO₂

A solution with chemical reagent sodium hexafluorosilicate (Na₂SiF₆) (Aldrich, Milwaukee, WI) was used for SiO₂ nanotube and nanowire LPD. The deposition conditions were 10 mM of Na₂SiF₆ for 24 hours with the solution held at pH 2.5 and temperature between 40-50 °C in a commercial AAO template. After 24 hours the solution remained clear with no observable precipitation.

3.4.2 CHARACTERIZATION OF SiO₂

TEM images did not show the presence of SiO₂ nanotubes or nanowires, just very small broken pieces resembling the composition of the AAO template. Characterization in the SEM showed that there was no evidence of SiO₂ deposition within the AAO template. The surface of the AAO template, however, had strange structures on the surface as depicted in Figure 33. The Si species, (SiOₓFᵧ), reacted with the AAO causing the formation of sodium fluoro-aluminate structures on the etched AAO template by mechanisms not fully understood. It appears that a thin layer of silica was coated on the AAO template and began to etch away the Al₂O₃ forming ball-like structures. Etching continued causing the stem and needle-like features shown on the surface of the template. The average coordination at the sites over the pores is higher than on the surface of the template. This increases the bonding interaction as the SiO₂ precursors are deposited. Higher SEM magnification
of the ball-like structures during early formation shows the growth of small particles which fused together as shown in Figure 34.

**Figure 33.** $\text{Na}_2\text{SiF}_6$ reacted with the porous AAO forming Na, Al, F, and O compositional structures by mechanisms not fully understood.
Figure 34. Small particles formed inside of the ball like structure which appeared to have merged together.

XEDS peaks showed that the ball-like structure was composed of predominantly Al, Na, and F as shown in Figure 35 which should be readily soluble in an aqueous environment. XEDS peaks for the needle like and base of the ball structures were composed of predominately the same structure as the porous AAO, Al₂O₃, shown in Figure 36.

XRD analysis was also done on the ball structures to confirm their composition of sodium aluminum fluoride as shown in Figure 37. The XRD analysis of the fracture surface of the AAO template was aligned vertically to detect the surface composition inside the pore. The Glancing-Incident XRD (GIXRD) were recorded on a Scintag Advanced Diffraction System with Cu K-alpha X-ray source with the X-ray fixed source at 1° and 0° sample tilt.
Figure 35. XEDS peaks for the ball-like structure formed when Na$_2$SiF$_6$ was deposited on an AAO template. The composition peaks matched with Na$_3$AlF$_6$. 
Figure 36. XEDS peaks for the needle-like structures and base of the ball-structure formed when Na$_2$SiF$_6$ was deposited on an AAO template. The peaks matched to a similar composition as the AAO template, Al$_2$O$_3$. 
Figure 37. XRD analysis of the ball-like structures formed after SiO₂ precursor LPD on AAO template, confirming their composition of Sodium Aluminum Fluoride.

3.5 DEPOSITION OF CO-AXIAL NANOTUBES

3.5.1 EXPERIMENTAL PROCEDURES FOR CO-AXIAL NANOTUBES

Coaxial nanotubes, another class of nanotube heterostructures, are both fundamentally interesting and have significant technological potential. Coaxial structures can be fabricated by preparing one metal oxide nanotubes in a template and then filling the tubes with another metal oxide.
Two metal oxides were separately synthesized using LPD in the commercial AAO template to create a co-axial structure. Initially, ZrO₂ was deposited with a solution of 10 mM of Na₂ZrF₆ with a pH of 2.5 and temperature between 40-50 °C for 24 hours. The template was removed and replaced in a 10 mM solution of (NH₄)₂TiF₆ with a pH of 2.5 and temperature between 40-50 °C for 24 hours.

A co-axial core-shell was also prepared by protecting the template with OTS to minimize the TiO₂ deposition and forming nanotubes. A TiO₂ shell with 10 mM (TiF₆)²⁻ solution was first deposited with a pH of 2.5 and temperature between 40-50 °C for 24 hours followed by depositing a ZrO₂ core with a 10 mM (ZrF₆)²⁻ solution with a pH of 2.5 and temperature between 40-50 °C for 24 hours. A schematic diagram in Figure 38 shows the structure of the TiO₂-ZrO₂ co-axial core-shell.

3.5.2 CHARACTERIZATION OF CO-AXIAL COMPOSITIONS

Since the deposition parameters for the two pure oxides are different, the co-axial wire is not homogeneous. A layer of ZrO₂ was formed within the TiO₂ core-shell structure which was confirmed in the TEM. Figure 39 shows how TiO₂ dominated and eradicated the already deposited ZrO₂. The microstructure of the nanowires was also very similar to the pure TiO₂ nanowires observed with fine filaments along the edges. The ZrO₂ dissolved back in the deposition solution of the TiO₂. The small amount of ZrO₂ in the system was well below the ZrO₂ solubility (Figure 40). The solubility of TiO₂ is shown in Figure 41. The fluorine (F) ions could also be a factor in increasing the solubility and chelating ZrO₂ back into the solution.
When TiO$_2$ was deposited on an OTS protected AAO template followed by ZrO$_2$ a co-axial structure was observed as depicted in the TEM Z-Contrast Image in Figure 42. The TiO$_2$ formed a core-shell and then there is a brighter band of ZrO$_2$ forming the co-axial structure.

Figure 38. Schematic diagram for the development of the co-axial core-shell. TiO$_2$ initially forms the outer nanotube which is then lined with a ZrO$_2$ core shell.

Figure 39. LPD of ZrO$_2$ core-shell followed by LPD of TiO$_2$. (a) Zr-M line; (b) Ti-L line; (c) O-K line. There are only trace amounts of Zr left in the nanotube.
Figure 40. Solubility of ZrO$_2$\textsuperscript{[69]}. 

Figure 41. Total titanium concentration vs. pH phase diagram at 50 °C drawn according to thermodynamic data indicating the solubility of TiO$_2$\textsuperscript{[70]}.  

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Figure 42. Co-axial core-shell of TiO$_2$ filled with ZrO$_2$ (i.e. the brighter contrast areas) imaged in the TEM Z-Contrast Image.
CHAPTER 4

DEPOSITION MECHANISMS

Generally, aqueous-chemical deposition of TiO₂ nanowires inside AAO templates, without the application of an external field is not possible[19]. This is because the isoelectric point (IEP) of aluminum oxide (pH 7-9[71]) is close to the IEP of precipitating TiO₂ sols (pH 6-7[71]), resulting in electrostatic repulsion between the two at most pH values. In the context of chemical deposition of thin films[72], it has been shown that the use of ammonium hexafluorotitanate ((NH₄)₂TiF₆) aqueous precursor results in Ti-containing clusters with a much reduced IEP (pH ~1.5)[73]. Thus, the (NH₄)₂TiF₆ precursor at pH 2.5 used in this research is expected to result in negatively charged Ti-containing clusters, while the AAO template surfaces are expected to be positively charged. This results in the heterogeneous nucleation and growth of TiO₂ crystals on the walls of the AAO substrate pores, creating nanotubes.

Using the LPD synthesis method, it is possible to exercise control over the geometry of the nanotubes and nanowires. The diameter and length can be controlled by tuning nanopore diameter and thickness of the AAO template,
respectively, and the nanotubes wall thickness can be controlled by processing conditions.

4.1 GROWTH METHODS

A novel growth method should satisfy three conditions: it must (i) explain how one-dimensional growth occurs, (ii) provide a kinetic and thermodynamic rationale, and (iii) be predictable and applicable to a wide variety of systems\textsuperscript{[74]}.

4.1.1 SURFACE NUCLEATION

The surface nucleation model requires heterogeneous nucleation of the solid state at the interface between the surface and the solution as depicted in Figure 43(a). Metastable supersaturation, which can be controlled by pH and concentration of the solution as shown in Figure 41 is critical for surface nucleation\textsuperscript{[69]}. The degree of supersaturation is high at pH 2.5. For a 1 mM LPD solution, there is metastable saturation, the solubility at pH 2.5 is approximately 2 \times 10^{-6} \text{ mM} so the solution is supersaturated (i.e. there is no bulk precipitation in the solution so it is metastable).

Heterogeneous catalytic reactions by solid materials only occur at the surfaces of the catalyst. For the same deposition of the metal oxides, the rate of the reaction is a function of the available surface area. Therefore, porous supports are usually needed. The greater the amount of surface accessible to reactants, the larger the amount of reactant converted to product per unit time for each unit of catalyst mass. Traditionally, the active component disperses throughout the entire surface
area of a suitable support. If the added amount of metal oxide is excessive, deposition will build up on top of the template and block the pore channels.

To increase surface area effectively, a small pore size is desired. However, if the pore size is too small, it will impede the passage of reactants or products and the effective surface area decreases. A mesoporous structure (50 - 100 nm) provided a significantly high surface area (> 1000 m²/g) and was still wide enough for the passage of molecules. The sign and magnitude of the surface charge is determined by the chemical nature of the oxide surface and by the pH of the solution.

The limits to which metal oxides can be used in template synthesis of nanotubes and nanowires are defined by the chemistry required to synthesize the metal oxides. All materials, in principle, could be synthesized within nanoporous membranes, provided a suitable chemical pathway could be developed. Typical concerns that should be addressed when developing new template synthetic methods include the following: (i) will the precursor solutions used to prepare the material have hydrophobic or hydrophilic behavior; (ii) will the deposition reaction proceed too fast resulting in pore blockage at the membrane surface before nanotube or nanowire growth can occur within the pores; and (iii) will the host membrane be stable both thermally and chemically during the reaction. The various methods that have been reported can be categorized based on characteristic approaches to maintaining the supersaturation of the solution so as to sustain the formation of the solid phase.
Solution chemistry and temperature will determine the degree of supersaturation of the system, which will have a strong influence on the ability of the liquid medium to supply material to the template pores. Increasing supersaturation should increase the rates of nucleation and growth of a solid, which may lead to increased growth rates of the nanotubes and nanowires. Figure 44 is a schematic plot of the number of nuclei (N) as a function of degree of supersaturation (S) which indicates that there is a narrow window where nucleation is favored for oriented nanostructures. In aqueous hydrolyzing systems, supersaturation of a solution can be increased by raising the temperature, raising the concentration of the metal oxide, or by changing the pH. The kinetics of crystallization became more rapid with an increased temperature and an optimum pH.

Figure 43. Surface nucleation (a) and particle attachment (b).
Figure 44. Idealized diagram for nucleation and growth[11].

Excessively high supersaturation typically leads to heavy bulk precipitation forming a thick deposition layer on the surface of the AAO template limiting the growth of nanotubes or nanowires inside the template. If the solution remains supersaturated after bulk precipitation occurs, growth can proceed due to heterogeneous nucleation or the attachment of nanoparticles. Optimizing the nanotube and nanowire growth rate involves balancing factors that increase supersaturation with those that favor a more controlled deposition rate.

The nanotubes and nanowires were produced by the deposition of ions on the inner walls of the pores of the AAO template. The shape of the nanotubes and nanowires matched that of the AAO pore channels, and nanotubes formed without formation of solid phase in the solution. Therefore, deposition can be concluded to have occurred through heterogeneous surface nucleation into the AAO. Negatively charged (MF₆)²⁻ ions were attracted to the surface of the positively charged AAO, and hydrolyzed into the metal oxide shown in the diagram in Figure 45.
mechanism for deposition is the formation of a tube which over time begins to fill, building into a solid wire structure as shown in Figure 46. Nanotubes were also formed with no solid phase in the solution. Observation of nanotube-nanowire combinations were frequently observed in the TEM when the pore channel was not completely filled.

![Diagram showing the formation of a tube with positively charged AAO template and negatively charged metal oxide](image)

**Figure 45.** The positive charge of the AAO template attracts the negatively charged metal oxide particles which build up layer by layer on the AAO template.
Figure 46. Growth mechanism for metal oxide nanotubes which are attracted to the oppositely charged pore walls of the AAO template and by surface nucleation build into nanowires with time.

4.1.2 ELECTROSTATIC INTERACTION

Most materials immersed in a polar aqueous solute can acquire surface electric charges from the preferential absorption of ions (generally negatively charged since cations are more easily hydrated and retained in solution), by the ionization or dissociation of surface groups (e.g. hydrolysis of cations). The charging of a surface in a liquid can come about either by the ionization of surface groups or by the adsorption of ions from the solution onto a previously uncharged surface. This surface charge affects the ion distribution near the surface in the polar solution: counter-ions will be attracted and co-ions will be repelled. Therefore, the diffuse electrical double layer is established.

The electrostatic interaction can be either attractive or repulsive, depending on the charge of interacting surfaces. For surface charges of the same sign, the
interaction is repulsive, while for surface charges of opposite signs, the interaction is attractive. The sign and magnitude of the surface charge is determined by the chemical nature of the oxide surface and by the pH of the solution. The pH at which zero charge is observed is the isoelectric point (IEP).

Metal oxide particles, if immersed in water, may have a charge corresponding to the binding of some H\(^+\) (or OH\(^-\)) ions by ion adsorption. Other surface reactions may happen between the particle surface and the OH\(^-\) or H\(^+\) ions in the solution via hydrolysis\(^{[69]}\).

\[
\begin{align*}
(a) & \quad -\text{M-OH} + \text{H}^+ = -\text{M-OH}_2^+ \\
(b) & \quad -\text{M-OH} + \text{OH}^- = -\text{M-O}^- + \text{H}_2\text{O}
\end{align*}
\]

While both of these reactions occur to some extent on all oxide surfaces, usually one will occur in a greater extent on a given oxide. At pH lower than the IEP, more H\(^+\) ions surround the particles and the surface charge is positive; at pH above the IEP, the surface charge is negative.

According to the theory of nucleation and growth\(^{[75]}\) the free energy of forming stable nuclei on a substrate is determined by four factors: (i) the degree of supersaturation S; (ii) the interfacial energy \(\sigma_{pl}\) between the particle (p) and the liquid (l); (iii) the interfacial energy \(\sigma_{ps}\) between the particle and the substrate (s); and (iv) the interfacial energy \(\sigma_{sl}\) between the substrate and the liquid:

\[
\Delta G = -RT \ln S + \sigma_{pl} + (\sigma_{ps} - \sigma_{sl}) A_{ps} \tag{4.1}
\]

where A is the surface area of the particle.
A few generalized solution synthesis concerns should be considered:

1. Controlling the solubility of the precursors and the degree of supersaturation so that massive precipitation is not the dominating reaction. Experimentally, this is accomplished by reducing the reaction temperature, and by reducing the precursor concentrations as much as possible, while at the same time allowing nucleation and growth to occur. A high turbidity of the solution is an indication of rapid precipitation and should be avoided.

2. Reducing the interfacial energy between the substrate and the particle. In literature, surface functionalization is widely used to ensure that nucleation is favored on the substrate rather than in the solution.

3. Ensuring that the kinetic growth of oriented nanostructures is more favored over non-oriented structures.

4.1.3 IONIC INTERACTION

The strong ionic interactions hold together the metal cations and oxygen anions that normally show a strong tendency in crystallization at elevated temperatures during lattice formation.

Interactions can be electrostatic, van der Waals, or short range repulsion forces as described by the DLVO theory\(^{[76]}\). In 1942, Derjaguin and Landau\(^{[77]}\) and Verwey and Overbeek\(^{[78]}\) (DLVO) suggested that the total energy of a colloidal system is the summation of the repulsion forces. The DLVO theory describes surface forces which act between two surfaces in close proximity\(^{[76]}\).
4.1.4 PARTICLE ATTACHMENT

In the particle attachment model, particles form in the supersaturated bulk solution and attach to the substrate (Figure 43 (b)). Therefore, supersaturation is essential, but not metastability. This method relies on substrate-particle and the metal oxide-particle interactions to form nanotubes and nanowires.

The net force is based on the interatomic interactions between particles and surfaces. Generally, if the net force between colloidal particles is attractive, they stick together and if the force is repulsive they repel each other. The DLVO theory is represented by the following equation[76]:

\[ V_{\text{tot}} = V_e + V_a \]  \hspace{1cm} (4.2)

where \( V_e \) is the electrical double-layer interaction and \( V_a \) is the van der Waals interaction.

4.1.5 PARTICLE-SUBSTRATE INTERACTIONS

The DLVO[76] theory describes the stability of colloid particles against agglomeration and sedimentation in aqueous solution. This theory of colloid science describes surface forces which act between two surfaces when they are in close proximity. The net force is based on all of the interatomic interactions between all particles and surfaces. Generally if this net force between the colloid particles is attractive, they will stick together.
The surface charge affects the ion distribution near the surface in the polar solution and counter-ions will be attracted while co-ions will be repulsed. A diffuse electrical double layer is established. The thickness of the double layer is dependent on the Debye length and varies inversely with the ions in the solution. As the number of available ions increases, the double layer thickness decreases. The double layer is linearly proportional to the Debye length\(^{[79]}\),

\[
\lambda_D = \sqrt{\frac{\varepsilon_0 k T_e}{n_e q_e^2}}
\] (4.3)

where \(\lambda_D\) is the Debye length, \(\varepsilon_0\) is the permittivity of free space, \(k\) is Boltzmann’s constant, \(q_e\) is the charge on an electron, \(T_e\) and \(T_i\) are the temperatures of the electrons and ions, respectively, and \(n_e\) is the density of electrons.

The different interfacial interactions between the template and the deposited particles may be attributed to the various adhesion strengths. The ultrasonic cleaning should have eliminated loose deposits of the metal oxides. The LPD rate as a function of hydrofluoric acid concentration is shown in Figure 47. The optimal HF deposition condition occurs using a low concentration of HF with 0.01 M H\(_2\)BO\(_3\). The rate of LPD TiO\(_2\) as a function of the time reacting with the ultrapure deionized water is shown in Figure 48. Increasing the time and temperature of the water will improve the deposition rate.
Figure 47. Deposition rate as a function of hydrofluoric acid concentration. A comparison of samples with and without HF pretreatment are also shown. (a) $\text{H}_3\text{BO}_3 = 0.01 \text{ M}$ (b) $\text{H}_3\text{BO}_3 = 0.005 \text{ M}$. 
Figure 48. Deposition rate of LPD TiO₂ as a function of the time reacting with the ultrapure deionized water\cite{80}.

4.1.6 PARTIAL CHARGE MODEL AND COMPLEXATION

The partial charge model, based on Sanderson's principle of electronegativity equalization in a compound, is a qualitative model for understanding the behavior of an element during hydrolysis, condensation, and complexation. Condensation of cations in the solution can occur only when the hydroxo ligand in the coordination sphere of the cation is present\cite{81}.
Niesen et al.⁶¹ applied the partial charge model to measure electronegativity and pH diagrams of complexants of titanium species by chlorine and fluorine for the deposition of a TiO₂ thin film. Their results show that stable fluorine complexes of titanium (IV) could be formed under acid conditions.

4.1.7 MICROSTRUCTURE CONTROL

HRTEM images at low concentration (early stages) appear amorphous in structure as seen in Figure 47 (a). This agrees with the ion by ion layer deposition method that the metal oxide first takes on the amorphous structure of the AAO template and then as the metal oxide wall thickens it relaxes to the crystalline anatase structure shown in Figure 47 (b).
Figure 49. HRTEM images of TiO$_2$ nanostructures. Low concentrations and early stages appear amorphous (a). Increasing concentration and time develops into the crystalline anatase structure (b).
The mechanism of formation of the metal oxide nanotubes and nanowires from acidified fluro-solutions is the buildup of particles on the pore walls of the template. In the early stages of growth, the particles are held together by a network of Ti-O- bonds. The nanotubes are initially obtained when this process is done in the alumina membrane and the particles adsorb to the pore walls. The pore walls are positively charged and the particles are negatively charged.

The nanotubes and nanowires were produced by the deposition of anatase films consisting of small particles on the inner walls of the pores of the AAO template. The shape of the anatase nanotubes and nanowires matched that of the AAO pore channels, and nanotubes formed without TiO₂ formation in the solution. Therefore, deposition can be concluded to have occurred through heterogeneous surface nucleation into the AAO template. Negatively charged (TiF₆)²⁻ ions were attracted to the surface of the positively charged AAO template, and hydrolyzed into TiO₂.

The precursor solutions were supersaturated with Ti⁺⁺ ions to produce crystal nuclei of anatase. Since Ti-F bonds are relatively stable, rapid hydrolysis and polymerization of the precursor molecules does not occur and such moderate reaction conditions led to the deposition of stable crystalline particles in the substrate through surface nucleation. As a consequence, crystalline anatase nanotubes and nanowires were directly obtained at a low temperature. Since no higher annealing is required for crystallization, the infiltration and nanotube and nanowire morphology are controlled by this technique.
The solution remained clear after 1 hour showing a low degree of TiO$_2$ formation in the solution. The aged solution (i.e. 12 and 24 hours) becomes turbid because of homogeneously nucleated anatase TiO$_2$ particles caused by a high degree of super saturation. A higher precursor concentration (> 1 mM) creates longer nanotubes and nanowires. The caveat is that increasing concentration will increase deposition on the outer surface which can block the pores and hinder deposition. Longer times led to an increase in non-uniform deposition since pore-blocking was not homogeneous.

The formation of tubes after a short immersion times indicates that the particles adsorb to the alumina template's pore walls. This is expected because the pore walls are negatively charged while the metal oxide particles are positively charged. It has also been observed that the rate of saturation is faster within the pore walls than within the solution. Nanotubes and nanowire growth has been observed while the solution remained completely clear. This was especially obvious with the ZrO$_2$ solution which after 24 hours still did not have any visible precipitates indicating that there was agglomeration of the particles. This is most likely due to the enhancement in the local concentration of the TiO$_2$ particles due to adsorption on the pore walls.

Prolonged deposition times lead to a layer of oxide forming on the template surface as the pores are being filled. If it is assumed that the nanoparticles are uniformly sized spheres, then the highest possible packing density is 74%[83]. This
would also be the highest achievable density of the nanowires. If there is a range of sizes in the nanoparticles, even denser packing would be possible.
CHAPTER 5

CONTROL OF NANOSTRUCTURE

LENGTH AND THICKNESS

5.1 OPTIMIZE PROPERTIES BY DEPOSITION RATE

Slower deposition minimizes template pore blocking while faster deposition increases nanotube and nanowire length. In order to create a deceleration of deposition, OTS has been used. In order to accelerate the deposition, several factors could be increased; (i) infiltration time; (ii) concentration; (iii) deposition temperature; (iv) pH; and (v) convection.

The mechanism by which LPD occurs is complex and varies between different oxide systems. The parameters that can be adjusted to optimize nanotube and nanowire properties and deposition rates include precursor concentration, temperature, infiltration time, convection in the substrate, and pH. Once established, however, the process is highly reproducible as shown by the different outcomes based on conditions of time and concentration shown in Table 1 and Table 2. Resulting nanotubes and nanowires for different controlled conditions are represented in Figure 50. The condition for obtaining only nanowires has not been

90
found (i.e. there may always be some nanotubes present due to pore blockage), but increasing concentration and time increases the length of the nanowires until the channel of the template becomes blocked by deposition.

The nanotubes and nanowires have uniform diameters throughout their entire length with a surface that is relatively smooth. The morphology of the nanotubes and nanowires is controllable since no annealing for crystallization is required. Figure 51 depicts statistically averaged lengths for varying conditions of infiltration time and precursor concentration. Increasing infiltration time and precursor concentration increases the length and wall thickness of the nanotubes and nanowires. Figure 51 also shows that the nanotube and nanowire length is increased by applying continuous ultrasonication synthesis and that the ZrO₂ nanotubes and nanowires are significantly longer than the TiO₂ nanotubes and nanowires under the same conditions.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6 hrs</td>
</tr>
<tr>
<td>5 mM</td>
<td>tubes/wires</td>
</tr>
<tr>
<td>10 mM</td>
<td>tubes/wires</td>
</tr>
<tr>
<td>15 mM</td>
<td>tubes/wires</td>
</tr>
<tr>
<td>20 mM</td>
<td>tubes/wires</td>
</tr>
<tr>
<td>10 mM OTS protected AAO</td>
<td>tubes</td>
</tr>
</tbody>
</table>

→ increase length

**Table 1.** Predicted outcome of nanotubes or nanowires based on different conditions of concentration or time for TiO₂.
<table>
<thead>
<tr>
<th>Concentration</th>
<th>1 hr</th>
<th>12 hrs</th>
<th>24 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1mM</td>
<td>Short thin walled tubes</td>
<td>tubes/wires</td>
<td>Long thin walled tubes/some wires</td>
</tr>
<tr>
<td>10 mM</td>
<td>tubes/wires</td>
<td>tubes/wires</td>
<td>tubes/wires</td>
</tr>
<tr>
<td>20 mM</td>
<td>Long thin walled tubes/some wires</td>
<td>tubes/wires</td>
<td>wires/tubes</td>
</tr>
</tbody>
</table>

→ increase length

↓ increase length and tube wall thickness

**Table 2.** Increasing the time and concentration will increase the length and thickness of the nanotube walls.
<table>
<thead>
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<th>Concentration</th>
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<th>12 hours</th>
<th>24 hours</th>
</tr>
</thead>
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<tr>
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<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
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<tr>
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<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>20 mM</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
</tr>
</tbody>
</table>

**Figure 50.** Varying the concentration and LPD deposition time yields different lengths and nanotube wall thicknesses.
Figure 51. Box plots representing statistically averaged lengths for varying conditions showing control of nanotube and nanowire length. (n = 30 for each condition)
CHAPTER 6

CONCLUSIONS

An innovative method, using a simple apparatus and easily achieved conditions, has been developed for a “bottom up” approach for building metal oxide nanotubes and nanowires. The synthesis of these metal oxide nanotubes and nanowires is a single step process at near-ambient temperature by combining the LPD method with a porous AAO template. The as-deposited metal oxide consists of a nano-crystalline phase embedded in an amorphous matrix, containing fluorine as the main impurity.

The growth method for the nanotubes and nanowires is surface nucleation along the walls of the AAO template pore channels due to the opposing charge of the template and metal oxides. There is a direct relation between the deposition time and concentration with the length of the nanotubes and nanowires. This method can be used for stable fluoride complexes to form metal oxide nanotubes and nanowires. This research indicates that using a porous template and controlled LPD technique, metal oxide nanotubes and nanowires can be grown which have many promising applications.
CHAPTER 7

SUGGESTIONS FOR FUTURE WORK

- Fabricate and measure more properties of devices of various nanotubes and nanowires of different metal oxides.
- The sensor properties can be measured for different reacting gas species.
- Develop and analyze applications for the LPD method nanotubes and nanowires. (e.g. sensors, microbial applications, or photovoltaics using UV light)
- Try working with other parameters. (e.g. using a track-etched template instead of AAO template)
- Develop more co-axial and combinations of metal oxide precursor solutions
APPENDIX A

APPROXIMATION OF THE NUMBER OF
NANOTUBES AND NANOWIRES
DISPERSED IN SOLUTION
APPENDIX A
NUMBER OF NANOTUBES AND NANOWIRES
IN SOLUTION APPROXIMATION

- AAO Commercial Template Pore Size: 0.02 μm
- Membrane Diameter: 43 mm → 40 mm useable
- Average Thickness: 60 μm

- Used 3/4 of a commercial AAO template estimated 500,000 pores therefore 1,000,000 possible nanotubes or nanowires (growth occurs on both sides of the template). The template was dissolved in 10 mL of NaOH and centrifuged and washed multiple times. The precipitate was then dispersed in 2 mL of water.
- 0.01 mL of solution was removed and dispersed in 1 mL of ethyl alcohol containing approximately 10,000 nanotubes or nanowires
- 0.005 mL (1 drop) of this solution dispersed for SEM or TEM work is approximately 50 nanotubes and nanowires


3. Feynman, R.P. *There's Plenty of Room at the Bottom: An Invitation To Enter a New World of Physics*. A transcript of his talk is available online and a published version appears in Caltech's Engineering and Science February 1960 issue: <http://www.zyvex.com/nanotech/feynman.html>.


