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Transition metal oxides (M\textsubscript{x}O\textsubscript{y}, M = Ti, W, Zn) prepared by electrochemical anodization: synthesis, modifications, and applications

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A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy.

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Abstract

In the past few decades, transition metal oxides (TMO) show various unique properties and wide applications due to their electronic configuration and multiple possible structures. Among different TMO, titanium dioxide (TiO$_2$), tungsten trioxide (WO$_3$), and zinc oxide (ZnO) are most commonly oxides used as catalyst, sensors and electric devices due to their unique physical and chemical properties. Electrochemical anodization is a facile and cost-effective way to produce 1D self-assembly metal oxides, which integrates the advantage of larger surface area, short diffusion path, low quantum confinement, high charge transfer efficiency and tunable electronic structures. Post-annealing is a possible way to rearrange the disordered atomic arrangement of the anodic oxides and tune their electronic structure. In addition, the decoration of the anodic oxides with metal nanoparticles is another efficient way to modify the as-synthesized anodic oxides, which helps suppress the recombination of the photo-generated charge carriers and prolong their life time. The as-prepared and modified anodic metal oxides exhibit various applications, including the photocatalyst, electrochemical catalyst and SERS substrates.

The pre-treatment of the Ti substrate and electrolyte were conducted before formal anodization. Their influence on the morphology and mechanical properties of the anodic TiO$_2$ were discussed. The results indicated that the regular TiO$_2$ NTs with the hierarchical shape was produced on the patterned Ti substrate prepared by two-step anodization. Although the regularity of TiO$_2$ NTs improved a lot with the increase of aging time, the pore size decreased as well as the surface homogeneity. The nanohardness and reduced modulus showed the obvious increase with the aging time and highest adhesion between TiO$_2$ and Ti substrate was achieved by anodizing in the 25 h aging electrolyte.
Anodic TiO₂ initially has an amorphous structure and crystallizes into anatase after thermal annealing. High resolution transmission electron microscopy and in situ synchrotron X-ray diffraction were employed to study the dynamic phase transformation process and the effect of annealing parameters on the atomic structure. At temperatures above 330°C the crystallization process began immediately and ceased within ~500 s. The material was not fully crystallized (crystallinity only ~70 wt.%), even when the annealing time was prolonged to 7000 s at an elevated temperature. The incomplete crystallization could be ascribed to the effect of grain boundaries, oxygen vacancies, and fluorine ions.

Besides the phase structure change of anodic TiO₂ after annealing, the electric resistivity and wettability of the TiO₂ were found to have a close relationship with the post heat treatment. The as-synthesized and annealed TiO₂ were used as the electroplating substrate for fabrication Ni-TiO₂ nanocomposite. The results reveal that the deposited Ni grows inside the nanotube on annealed TiO₂ substrate, while it only forms a compact layer on the top of as-anodized. The resultant Ni-TiO₂ nanocomposite on annealed TiO₂ substrates also exhibited better oxygen evolution performance than on amorphous substrates in terms of low overpotential at a current density of 10 mA/cm² and small Tafel slope.

The modification of TiO₂ can also be achieved by a novel technique that combines magnetron sputtering and thermal dewetting. The obtained Cu-TiO₂ nanocomposite catalyst exhibited 4-fold increase in the photodegradation rate of methylene blue aqueous solution under solar light irradiation than anatase TiO₂ prepared with same anodization conditions. The enhanced photocatalytic activity was attributed to the synergistic effect of Schottky barrier and surface plasmon resonance.

Similar to anodic TiO₂, regular self-organized nanoporous WO₃ was prepared
through anodization in the electrolyte containing ethylene glycol, ammonium fluoride and DI water, which was subsequently used as a template for deposition of Ag nanoparticles by magnetron sputtering and thermal dewetting. The synthesized Ag-WO$_3$ nanocomposites showed large SERS enhancement factor of $\sim 2.1 \times 10^7$ and a low detection limit of $\sim 1 \times 10^{-6}$ M Rhodamine B. The visible light responding behaviour of WO$_3$, synergistic interaction between Ag nanoparticles and the WO$_3$ substrate, and the plasmonic behaviour of Ag collectively contribute to the enhanced Raman scattering.

Although TiO$_2$ nanotube and WO$_3$ nanoporous structure can be successfully prepared in the ethylene glycol electrolyte containing the NH$_4$F, it did not work for anodic ZnO. A new type of self-assembled Zinc oxide (ZnO) nanostructure has been prepared by electrochemical anodization of Zinc foil in NaOH aqueous electrolyte. The experimental results indicate that the primary factor affecting anodic nanostructure is the applied voltage, while anodization time and electrolyte concentration also play significant roles in tailoring nanorod morphology.
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First of all, I would like to express my greatest thanks and gratitude to my supervisor Prof. Wei Gao for his continuous support and encouragement. His creative thinking and exploration spirit set a good example for all our group members. Without his patient guidance and constant inspiration, this thesis would never come true. I would also like to have my great appreciation for the help from my co-supervisor Dr. Michael Hodgson and my advisor Dr. Balan Zhu, who have imparted precious experimental experience to me.

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CHAPTER 1

Introduction

Transition metal oxides are composed of transition metals surrounded by the oxygen atoms, which form a wide structural variety, such as monoxide, dioxide and perovskite etc. Due to their unique physical and chemical properties, transition metal oxides have been widely used as catalyst, sensors, and energy storage or electrochromic device. It is well known that the properties are closely related with nanostructures due to the quantum or size effect. Recently, there are a large variety of approaches that have been reported to fabricate well-defined nanostructures. Electrochemical anodization is a fast and cost-effective way to produce self-assembly transition metal oxides. Although regular morphologies can be achieved through anodization technique, the intrinsic drawbacks of transition metal oxides also limit their applications, which could be solved via modification of the as-synthesized metal oxides. In this thesis, the processing window for three common metal oxides were explored. Different modification methods were employed to further improve their properties and potential applications of the modified metal oxides were studied consequently.
1.1 Transition metal oxide

1.1.1 Background information

Transition metal oxides (TMO) are the ionic compounds that are composed of positive transition metallic and negative oxygen ions. The most common type is the binary oxides, which are composed of a metallic element and oxygen, such as titanium dioxide (TiO$_2$) and tungsten trioxide (WO$_3$). The binary oxides can also be developed into ternary oxide or mixed transition-metal oxides, where additional metallic elements are present with the formula of $A_{x}B_{3-x}O_{4}$, where $A, B$ are transition metal.$^1$

1.1.2 Electronic band structure

The transition metals generally conclude the elements of groups 4-11 in the periodic table with incomplete $d$ shell. Compared to the metals that have a continuous band of electronic state, the electron-hole pairs of TMO are separated into conduction and valance band. The valence band can be ascribed to the fully filled 2$p$ orbitals originated from oxygen anion, while the sparsely populated $d$ orbitals of the metal cation form the conduction band with high energy.$^2$ Because of the incompletely filled $d$-shell, the TMO show various unique properties, such as high dielectric constants,$^3, 4$ wide band gap,$^5, 6$ and electrochromic characters.$^7, 8$

1.1.3 Applications

In the recent decades, transition metal oxides have attracted great attention in the electronic, magnetic and optical applications.$^9, 11$ The special electrical and magnetic properties of transition metal oxides may derive from the unique electronic structures, that is the $d$-shells of metallic ions was not fully filled by electrons.$^{12}$ In addition, the transition metal oxides always exhibit mixed valence, where more than one oxidation states of metal ions would be present. The properties of such oxides always depend on the electron transfer rate between different oxidation states, such as the catalysis,
batteries and memristors. All these features make the transition metal oxides possessing special functional properties which can be used in a variety of applications.

Transition metal oxide have been extensively investigated as the effective photocatalysts. TiO$_2$ were first used as a photocatalyst to split water under irradiation of light in 1972 by Honda and Fujishima. From then on, a great deal of effort has been made on such promising photocatalyst for environmental purification, self-cleaning materials, advanced solar energy conversion, cancer treatment, and highly efficient antibacterial applications. There are many other metal oxides with a proper band gap that can be used as potential photocatalysts, such as iron oxide, tungsten trioxide, and tin oxide. However, the major shortcomings of the photocatalyst lie in the inadequate visible light absorption and fast recombination of photo-generated electron-hole charge carriers. Much attempt has been made to improve their photocatalytic activities, including heterojunction formation and metal or non-metal ions doping.

Dye-sensitised solar cells (DSSCs) are considered as the cost-effective and environmentally friendly way to replace the fossil fuels. Because of the tuneable morphology, and chemical and thermal stability of transition metal oxides, both the binary metal oxides and ternary compounds have been investigated as the photoelectrode material in DSSCs. The flower-like α-Fe$_2$O$_3$ exhibited high surface area and excellent electron mobility. The transparent Zn$_2$SnO$_4$ electrode improved the light harvest and had the large photovoltaic conversion efficiency. Transparent and conductive Zinc oxide (ZnO), and the combination of the ZnO nanowires and TiO$_2$ nanoparticles were synthesized. The hybrid nanostructure showed five times higher conversion efficiency than that of the bare ZnO.
Supercapacitors have attracted much attention over the last decades due to their potential application in the energy storage field. The electrode materials for the superconductor are supposed to have the specific chemical and physical properties, including conductivity, thermal stability, corrosion-resistivity and controlled pore size with large surface area. Several transition metal oxides have been studied as the supercapacitor electrode with high capacitance, such as ruthenium oxide and iridium oxide. Attempts are also made to involve other cost-effective oxides in supercapacitor devices, including nickel oxide and manganese oxide.

Besides the green energy production and storage, the portable electronic devices to harness this renewable energy are also an important part. Lithium-ion batteries have been widely used as the energy storage device for various electric appliances from mobile phone to electric vehicles. Compared to the commercial anode made of graphite, the electrode composed of transition metal oxides exhibited better stability, fast ion mobility, and high reversible capacity. The traditional binary metal oxides were first studied as the batteries anode. Various transition metal oxides could act as the potential anode due to the high capacitance and power density, but their practical applications were limited by the inevitable negative situation during the electrochemical reactions, including volume change and poor conductivity. Recently, conductive materials modification and ternary transition metal oxide preparation have been proved as an effective way to solve these problems.

1.2 Typical transition metal oxides (TMO)

Over the past decades, the TMO with the metal elements ranging from high melting-points (tungsten, tantalum, and nickel) to low melting-points (Zn and Sn) have been widely investigated. The most commonly studied oxides are TiO₂, WO₃, and ZnO, which find applications in catalyst, gas sensing and electrochromic devices. However,
each of the above three oxides also exhibits distinct physical and chemical properties, such as energy band structures, electric conductivity and chemical stabilities.

1.2.1 TiO$_2$

As the typical transition metal oxide, titanium oxides exhibit different valences with stoichiometric and non-stoichiometric chemical formula and various crystalline phases, including tetragonal, orthorhombic, monoclinic, hexagonal, triclinic and rhombohedral.$^{34}$ Normally TiO$_2$ can be assigned to three crystalline structures with structure parameters listed in Table 1.1. Anatase and rutile phases are relatively stable,$^{35}$ while the brookite, as the metastable phase, is usually a by-product and can be transformed to rutile at elevated temperature.$^{36}$ TiO$_2$ is an $n$-type semiconductor with indirectly band gap that is closely dependent on the phase structure. For example, anatase has the largest band gap of $\sim$3.2 eV, while that of Rutile and Brookite are 3.0 eV and 3.14 eV, respectively. The band gap difference of the above three phases can be ascribed to the different crystalline structure, resulting in distinct coupling effect between O$_{2p}$ and Ti$_{3d}$ orbitals.$^{34}$

<table>
<thead>
<tr>
<th>Crystal Form</th>
<th>Crystal system</th>
<th>Unit cell Parameters (nm)</th>
<th>Crystalline structures$^{37}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>Tetragonal</td>
<td>a 0.379 b 0.379 c 0.951</td>
<td></td>
</tr>
<tr>
<td>Rutile</td>
<td>Tetragonal</td>
<td>a 0.459 b 0.459 c 0.296</td>
<td></td>
</tr>
</tbody>
</table>
TiO$_2$ has always been considered as the most popular TMO because it is a versatile material and has the unique physical and chemical properties. Its wide applications cover the daily life and various functional areas, including pigments, cosmetics, biomedicine, photocatalyst, photovoltaics, and energy storage. Since Fujishima and Honda found the potential of TiO$_2$ as a photocatalyst for water splitting under ultraviolet light, much efforts have been made on broadening the light absorption, increasing reactive sites or reducing the photo-generated charge carriers recombination rate.

Another potential application of TiO$_2$ is the DSSC due to the suitable conduction band position, to where the electrons of organic dyes can be injected from the lowest unoccupied molecular orbital. The advantages of high conductivity, fast ion exchange and compensation, and tuneable morphology also make TiO$_2$ a potential candidate for electrochromic devices.

### 1.2.2 WO$_3$

Tungsten oxides are normally formed by a network of WO$_6$ octahedra with sharing corners and edges, and exhibit various valences, including the monovalent oxides and mixed valence oxide. Tungsten oxides also show various crystalline phases, including monoclinic, triclinic, orthorhombic and tetragonal. The phase transitions could happen easily during the annealing process and some phase change are partially reversible as shown in Figure 1.1. Moreover, the transition behaviour could be altered when the size is reduced, resulting in the enhanced surface energy and decreased
Similar to TiO$_2$, WO$_3$ is a $n$-type semiconductor with wide band gap. The amorphous phase with randomly oriented WO$_6$ octahedra exhibits relatively large band gap of ~3.25 eV, while the crystalline WO$_3$ with different distortion have the band gap between 2.4 and 2.8 eV due to the change of W 5d orbitals. Compared to the TiO$_2$ and ZnO, the narrowed band gap of WO$_3$ expand the photoresponse spectra to the visible region, which is a significant advantage for photocatalytic and photoelectrocatalytic applications. Another feature of WO$_3$ is the nonstoichiometric properties, as its lattice can accommodate quite a few of oxygen deficiency. This has a great effect on the structure changes, optical properties, and electronic properties. It is reported that WO$_3$ with high substoichiometry degree exhibits blue colour and good conductivity, while the one with low oxygen vacancy is transparent and resistive.

Figure 1.1 Stability temperature domains of the different polymorphs of WO$_3$.56
WO₃ is a well-known electrochromic material with the promising application as “smart windows”, which displays colour changes when the positive and negative potential are applied. Expect for the electrochromism, the photochromic, gasochromic and thermochromic properties of WO₃ have also attracted much attention. As another photocatalyst, WO₃ has not only the suitable conduction and valence band position with narrow band gap but also the high stability in acidic solution, resulting in its efficient photo-oxidising ability of the organic contaminant under solar light. With regards to other applications, such as DSSC and sensing devices, WO₃ with the large specific surface area are required to have effective contact area with fluids or analyte.

1.2.3 ZnO

Unlike the TiO₂ and WO₃, zinc oxide only has two molecular formulas with ZnO and ZnO₂ and two typical crystalline phases (hexagonal and cubic). Theoretically ZnO exhibits three crystalline structures, but the rock-salt and zinc-blende is not stable under ambient conditions. The thermodynamically stable wurtzite structure is characterized by two bonding sublattices of Zn²⁺ and O²⁻, which is surrounded by a tetrahedral of O ions and vice-versa as shown in Figure 1.2. ZnO is a II-VI semiconductor materials with a direct wide band gap between 3.1 and 3.37 eV. Although the band gap is wide, ZnO shows a large solar absorption spectrum and light quantum efficiency compared to TiO₂, which makes ZnO a potential photocatalyst for the environmental treatment. The large excitonic binding energy (60 meV) of ZnO contributes to an efficient excitonic emission even at room temperature, which could be used in optoelectronic devices.

The most interesting exploration of ZnO is the mechanical-electrical conversion device “nanogenerator”, which is based on its piezoelectric property. The generator
developed by Wang et al. has the sandwich structure with zigzag Si coated with Pt on top, well-aligned ZnO nanowire in the middle and conductive GaN as substrate.\textsuperscript{73} With the help of ultrasonic wave, the ZnO nanowires moved laterally and created positive and negative piezoelectric potential on the side surface, where the electricity would be produced and output through electrode. In addition, the applications of ZnO as transparent-conductive films, sensors\textsuperscript{74} and solar cells\textsuperscript{75} have also been reported.

![ZnO crystal structure](image1.png)

Figure 1.2 (a) Hexagonal wurtzite crystal structure of ZnO, (b) Hexagonal prism of ZnO crystal showing different crystallographic faces.\textsuperscript{76}

1.3 Synthesis of TiO$_2$, WO$_3$ and ZnO nanostructure

It is known that the properties of nanomaterials are quite different from that of bulk materials due to the surface effect and quantum effect.\textsuperscript{77,78} Currently the advanced materials preparation techniques motivate the development of nanomaterials in different dimensions, including 0 D (nanoparticles), 1 D (nanowires, nanorods, nanotubes and nanofibers), 2 D (nanosheets and nanodisks) and 3 D (nanoflowers, core-shell and urchin-like) structures. A large variety of approaches have been reported to fabricate TiO$_2$, WO$_3$ and ZnO nanostructures. These techniques can be generally classified into two types: vapor-phase based and liquid-phase based methods.

1.3.1 Vapor-phase synthesis
The vapour-phase deposition typically contains two processes: evaporation of the source materials high temperature and condensation on the targeted substrates at relatively low temperature. The principle of this method is the reaction between metal vapours and oxidants to form metal oxides. The processing parameters, including starter materials type, temperature and pressure, should be carefully controlled to synthesize the nanostructures with expected size, morphology and crystallinity.

1.3.1.1 Physical vapour deposition

Physical vapour deposition process is a purely physical reaction based on the evaporation of metal or substoichiometric metal oxides as the source materials to produce the stoichiometric metal oxides. There are many techniques to achieve this purpose, such as electro-beam deposition, pulsed-laser deposition, and thermal evaporation, depending on the evaporation energy source. Among them, sputtering deposition is well established physical vapour deposition method. During sputtering process, the atoms of solid target materials are ejected into the plasma phase through bombarding with energetic particles. Then the escaped target materials atoms deposit on the substrate to form thin films with various nanostructures.

The uniform and dense TiO$_2$ thin film was prepared by Hasan et al. through radio frequency reactive magnetron sputtering using a mixture of Ar and O$_2$ atmosphere and the effects of substrate temperature on the optical property was discussed. The sputtered TiO$_2$ grown by high power impulse magnetron sputtering method had larger density and could be used as protection layer for photocathode in hydrogen evolution.

As for the WO$_3$, quality thin films were produced by reactive magnetron sputtering under different gas pressure. Compared to the polycrystalline WO$_3$ fabricated under low pressure, that prepared at high pressure had less dense porous morphology but higher water photooxidation efficiency. Gao et al. successfully prepared different
ZnO nanostructures through both direct current and radio frequency sputtering methods and found the ZnO produced by radio frequency are more conductive than that using direct current sputtering.\textsuperscript{84, 85}

1.3.1.2 Chemical vapour deposition

The main difference between the physical vapour deposition and the chemical vapour deposition is that whether or not chemical reactions occur during the deposition process as shown in Figure 1.3. In the chemical vapour deposition process, the reactant species (normally using volatile precursors) are delivered to the coating chamber with the help of carrier gases. Meantime, the dissociations of the reactive gas and precursors take place at specific pressures to produce resultant compounds on the target substrate. However, the chemical vapour deposition also has its drawbacks, including the high deposition temperature, slow deposition rates and chemical contamination.\textsuperscript{33}

Thick TiO\textsubscript{2} films and nanoparticles synthesized in a mixture of helium and oxygen atmosphere using titanium tetraisopropoxide were reported by Seifried et al. and the as-prepared film had the thickness of $\sim 150 \ \mu\text{m}$.\textsuperscript{86} Other morphologies, such as nanorods, nanowires and even mesoporous microspheres could also be fabricated via chemical vapor deposition.\textsuperscript{87-89} It was found that the WO\textsubscript{3} nanostructures synthesized by chemical vapour deposition have close relationship with the selection of reactants, with which the cube-like crystals, needles, wires and plates structures were formed.\textsuperscript{90, 91} Similarly the various kinds of ZnO nanostructures can be fabricated through chemical vapour deposition, including nanoplatelets, nanorods, and nanotubes.\textsuperscript{92-94}
1.3.2 Liquid-phase synthesis

Compared to the vapour-phase synthesis techniques, the liquid phase methods provide a different way to produce metal oxides and have the following advantages: i). low cost. The vapour phase deposition usually requires expensive equipment; ii). shape control. The random distribution mechanism or the high temperature conditions of vapour phase deposition approaches have a negative impact on the nanostructures synthesized. In the liquid phase deposition process, the growth of metal oxides is performed in an aqueous or organic solution at a relatively low temperature. It is usually a thermodynamically equilibrium reactions, which can be precisely controllable through tuning the conditions.

1.3.2.1 Sol-gel method

The sol-gel method is a versatile technique and involves the transition from a colloidal suspension “Sol” to a solid “Gel” phase. The inorganic metal salts or organic compounds are usually employed as precursors to produce the “sol” through hydrolysis and polymerization reactions. The monolithic “gel” will be formed when the hydroxide particles size exceeds the critical value and the films that contain “sol-gel” are deposited onto the substrate via dip-coating, spinning or dorp-casting. The further
drying treatment is conducted to remove the remaining solvent to convert films to dense solid materials.

TiO₂ nanoparticles formation could use titanium tetraisopropoxide as the precursor and the growth rate of particles increased with the temperature.⁹⁶ Recently the carbon and nitrogen doped TiO₂ was also prepared through the addition of glucose as carbon source and ethylenediamine as a nitrogen source to the sol, which exhibits the enhanced photocatalytic property.⁹⁷, ⁹⁸ There are a variety of precursors that can be used for WO₃ sol preparation, including WOCl₄, WCl₆ and tungstic acid.⁹⁹, ¹⁰⁰ Instead of nanoparticles morphology, Hilliard et al. reported a cost-effective method to synthesize mesoporous WO₃ nanostructure with incorporating a block polymer to the sol-gel process. As for the sol-gel process of ZnO, nanoparticles, nanowires and nanotubes have been successfully produced.¹⁰¹, ¹⁰²

1.3.2.2 Hydrothermal method

Hydrothermal method is a facile and cost-effective liquid phase technique to synthesize not only the nanoparticles but also the complicated nanostructure configurations. The reactions are always conducted under high temperature (above the boiling point of water or other solvents) and pressure (vapour saturation pressure) for a certain period to allow the nucleation and growing of crystals.¹⁰³ Therefore, stainless-steel vessels with hermetic seal called “autoclave” are required to suffer from these harsh conditions. During the hydrothermal reactions, the solute dissolves at the hotter end, and then hydrolysis and condensation happened at the cooler end, followed by the nucleation around deposited seeds and the desired crystal growth.¹⁰⁴

TiO₂ nanoparticles can be obtained both in the water and acidic ethanol-water solution through hydrothermal reactions.¹⁰⁵, ¹⁰⁶ Even the TiO₂ nanorods with anatase, Rutile and brookite phase structure can be fabricated through regulating the pH values.
during the hydrothermal process. In terms of hydrothermal synthesis of WO₃, the tungstic acid solutions have been extensively used. All kinds of WO₃ nanostructures, such as nanorods and nanoplates, with different crystallinity can be prepared by adding sulphate and organic acid into the above precursors. The hydrothermal method of preparing ZnO structures was first reported by Verges et al., but this technique did not attract more attention until Vayssieres et al. successfully synthesized ZnO nanowires on glass and silicon substrate. After the preparation of different kinds of interesting ZnO nanostructures, the emphasis has switched to the modification of ZnO during the hydrothermal process. The PEO₁₉-B-PPO₃ was added as the nucleation agent to tailor the optical band gap of resultant ZnO. The photocatalytic efficiencies of metal-doped ZnO prepared by hydrothermal method were also studied, which exhibit different enhancement mechanism.

1.3.2.3 Electrodeposition

Electrodeposition is a common technique to produce metallic coating involving the reduction of the metallic ions in the electrolyte for the purpose of corrosion prevention or improving the mechanical properties. However, the metal oxide can also be deposited on the cathode in the acidic electrolyte containing metal complexes of hydroxycarboxylic acids with applied external power. For example, the carboxylic acid is released from complexes with metal ions in the hydroxycarboxylic acid electrolyte during the electrochemical deposition, while hydroxyl agents are deprotonated again. The generation of hydroxyl leads to the increase of local pH and consumes the buffer capacity of the solution, resulting in the accumulation and precipitation of metal hydroxides or oxides.

The preparation of compact TiO₂ layer was reported as the blocking layers for perovskite solar cells. The morphology of electrodeposited TiO₂ can be further
improved by using surfactants as templates, which enhances its optical properties.\textsuperscript{117, 118} The peroxotungstic acid solution is the most common electrolyte for WO\textsubscript{3} electrodeposition,\textsuperscript{119} but Wang \textit{et al.} also successfully produced “pebble-beach” like morphology in a special aqueous sodium tungstate solution.\textsuperscript{120} Porous WO\textsubscript{3} layer prepared through electrodeposition only requires a small potential and short deposition time, while too high voltages or excessively long duration time may lead to the densification of porous nanostructures.\textsuperscript{121, 122}

Normally the as-prepared tungsten oxides exist in hydrate form, which can be transformed to the crystalline phase through annealing at 400°C.\textsuperscript{123} ZnO nanowires and nanotube arrays were synthesized by the electrochemical deposition.\textsuperscript{124, 125} Recently, the well-defined ZnO nanostructures with large surface areas, such as nanorods and nanoplates, are desired in the solar cell and sensor applications.\textsuperscript{126} Either the pre-spread of ZnO seeds or the template-assisted technique could help control the uniformity of the synthesized ZnO.\textsuperscript{127, 128}

\subsection*{1.4 Electrochemical anodization}

Among all kinds of nanostructures, 1 D nanomaterials, such as nanotubes, nanorods, and nanofibers, has the larger surface area, short diffusion path, low quantum confinement, high charge transfer efficiency and tunable electronic structures, which makes the 1 D nanostructures as the building blocks for many applications.\textsuperscript{33, 129} Electrochemical anodization is a facile and cost-effective way to produce 1 D self-assembly transition metal oxides.\textsuperscript{130} It refers to the electrochemical oxidation of the cathodic metal layer to surface metal oxide layer under the applied bias.\textsuperscript{131} The synthesis of TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} nanotubular or nanoporous structures has been extensively studied during the past decades.\textsuperscript{132, 133} Recently, highly ordered nanostructures prepared
by anodization based on other transition metals (Hf, Ta, Nb) as well as the metal alloys (TiNb and TiZr) are also reported.134-138

Electrochemical anodization can be regarded as the reverse of the above electrodeposition. In a typical anodization apparatus, the transition metal is used as the working electrode and platinum foil always as the counter electrode shown in Figure 1.4. Both of them are immersed in the electrolyte, which can be the aqueous or organic based solution. When the electrical current is applied between two electrodes, the water in the electrolyte breaks down into oxygen-containing agent, which participate the oxidation on the anode.

![Figure 1.4 Schematic diagrams of set-up for anodization experiment.139](image)

### 1.4.1 Formation and growth mechanism

During the electrochemical anodization process, a series of reactions take place both on the anode and cathode. Using the titanium anodization as the example, the oxidation of titanium and dissolution of the as-synthesized TiO₂ can be presumed:

\[
Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^- \quad \text{Eq. 1.1}
\]

\[
TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O \quad \text{Eq. 1.2}
\]
In the meantime, the hydrogen evolution reaction happens at the cathode:

\[ 2H^+ + 2e^- \rightarrow H_2 \quad \text{Eq. 1.3} \]

The reactions occurred on the anode have the direct relationship with the TiO_2 formation. To be specific, there are three dynamic processes competing with each other to produce different TiO_2 nanostructures: (1) the field-assisted oxidation, (2) the field-assisted dissolution and (3) chemical dissolution. The oxygen-containing agents migrate through the electrolyte and the formed oxide layer to the Ti/TiO_2 interface under the action of the electrical field induced by the applied external current or potential, resulting in the oxidation of Ti substrate as shown in Figure 1.5a. Due to the positive potential on the anode, the etching components, such as fluorine (F⁻), are driven to the interface of electrolyte and TiO_2 layer, and react with TiO_2 to form soluble [TiF_6]^{2-} complex (Figure 1.5b). Due to the small radius of F⁻, it is possible for them to be transported through the oxide layer and produce F⁻ rich layer between the oxide and metal substrate. The last but not the least, the chemical dissolution can attack and etch the surface and/or the inner part of oxide, which has a significant effect on the shape of the synthesized nanostructure.

Dong et al. reported that the anodic TiO_2 nanotube mouth could be excessively corroded to produce the nanowires morphology if the anodic TiO_2 exposed to the electrolyte for a long time. However, the regular TiO_2 nanotube would not be fabricated if the dynamic equilibrium was broken. A compact anodic TiO_2 layer could be fabricated if the oxidation rate exceeded the dissolution rate due to the intrinsic insolubility of the synthesized oxide layer, while the electropolishing may happen when the oxide layer was soluble in the anodization electrolyte.
The growth of TiO$_2$ nanotubes can be vividly revealed by the current-time curve as shown in Figure 1.6. The whole process has three distinct stages. At the beginning, the current decreases sharply with the prolonging reaction time. It can be ascribed to the formation and thickening of an initial compact oxide layer, which exhibits the high electrical resistance. An obvious rise of current can be found following the decreased trend. At this stage, the compact oxide layer is corroded by the etching component in the electrolyte under the electric field. Small etching pores start to show up on the surface of the compact oxide layer and increase the conductivity of the whole layer. Then the oxidation and dissolution process gradually achieve an equilibrium state and the current does not change a lot at the final stage, which leads to the continuous growth of tube shape. As for the detailed explanation on the tubular or porous shape formation of anodic TiO$_2$ and Al$_2$O$_3$, a plausible theory about oxide volume expansion, resulting stress and critical field strength has been proposed.$^{144-146}$
1.4.2 Influencing factors

Fabrication of self-organized transition metal oxide nanostructures with homogeneous morphology depend on several key anodization parameters, including the electrolyte composition, current density or potential, temperature and duration time.

1.4.2.1 Electrolyte composition

The morphology of anodic TiO$_2$ nanostructures is highly dependent on the electrolyte conditions, including the type of the solvent, concentration of etching component, pH value and the water content. It is well known that the electrolyte for Ti anodization has evolved through four generation. The first generation of the electrolyte is mainly the aqueous based electrolytes together with different acids, such as hydrofluoric acid, sulphuric acid and phosphoric acid. The great improvement of anodic TiO$_2$ nanostructure was achieved through adopting the second generation of electrolyte-buffered electrolyte, in which the pH value was adjusted to around 3-5 by adding the NaOH or citric acid. The solvent of the third generation changed from aqueous solution to the polar organic electrolytes. The mobility of reactant was reduced with the help of organic-based electrolyte with high viscosity, which slows down the reaction rate and smooth the morphology. However, due to the environmental
consideration and safety issues of the electrolyte containing F–, the fourth generation electrolyte has been developed. The TiO2 nanotube bundles were prepared by anodization in a perchloric acid solution.155 In addition, the aqueous hydrochloric acid and hydrogen peroxide were able to produce anodic TiO2 nanotube,156-158 but the thickness of the as-prepared TiO2 layer is limited.

Similar to the TiO2, both the aqueous-based electrolyte and organic based electrolyte were investigated to produce uniform self-organized WO3 nanostructures. However, the morphology control seems not as easy as that for TiO2 anodization, which could be ascribed to the fast dissolution rate of WO3. Grimes et al.159 first reported that nanoporous WO3 could be prepared through anodization in oxalic acid. Different kinds of aqueous based and organic based electrolytes have been tried to increase the uniformity and thickness of WO3 layer.160-162 The common anodic WO3 shape reported was nanoporous structures with wide pore size and limited layer thickness as seen in Table 1.2.

Table 1.2 Various electrolyte conditions for WO3 anodization

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Power</th>
<th>Time (h)</th>
<th>Morphology</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous electrolyte</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2 wt.% NaF</td>
<td>60V</td>
<td>0.5</td>
<td>Nanoporous</td>
<td>Tsuchiya163</td>
</tr>
<tr>
<td>0.25M oxalic acid</td>
<td>6.5-8 mA/cm²</td>
<td>0.5</td>
<td>Nanoporous</td>
<td>Mukherjee159</td>
</tr>
<tr>
<td>1M Na2SO4 + 0.5 wt.% NaF</td>
<td>50V</td>
<td>0.5</td>
<td>Nanoporous</td>
<td>Li164</td>
</tr>
<tr>
<td>1M H2SO4 + 0.5 wt.% NaF</td>
<td>40V</td>
<td>1</td>
<td>Nanoporous</td>
<td>Berger162</td>
</tr>
<tr>
<td>0.3 M oxalic acid</td>
<td>35V or 55V</td>
<td>1-4</td>
<td>Nanobowl</td>
<td>De Tacconi165</td>
</tr>
<tr>
<td>0.2 wt.% NaF + 0.3 wt.% HF</td>
<td>60V</td>
<td>1</td>
<td>Nanoporous</td>
<td>Guo166</td>
</tr>
<tr>
<td>H3PO4+8M HF</td>
<td>40V</td>
<td>0.1-2</td>
<td>Nanoporous</td>
<td>Yang167</td>
</tr>
<tr>
<td>Molten ortho-phosphoric acid</td>
<td>5V</td>
<td>1</td>
<td>Nanochannel</td>
<td>Altomare168</td>
</tr>
<tr>
<td>Organic electrolyte</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.15M NH4F/glycerol</td>
<td>20-35V</td>
<td>5-10</td>
<td>Nanoholes</td>
<td>De Tacconi165</td>
</tr>
<tr>
<td>0.5 wt.% NH4F/ethylene glycol</td>
<td>20-60V</td>
<td>1</td>
<td>Nanoporous</td>
<td>Zheng169</td>
</tr>
<tr>
<td>0.5g NH4F/ethylene glycol</td>
<td>10V</td>
<td>1.5</td>
<td>Nanoporous</td>
<td>Ou161</td>
</tr>
<tr>
<td>Anhydrous 10 wt.% K2HPO4/Glycerol</td>
<td>50V</td>
<td>6-24</td>
<td>Mesosponge</td>
<td>Lee170</td>
</tr>
<tr>
<td>NMF, DMSO and DMF</td>
<td>40V</td>
<td>48-72</td>
<td>Worm-like nanostructure</td>
<td>Cristino171</td>
</tr>
<tr>
<td>0.2M NH4NO3/ethylene glycol</td>
<td>10</td>
<td>0.6</td>
<td>Nanochannel</td>
<td>Wei172</td>
</tr>
</tbody>
</table>
Compared to the TiO$_2$ and WO$_3$, the processing window for anodic ZnO is relatively narrow due to the amphoteric nature of ZnO. In terms of acidic electrolytes, the formation of ZnO stripe arrays and nanosheet could be observed on the surface of Zn foil after anodization. Ng et al.\textsuperscript{173} successfully fabricated ZnO nanostripes via anodization method in the electrolyte of the acidified ethanol. Sung et al.\textsuperscript{174} prepared polygonal nanoflakes perpendicular to the surface of ZnO through anodization of Zn in ethanolic H$_2$SO$_4$. Flake-like nanostructures were also obtained in H$_3$PO$_4$, HCl and HNO$_3$ solution\textsuperscript{175}. Therefore, it can be presumed that the chemical etching dominates in the formation of strip arrays introduced by preferential etching of crystal orientation of original foil, while acid ions contribute to the nanosheet formation with the help of electrical power. The speculation can be confirmed by the fact that nanosheets and sunflower shape were synthesized in (NH$_4$)$_2$SO$_4$ and NH$_4$Cl solutions without H$^+$.\textsuperscript{176} Moreover, Zn anodization in F$^-$ ion containing electrolyte was able to give birth to nanowires, indicating the special etching behavior of F$^-$ during anodic ZnO growth.\textsuperscript{177,178}

As for the alkaline electrolytes, the fabrication of ZnO nanoplates\textsuperscript{179} and nanoparticles\textsuperscript{180} has been reported. Recently, the porous ZnO film composed of straight cells were fabricated in 0.1 M NaOH aqueous solution with the addition of the ethylene glycol, which might be attributed to the dissolution of amorphous oxide or hydroxide during the anodization process.\textsuperscript{181} Different alkaline solution were also tried as the anodization electrolyte, but only the corrosion of zinc substrate was found.\textsuperscript{182}

1.4.2.2 Anodization voltage

As discussed above, the formation of self-organized TMO nanostructure derives from the competition of field-assisted oxidation, dissolution and chemical dissolution
process. The applied voltage determines the electric field across the barrier oxide layer, which not only accelerates the oxidation reaction by driving more oxygen-containing agents to the metal substrate but also promote the dissolution of the synthesized metal oxides. The immediate consequent of the increasing anodization voltage is that the time of reaching dynamic equilibrium during anodization reaction will be shortened.\textsuperscript{169}

As shown in Figure 1.7, the inner diameter of the anodic TiO\textsubscript{2} nanotubes has a linear relationship with voltage, while the thickness of TiO\textsubscript{2} layer has a different trend. Excessively high anodization voltage may cause the micro-arc oxidation of Ti and produced the porous TiO\textsubscript{2} film with micro-sized holes.\textsuperscript{183} On the other hand, Ti anodization in the acidic electrolytes under too large anodization voltage would permanently dissolve the formed oxide layer and eliminate the tubular shape.\textsuperscript{184}

As for the anodic WO\textsubscript{3}, the nanostructures gradually evolved from nanoholes to hexagonal pore and finally formed the nanoporous structures with increasing voltage.\textsuperscript{50} The oxide layer thickness and pore size of anodic WO\textsubscript{3} nanochannel also increase with the rise of the voltage.\textsuperscript{168} The high voltage applied during Zn anodization leads to the formation of dense and thick ZnO nanostructure,\textsuperscript{175} while it also produced irregular shape due to the fast dissolution and severe oxidation.\textsuperscript{174, 185} In addition, the voltage also has an effect on the etching mechanism of Zn anodization. It was demonstrated that H\textsuperscript{+} ions contributed to the dissolution process at a low potential, whereas anions play an important role in dissolution at high potential.\textsuperscript{174}
1.4.2.3 Temperature

The temperature of electrolyte generally affects the dissolution rate of the as-formed TMO nanostructures. At low temperatures, the mobility of the etching component was suppressed, resulting in the moderate dissolution rate, while the viscosity of the electrolyte decreased at high temperatures, leading to the fast movement of the etching agent and irregular oxide structures. The diameter of the anodic TiO$_2$ nanotubes was independent of temperature in the aqueous electrolyte, but it increases with the temperature in the organic solution due to the fast dissolution rate.\textsuperscript{187} It has also been reported that the desired Ti anodization temperature is between 0 and 40°C. Only non-uniform TiO$_2$ nanotubes could be formed at the temperature above 40°C in the glycerol electrolyte, which did not exhibit good mechanical properties.\textsuperscript{188}

Recently, a report indicated that the elevated electrolyte temperature effectively improved the morphology of anodic WO$_3$.\textsuperscript{189} In the phosphoric electrolyte, high-temperature of ~100°C was necessary to produce mesoporous or nanochannel WO$_3$.\textsuperscript{168, 170} Lee 	extit{et al.}\textsuperscript{171} stated preheating procedure is essential to produce mesoporous WO$_3$ and layer thickness increased with electrolyte temperature.
As for the Zn anodization, the influence of the temperature is different depending on the pH of electrolyte used. For acidic electrolytes, the temperature only worked for Zn anodization under low voltage, while it can be ignored under high voltage.\textsuperscript{175} In the alkaline solution, the situation is complicated. The temperature did not have a significant influence on nanostructures obtained in NaOH electrolyte at 1 V, but the reduction of temperature resulted in an almost featureless surface under 40 V.\textsuperscript{175} However, Hu et al.\textsuperscript{185} found that high reaction temperature did not promote the formation of nanowire, and the well-ordered nanowire arrays were observed at a low temperature.

1.4.2.4 Duration time

The identification of the optimized anodization duration should be based on the determination of the other anodization conditions, including electrolyte, potential and temperature. Generally, the morphology and thickness of anodic nanostructures improve with the anodization time. Short time always produces the immature nanostructures, such as small pore size and thin oxide layer, while the prolonged duration could also have the possibility of over-etching. As for the TiO$_2$, The dynamic equilibrium of the oxidation and dissolution can be reached within 2 h in the aqueous electrolyte and the as-synthesized oxide layer would not be longer than a few micrometers.\textsuperscript{153} The reaction process in the organic electrolyte is much slower due to the high viscosity of solution, but it is possible to prepare TiO$_2$ nanotubes as long as 1000 μm.\textsuperscript{190} The influence of the time for WO$_3$ and ZnO is almost the same with that of TiO$_2$.\textsuperscript{170, 191-193}

1.5 Modification of anodic metal oxide

Despite the anodic TiO$_2$, WO$_3$ and ZnO with 1D nanostructures exhibit various desirable properties, the modification of these semiconductors can overcome some of their intrinsic drawbacks,\textsuperscript{194, 195} such as fast recombination rate of photo-generated
charge carriers and limited visible light absorption, as well extend their applications. The modifications are usually conducted by: 1) heat treatment, 2) doping with other element, and 3) decoration with semiconductors.

1.5.1 Heat treatment

As the anodic oxides formed by anodization have the amorphous structure that exhibits poor performance due to the disordered atomic arrangement, post heat treatment is designed to heal these defects and tailor electronic structure to improve their properties. The transformation of TiO$_2$ from amorphous to crystalline anatase phase started around 280°C, while the rutile phase appeared at annealing temperature above 450°C with complete transformation around 800°C. Besides, the post annealing has a significant effect on the chemical composition of anodic TiO$_2$ prepared in the F$^-$ containing electrolyte. It could help remove the F$^-$ ions substituted in the TiO$_2$ lattice structures at the temperature between 300 and 600°C and even create the oxygen vacancy in the oxygen-deficient atmosphere, which improves the light absorption and electrochemical activity. Besides the conductivity of TiO$_2$ layer increased with the formation of anatase phase, deterioration of conductivity occurs in the presence of rutile phase.

The WO$_3$ annealed at 400°C exhibited obviously larger photocurrent than the nonannealed sample. The crystallinity of anodic WO$_3$ increased with the annealing temperature. However, the performance of WO$_3$ did not have a positive relationship with the crystallinity as Charlene et al. stated that WO$_3$ annealed at 400°C showed higher photoelectrochemical property than that at 600°C.

As for ZnO, thermal annealing had a significant effect on the structure rather than the morphology. Since the crystalline phase and exposed facets did not change a lot at the different annealing temperature, the difference of photocatalytic activity of ZnO
should originate from different crystalline degree and defects. Kwok et al. reported that the post-annealing was an effective way to improve crystalline quality and optical properties due to the decrease in the surface defects. Therefore, appropriate selection of the heat treatment conditions, such as the temperature (heating or cooling rate), atmosphere and time, are important for tuning the performance of TMO.

1.5.2 Doping

Doping with non-metal or metal elements into the oxide lattice structure has been extensively investigated during the past two decades. It is a versatile technique to achieve bandgap engineering of TMO by introducing an impurity element with shallow energy level, which prevents the charge carrier recombination and enhances the light absorption (Figure 1.8). The nitrogen doped TiO$_2$ could be easily prepared by anodizing Ti in the organic electrolyte containing the nitrogen precursor. The multiple doping of N, C and Ni into TiO$_2$ could also be made through the one-step anodization in the electrolytes that contains K$_2$[Ni(CN)$_4$], which exhibit the ten times larger photocurrent density than the undoped TiO$_2$. However, the N-WO$_3$ could not be synthesized directly through anodization. The subsequent thermal treatment of anodic WO$_3$ with ammonium hydroxide was required, resulting in the reduced bandgap and enhanced oxygen evolution property.

As for ZnO, there are few literatures discussing the method for doping anodic ZnO, which might be due to its instability. But the metal and non-metal doped ZnO could be fabricated through other techniques, such as electrodeposition and vapour transport oxidation.
1.5.3 Decoration

Another promising modification method is decorating the TMO nanostructures with noble metal nanoparticles, which have the two main functions in improving the properties of modified TMO:\(^\text{212}\)

1. Surface plasmon resonance. The metal nanoparticles have the surface plasmon resonance effect under the illumination of light with proper wavelength due to the induced enhanced electric field. The photoexcited electrons with sufficient energy around the metal particles may transfer and react with electron acceptors, which enhance the photocatalytic or photoelectrocatalytic properties.

2. Schottky barrier. Due to the large work function, the Schottky barrier is formed at the metal nanoparticles and metal oxide interfaces. This solid-state junction promotes the charge separation and prolongs the lifetime of photo-generated charge carriers. The Au decorated TiO\(_2\) nanotube arrays were reported as efficient photoelectrode,\(^\text{213}\) recyclable sensor\(^\text{214}\) and direct alcohol fuel cells.\(^\text{215}\)

However, the decoration of anodic WO\(_3\) and ZnO has rarely been reported. Except for the metal particles decorations, the semiconductors could also be used to improve
the TMO properties through the formation of the heterojunction and changing the band bending.\textsuperscript{147}

![Diagram](image.png)

Figure 1.9 (a) Schematic illustration of fabricating single catalytic particles embedded in self-organized TiO\textsubscript{2} nanotubes; (b) SEM images of Au catalyst nanoparticles.\textsuperscript{216}

1.6 Research objectives

The transition metal oxides with 1 D nanostructure, especially the TiO\textsubscript{2}, WO\textsubscript{3} and ZnO, have attracted much attention due to their wide applications in photocatalysts, sensors, electrochromic devices, and supercapacitors. Electrochemical anodization is a versatile and cost-effective way to prepare self-organized nanostructures of these transition metal oxides. According to the literature review, although a number of excellent works have been performed with respect to the anodization preparation, modification and applications, relatively little work discusses the questions as follows:

(1) Effect of Ti substrate pretreatment and electrolyte aging on the Ti anodization

Two-step anodization is a simple and effective way to produce well-aligned TiO\textsubscript{2} nanotubes. The first anodization acts as the pre-treatment process and produces concaves on Ti substrate that guide the growth of TiO\textsubscript{2} in the second stage of anodization. However, the evolution process from etching pits to nanotubes inside the
concave is not clear. The aging treatment has a significant influence on the electrolyte conductivity and thus affects the reaction rate during anodization. But the research on the changes of mechanical property induced by using the aging electrolyte has been rarely conducted.

(2) The crystallization process of TiO\textsubscript{2} during the post-annealing treatment.

Generally, the anodic TiO\textsubscript{2} fully transforms from amorphous to anatase phase when annealed at \textasciitilde450\textdegree C. But the onset temperature and the completion time of the phase transformation still need to be studied. Besides, the dynamic crystallization process of TiO\textsubscript{2} during annealing should also be paid attention to, because it may has a close relationship with the formation of deficient TiO\textsubscript{2}.

(3) The effect of TiO\textsubscript{2} crystallinity on the electrodeposition behaviour of Ni

Recently, filling the anodic TiO\textsubscript{2} nanotubes with metals has been extensively studied due to its potential applications in energy storage and electrical device. The electrodeposition technique is a simple and fast way to obtain this kind of hybrid nanostructure. However, the deposited metals may enter the inside of annealed TiO\textsubscript{2} tubes, as well as stacking and aggregating into dense layer on the top of amorphous TiO\textsubscript{2}. The mechanism of the different electrodeposition behaviour between the amorphous and annealed TiO\textsubscript{2} is not fully understood.

(4) Photocatalytic activities of TiO\textsubscript{2} enhanced by Cu nanoparticles

TiO\textsubscript{2} has been exploited as the leading photocatalyst. During the past decades, the photocatalytic performance of TiO\textsubscript{2} has been improved by decoration of various noble metals nanoparticles, including Au, Pt and Ag. The common method of decorating noble metals, such as photoreduction and atomic layer deposition, may not produce the well-dispersed metal nanoparticles. Compared to the noble metals, Cu is a conventional metal that has proper work function and low cost. The uniform deposition and
distribution of Cu nanoparticles can be achieved by magnetron sputtering and thermal
dewetting. But the photocatalytic property of this Cu/TiO$_2$ has rarely been reported.

(5) Research on the electrochemical anodization of WO$_3$ and ZnO

Compared to the anodic TiO$_2$, the successful preparations of WO$_3$ and ZnO with
the 1D nanostructures, such as nanoporous, nanoroads and nanotubes, through
anodization were seldom reported. The anodic WO$_3$ prepared in the aqueous electrolyte
reported so far were partially ordered. Although the WO$_3$ with nanochannel structure
was obtained in the phosphoric electrolyte, the high temperature of $\sim$100°C was required.
As for the ZnO, only the nanoparticles, nanoplate, nanoflake or nanoflower shapes were
synthesized through anodization. It is interesting to conduct research to see if we can
produce anodic WO$_3$ and ZnO with 1D nanostructure under the common conditions.

1.7 Thesis framework

The thesis is structured based on the questions in above Section 1.6:

Chapter 1 firstly introduces the research background of transition metal oxides,
followed by the detailed information of the subjects in this thesis of TiO$_2$, WO$_3$ and
ZnO, including their crystal structure, electronic structure and applications. Then the
common preparation methods of TiO$_2$, WO$_3$ and ZnO are discussed, and the techniques
adopted in this thesis are further described, such as the electrochemical anodization,
heat treatment, and metal decoration.

Chapter 2 discusses the effect of different pre-treatment methods of Ti substrate
on the morphology of anodic TiO$_2$. And the mechanism of nanostructure evolution
during two-step anodization is proposed. In addition, the mechanical and tribological
properties of TiO$_2$ synthesized in different aging electrolytes are characterized through
Nanoindentation.
Chapter 3 illustrates the dynamic change of crystallinity, crystal size and even the lattice parameters through *in-situ* synchrotron X-ray diffraction technique, which reveal the formation mechanism of the oxygen-deficient black TiO$_2$.

Chapter 4 investigates the effect of crystallinity on the platability of TiO$_2$ NTs and proves the electroplating technique is a feasible method to modify TiO$_2$ nanotube arrays with metals. The formation mechanism of the different deposited Ni nanostructure is discussed based on the conductivity and wettability test. The application of the hybrid Ni-TiO$_2$ nanocomposites as a catalyst for oxygen production is also explored.

Chapter 5 describes that the combination of magnetron sputtering and thermal dewetting is a novel method of uniformly depositing Cu nanoparticles on the anodic TiO$_2$ nanotube arrays. The photocatalytic activity of modified Cu-TiO$_2$ nanocomposites is characterized by decomposition of methylene blue dye solution under the simulated solar light.

Chapter 6 presents a comprehensive study of tungsten anodization, including the effect of temperature, water content, voltage, fluorine ions and anodization duration time. The obtained nanoporous WO$_3$ are modified with Ag nanoparticles and tested as an efficient SERS substrate for organic pollutant detection.

Chapter 7 studies the possibility of using aqueous NaOH solution as the electrolyte for Zn anodization. Different electrolyte concentration and voltages are tested to find the optimal conditions. In addition, the optical properties of anodized ZnO nanorod are measured.

Finally, Chapter 8 presents the conclusions and future research work.
CHAPTER 2

Effect of pre-treatment on TiO$_2$ nanotube by Anodization

The technological processes of electrochemical anodization could be classified into three parts: pre-anodization process, anodizing process, and post-anodization process. In the past few decades, the anodizing process of Ti anodization has been studied, including electrical loading mode (constant current, constant voltage or different current/voltage profile), electrolyte composition, and anodization temperature and duration time. Recently more attention has been put on the post-anodization, such as modification of anodic TiO$_2$ with different materials and self-doped oxygen vacancy. However, there is little research on the pre-anodization process. In this chapter, the studies on the influence of pretreatment of Ti foil and electrolyte were conducted to fill this research gap.

* This chapter is partially based on a journal paper published in International Journal of Modern Physics B:
CHAPTER ABSTRACT

TiO₂ nanotube arrays (NTs) were prepared through conventional electrochemical anodization on Ti substrates with different pretreatments or in the electrolyte of different aging times. The as-received, electropolished and patterned Ti substrates were adopted to illustrate the effect of Ti surface conditions on the as-anodic TiO₂ morphology. The anodization of spare Ti foils was performed with different durations to age the electrolytes. The dependence of morphology, mechanical and tribological properties of the as-synthesized TiO₂ on aging time was studied. The results indicated that the regular TiO₂ NTs with the hierarchical lotus root shape was produced on the patterned Ti substrate, which has a better surface topography than that on the as-received and electropolished Ti.

Although the regularity of TiO₂ NTs improved a lot with the increase of aging time, the single pore size decreased as well as the surface homogeneity. The nanohardness and reduced modulus showed the obvious increase with the aging time from 0.01 GPa to 2.17 GPa and 4 GPa to 62 GPa, respectively. The highest adhesion between TiO₂ and Ti substrate was achieved by anodizing in the 25 h aging electrolyte with delamination force of ~750 μN. Based on the morphology and mechanical properties of anodic TiO₂ NTs, optimal pretreatment conditions for Ti anodization are the combination of patterned substrate prepared by two-step anodization and the aging electrolyte of 25 h.

2.1 Introduction

Due to the wide band gap and good chemical stability, titanium dioxide (TiO₂) has been widely investigated as a promising material for photochemical applications. Recently TiO₂ nanotubes (NTs) with high-aspect-ratio and precisely controlled
morphology have attracted tremendous attention. So far several techniques are
developed to fabricate ordered TiO$_2$. Among these, electrochemical anodization is a
simple and convenient way to produce regular NTs.

Much efforts have been made to improve the regularity of anodic TiO$_2$ NTs,
including optimizing key anodization conditions and introduction of imprint moulds.
Focused ion beam lithography and nanoimprint lithography are two patterning
techniques to create periodic patterns on Ti surface for highly ordered anodic TiO$_2$ NTs.
While these methods are highly controllable to create patterns, the main shortcomings
are low efficiency and high cost. Compared to these techniques, two-step anodization is
an effective way to produce highly-aligned TiO$_2$ NTs. This technique has been studied,
but little research was carried out on the mechanism of anodic nanostructure evolution
during process.

Except for the pretreatment of the Ti substrate before anodization, it is well
known that the morphology of self-organized TiO$_2$ is closed related to the electrolyte
age. The fresh electrolyte was reported to produce the nanotube arrays with high
length to width ratio, while aging electrolyte only gave birth to the one with low aspect
ratio. S. Li et al. stated that the aging duration has an effect on the formation of
concave rings outside TiO$_2$ tube walls. Not only the topography but also the imprint
pattern left by first anodization was also influenced by the aging time.

Although various TiO$_2$ nanostructures were developed according to different
applications, the mechanical properties, especially the adhesion between TiO$_2$ layer
synthesized and Ti substrate, have always been neglected. K. Gulati et al. first discussed
the stability of anodic oxide layer prepared on Ti wires, but only the qualitative analysis
was given based on the visual cracks number or delamination.

In this work, we report the effects of different surface treatment of Ti substrate
and aging electrolyte on the TiO$_2$ morphology. The mechanical and tribological properties were also characterized through Nanoindentation and Nanoscratch tests. All these results may provide an idea of fabricating the anodic TiO$_2$ layer with regular shape and good mechanical property.

2.2 Experimental section

Prior to anodization, all Titanium (Ti) foils were ultrasonically cleaned in DI water for 5 min. There are three types of Ti foils with different pre-treatment procedures employed in the anodization experiments, as-received Ti foils, electropolishing Ti foils and patterned Ti foils. The electropolished Ti foils were prepared in electrolyte with glacial acid and perchloric acid (volume ratio of 9:1) under 40 V. As for the patterned Ti foils, two-step anodization technique was adopted. The as-received Ti foils were used as anode with Ti mesh as cathode at a distance of 3 cm in a two-electrode cell. The first anodization was performed at in the ethylene glycol base solution with 0.25 wt.% NH$_4$F and 2 vol.% DI water under 60 V for 10 h. Then the as-formed TiO$_2$ layers were peeled off, leaving Ti foil with ripples for the second-step anodization.

All the Ti foils were anodized at 60 V for 60 min in the electrolyte with the same composition as above. In order to further investigate the formation mechanism of patterned anodization, the etching pits behaviour was studied through anodization on polished Ti foils under voltages between 60 and 90 V for 1, 3 and 5 min. The nanostructure evolution process was simulated through a Finite Element Method (FEA) using Matlab according to the theoretical model proposed by Cheng et al..

The “Age” of electrolyte refers to the anodization duration of electrolyte prior to the formal experiment. Before the initiation of anodization, the electrolyte was “aging” for 0 h, 10 h, 25 h, 55 h and 73 h, respectively at 60V in in ethylene glycol containing 0.25 wt.% NH$_4$F and 2 vol.% DI water. Then as-formed TiO$_2$ layers were peeled off.
ultrasonically and Ti foils were used for anode in second anodization in the aging electrolyte at 60 V for 3 h. The obtained TiO₂ layer was washed in distilled water and ethanol for the characterization.

Nanoindentation and nanoscratch tests were conducted using a Hysitron TI950 Triboindenter to evaluate the mechanical and tribological properties of TiO₂ NTs. Two types of depth controlled load-function were used in the nanoindentation to avoid the influence from Ti substrate, which are 10% of TiO₂ layer thickness and a constant depth of 500 nm, respectively. The load-displacement curves were recorded to calculate the nanohardness and reduced modulus. The nanoscratch was performed with the normal load increasing from 0 to 2000 μN. The delamination was determined based on the analysis of scratch depth, friction coefficient and friction force.

2.3 Results and discussions

2.3.1 Effect of Ti foil surface on the anodized TiO₂ nanotube arrays

Morphologies of anodic TiO₂ NTs on different Ti substrates were shown in Figure 2.1. The rough Ti substrate gave birth to the non-uniform arrangement of TiO₂ nanotubes (Figure 2.1a). Texture of the as-received Ti might guide the nanotube formation during anodization, resulting in the regular distribution of the nanopores in one area, while randomly allocated nanopores in other area. Compared to the untreated Ti substrate, the polished one produced more regular nanotubes (Figure 2.1b).

Although the shape of tubes was neither round nor hexagonal, the regularity improved a lot. Hierarchical lotus root nanostructures with cells shape around the tube mouth and small pores inside were fabricated on the patterned Ti substrate (Figure 2.1c). The morphology difference could be attributed to the electric field distribution (EFD). The formation of TiO₂ is a dynamic equilibrium process between oxide formation and dissolution assisted by electrical field. The unpolished Ti foil had the rough surface and
resultant non-uniform EFD, leading to the different growth rate of TiO₂ NTs on the surface. Electropolishing helps equalize the difference and ensure uniform growth over the surface. However, the patterned Ti caused EFD to focus at bottom of ripples, acting as preferential pore formation centre. From the length variation in Figure 2.1 inset, it could be found that the polished Ti produced thicker oxide layer than untreated and patterned substrate. Although the polished Ti could produce uniform nanotubes and thick oxide layer, it is not applicable for massive production due to the poor repeatability and the strong acid involved.

The electrochemically etched pits with different anodization voltages and durations were shown in Figure 2.2. Small etching pits with the size of ~30 nm nucleated are randomly distributed on the surface with irregular shape (Figure 2.2a). With prolonging the time, these pits expanded until they met each other with the size increased to ~58 nm (Figure 2.2b). However, the density of etched pits did not change much. The etching process under different voltages is similar to that under 90 V as shown in Figure 2.2c. The nanopore size increases with time and voltages, while the pore number fluctuates between 11 and 14 in an arbitrary line with the length of 1 µm. Therefore, it can be concluded that the anodization voltage and time affect growing rate.
of the etching pores rather than the pore density.

Figure 2.2 Etching pits on polishing Ti substrate at 90V for: (a) 1min, (b) 5min and (c) Nanopore size and nanopore numbers with different anodization voltage and duration time.

The etching pits density basically remained unchanged during reaction on flat substrate, but the case is not the same on the patterned substrate. The hierarchical TiO₂ nanostructures with porous structure atop and tubular shape formed underneath were produced as shown in Figure 2.3. The size of porous cells matched well with that of imprints left by first anodization. Inside each cell, it could be found that a few of nanotubes were developed and each small pore corresponds to one tube. Compared to the polished Ti foil, the patterned substrate produced smaller pores with larger pore density (Figure 2.3a). In addition, these small pores gradually emerged into the wider pores as the anodization progresses (Figure 2.3b).

Figure 2.3 Hierarchical morphologies of TiO₂ by two-step anodizing at 90 V with: (a) 15 min, and (b) 60 min.
It is known that three processes compete with each other and contribute to the formation of TiO$_2$ NTs: field-assisted oxidation, field-assisted dissolution and chemical dissolution.$^{14}$ As the dimples created by first anodization have the curved shape, current and electric field are prone to have the local concentrated distribution at the tube bottom as shown in Figure 2.4. The fluoride ions (F$^-$) tend to immigrate to the electrolyte/oxide interface, dissolve the formed oxide layer and release the [TiF$_6$]$^{2-}$ anion back to electrolyte in the central areas of dimples, which is illustrated by the current distribution in Figure 2.4a. The large current would directly lead to the fast dissolution and form small pores (3-4 per ripple) in this region, which is consistent with the pores formation shown in Figure 2.3a.

Due to the highly effective voltage distributed at the oxide/metal interface shown in Figure 2.4b, the oxygen-containing ions are driven to deep tube bottom, where oxidation occurred exclusively. As the anodization reaction went on, the synthesized nanotubes inside the ripples leaned on each other at certain angle rather than parallel distributed. The tube walls could be thinned and joint point at the bottom would be penetrated because of the chemical dissolution effect, resulting in the emerging of the neighbouring nanotubes into large pores (Figure 2.3b). Similar results were also reported in the formation of multipodal TiO$_2$ nanotubes.$^{15}$
Figure 2.4 Simulation of current density and voltage during electrochemical anodization.

2.3.2 Effect of electrolyte aging time on the anodized TiO$_2$ nanotube arrays

The influence of aging electrolyte on the TiO$_2$ NTs morphology can be found in Figure 2.5. The irregular TiO$_2$ surface composted of tangled nanowires was produced in the fresh electrolyte (Figure 2.5a). However, the uniformity improved a lot when the electrolyte aged for 10 h and 25 h. When the aging time exceed more than 55 h, the nanoporous size was significantly reduced and the surface condition was not homogenous from visual inspection (Inset in Figures 2.5 d and 2.5e).

The morphology difference between aging time could be revealed by the current density (CD) during anodization (Figure 2.5f). CD of all the aging electrolyte exhibit typical I-t relationship for TiO$_2$ NTs formation. The fast CD decay can be ascribed to the initial oxide layer formation. Small etching pits then appear and evolve into pores after the CD achieving the lowest point. Finally, the CD falls back to a constant value, indicating the extension of the regular nanotube. However, the final CD values of different aging time deviated greatly from each other and decreased with the increase of aging time.

It was reported that both water and F$^-$ in the electrolyte were consumed with prolonging reaction time. The water provides not only hydroxyl ions for the oxidation of Ti but also the H$^+$ for dissolution of TiO$_2$, while F$^-$ contributes to the formation of soluble [TiF$_6$]$^{2-}$ ions.$^{12}$ This directly leads to the reduced conductivity of electrolyte. Therefore, the potential drop caused by the electrical resistivity of electrolyte becomes more obvious, resulting in the decrease of voltage applied on the anode and the produced CD.

Due to the moderate content of H$^+$ and F$^-$, the excessive chemical dissolution of tube mouth (Figure 2.5a) was suppressed and the uniform porous nanostructure were
obtained. However, the effective potential and reaction ions were too low to produce thick oxide layer with large pore size, leading to the formation of narrowly etched nanoholes. The oxide layer produced in 73 h aging electrolyte was not even enough to fully cover the foil surface (Inset in Figure 2.5e).

Figure 2.5 SEM images of anodized TiO$_2$ NTs in different electrolyte: (a) Fresh, (b) 10 h aging, (c) 25 h aging, (d) 55 h aging and (e) 73 h aging; (f) Current density VS time curve.

The anodic TiO$_2$ produced in the aging electrolyte showed enhanced mechanical properties compared to that in fresh electrolyte as shown in Figures 2.6a and 2.6b. For both 10% depth and 500 nm loading function, the nanohardness increased significantly from 0.01 GPa to 2.17 GPa with the aging time. The reduced modulus also had the similar change, while it showed a declined trend when aging time was longer than 55 h. Moreover, the results obtained through the 500 nm controlled and 10% depth-controlled loading mode were quite close to each other, indicating that the mechanical properties of anodic TiO$_2$ are consistent along the depth direction.

As seen from the Figure 2.5a, the surface of TiO$_2$ was covered by the excessive etched TiO$_2$ tubes with “nano-whiskers” shape. It is common that this loose structure
had poor mechanical property. With the increase of aging time, the morphology of synthesized nanotube becomes more uniform without collapsed tube debris, which were mechanically stable and had the acceptable performance. When the aging time was too long, the anodic TiO$_2$ exhibited large nanohardness and reduced modulus, which is similar to the bulk materials.$^{16}$ But the nanotubular shape advantage disappeared due to the shrunken pores.

The adhesion is another important property that should be considered for the practical applications of anodic TiO$_2$ layer, because the easy delamination of oxide layer may cause TiO$_2$ particle pollutant and deteriorate the performance. As shown in Figure 2.6c, the critical failure force of anodic TiO$_2$ increased with prolonging the electrolyte aging time then dropped significantly to a low level, indicating that the adhesive strength between TiO$_2$ oxide layer and Ti substrate rose at first and then reduced.

The improved adhesion performance could be attributed to the thick barrier layer produced and the moderate reaction rate in the “old” electrolyte. Due to the fast dissolution of TiO$_2$ inside the nanotubes in the fresh electrolyte, the thinner barrier layer could be obtained with the reduced stability.$^{17}$ In the meantime, good conductivity and high ions concentration of fresh electrolyte lead to the fast oxide formation and dissolution rate and the high residual compressive stress remained in the TiO$_2$/Ti interface.$^{18}$ However, the longer aging time (>25 h) did not induce the further improvement in adhesion, which might be related to the inhomogeneous oxide layer synthesized (inset in Figures 2.5d and e), which would be studied in the future.
2.4 Conclusions

This chapter studies the effect of pre-treatment of Ti foils and anodization electrolyte on the anodic TiO$_2$ morphology. The as-received Ti foil only produces random distributed TiO$_2$ nanotubes, while the regularity of nanostructure prepared on polished and patterned Ti foil improves a lot. This is closely related to the different TiO$_2$ growth rate induced by the electric filed distribution across the surface area. The electrolyte after aging treatment exhibits less water and fluoride content, and lower conductivity. The dissolution rate of synthesized TiO$_2$ and effective potential applied on the anode are decreased in the aging electrolyte, resulting in the formation of TiO$_2$ with smooth topography, narrow pore size and thicker barrier layer. In addition, the mechanical and adhesive properties of TiO$_2$ prepared in the aging electrolyte are also enhanced. Therefore, the patterned Ti foil and the aging electrolyte are the optimized pre-treatment conditions for Ti anodization to produce regular TiO$_2$ NTs with high mechanical property and good adhesion.
CHAPTER 3

Effect of post annealing on TiO$_2$ nanotube by Anodization

Following the studies of the pretreatment of Ti substrate and electrolyte before anodization in Chapter 2, the effect of post annealing was investigated as the first part of “post anodization process” mentioned in Chapter 2. Generally the as-anodized TiO$_2$ NTs have an amorphous structure with poor electrical conductivity and photocatalytic activity, which limits the practical application of anodic TiO$_2$ NTs. Heat treatment after anodization is considered as the essential step to stimulate the potential of anodic TiO$_2$ NTs through re-arrangement of Ti and O atoms. In this chapter, the \textit{in situ} synchrotron X-ray diffraction technique was employed to illustrate the dynamic change of crystallinity, crystal size and lattice parameters, which may help reveal the formation mechanism of the oxygen-deficient black TiO$_2$.

* This chapter is based on a journal paper under submission to: The Journal of Physical Chemistry Letters:
J. Dong; J. Dong, B. Ingham, T. Kemmitt, S. Wei, W. Gao. “Controlling the incomplete crystallization of black TiO$_2$”
CHAPTER ABSTRACT

Anodized black TiO$_2$ is oxygen-deficient and in the form of tubular morphology, which initially has an amorphous structure and crystallizes into anatase after thermal annealing. High resolution transmission electron microscopy and in situ synchrotron X-ray diffraction were employed to study the dynamic phase transformation process and the effect of annealing parameters on the atomic structure. At temperatures above 330°C the crystallization process began immediately and ceased within ~500 s. The material was not fully crystallized (crystallinity only ~70 wt.%), even when the annealing time was prolonged to 7000 s at an elevated temperature. The incomplete crystallization of black TiO$_2$ could be ascribed to the effect of grain boundaries, oxygen vacancies, and fluorine ions, each of which can be controlled by adjusting the annealing conditions. As oxygen-deficient black TiO$_2$ has unique electrical and catalytic properties, this work may provide a new approach to further tune its properties through thermal treatment.

3.1 Introduction

There is increasing interest in the use of nanostructured titanium dioxide (TiO$_2$), especially arrays of TiO$_2$ nanotubes (NTs), in various applications such as environmental technology and energy conversion.$^{1-3}$ Its electronic and catalytic properties are closely related to morphology and crystallinity, which can be controlled by the preparation conditions and subsequent treatment.$^{4-10}$ Simple electrochemical anodization techniques have been used to produce various morphologies such as nano-ribbon and nano-bamboo structures.$^{11}$ Post-treatment methods are then used to tailor the properties of TiO$_2$ for potential applications.

It is well known that as-synthesized anodic TiO$_2$ NTs with amorphous structure
exhibit poor performance due to the intrinsic disordered atomic arrangement of Ti and O. However, when TiO$_2$ NTs are transformed to crystalline state, they have better catalytic and electrochemical activity, higher solar conversion efficiency, faster electron mobility, stronger adsorption ability and are more suitable for biomedical applications than the amorphous phase. These properties are also influenced by the overall degree of crystallinity, crystal phase composition, atomic defects and grain size. The anatase structure is superior to rutile in conducting devices, solar cell applications and photocatalytic activity. In addition to the influence on the electrical and chemical properties of TiO$_2$, crystallinity can also affect its mechanical properties.

As the crystal structure has excellent performance, the methods to induce phase changes in TiO$_2$ have been studied extensively. Crystallisation was observed during anodization at high voltage, for long anodization times or using a hot electrolyte, which could be attributed to the enhanced dissolution of amorphous phase. Crystalline TiO$_2$ can also be formed by simply soaking the material in deionized water for three days, but in this case the tubular shape transforms into nanowires. The most common approach to induce crystallinity is thermal annealing, with anatase being formed at temperatures between 300-500°C. Above 550°C rutile begins to form and the electronic properties decline. Both the annealing temperature and the thermal history (i.e. ramp rates and hold times) have a profound effect on the TiO$_2$ crystallinity and the electronic and catalytic properties. There are significant variations in key aspects of the crystallization process, such as reported onset temperature and degree of crystallization.

The thermal annealing process can affect the type and density of atomic defects. Our group has prepared oxygen-deficient black TiO$_{2-x}$ by an anodization and thermal
annealing process.\textsuperscript{32, 33} Black and oxygen-deficient TiO\textsubscript{2} has attracted much interest since it was synthesized by Chen \textit{et al.} via hydrogen generation under high pressure and high temperature.\textsuperscript{34} The improved photocatalytic performance of their material was due to its unique structure of a crystalline core covered by a reduced amorphous layer.\textsuperscript{34}

In a similar vein, we found that our oxygen-deficient black TiO\textsubscript{2} has unique microwave absorption properties arising from differences in oxygen vacancy concentration across the crystalline-amorphous boundary.\textsuperscript{35} Some other physical and chemical properties, such as optical absorption\textsuperscript{36} and catalytic activity\textsuperscript{37} are also highly dependent on the extent of atomic defects. To understand driving forces behind this, it is necessary to further investigate the black TiO\textsubscript{2-x} from the perspective of atomic defects in its lattice structure.

In this chapter, \textit{in situ} synchrotron X-ray diffraction (XRD) was used to characterize the dynamic crystallization process of anodic TiO\textsubscript{2} NT. The crystallization behaviour of TiO\textsubscript{2} under non-isothermal and isothermal annealing is discussed. The mechanism of incomplete crystallization for oxygen-deficient TiO\textsubscript{2} produced by anodization is proposed. These results will help in design of thermal annealing profiles in order to engineer black TiO\textsubscript{2} and control its properties.

\textbf{3.2 Experimental section}

\textbf{3.2.1 Sample Preparation}

Titanium foils (99.96\%, 0.3 mm thick) were used as anodes in a two-electrode cell with a platinum plate as the cathode. The foils were prepared by polishing to remove the residual oxide film, ultrasonically cleaning in acetone and deionized water, followed by drying in a nitrogen atmosphere. The electrochemical anodization was performed at 60 V with controlled time intervals in an electrolyte of ethylene glycol (99.8\%, Sigma-Aldrich) containing 0.25 wt.% NH\textsubscript{4}F (98\%, Sigma-Aldrich) and 2 vol.% deionized
water. The as-synthesized TiO$_2$ samples were cleaned in distilled water and ethanol to remove residual electrolyte and kept in ethanol for 12 h at room temperature.

3.2.2 Characterization

High-resolution transmission electron microscopy (HRTEM, Philips Tecnai G$^2$ F20, 200 kV) was used to characterise the morphology and lattice structure. The fluorine ion concentration was measured by X-ray photoelectron spectroscopy (XPS, PHI Quantera-II SXM) using monochromatic Al K$_\alpha$ X-rays source with a power of 100 W and pass energy of 20 eV. The C 1s peak at 284.8 eV was used for energy calibration.

3.2.3 Synchrotron measurements

In situ synchrotron X-ray diffraction experiments were conducted at the Powder Diffraction beam line at the Australian Synchrotron. Powder samples were loaded in 0.5 mm quartz capillaries. An Al$_2$O$_3$ crystallinity standard (NIST, certified 91.75%) was thoroughly mixed with the as-synthesized TiO$_2$ before annealing, acting as the reference for calculation of crystallinity.

Measurements were recorded using a Mythen Detector, spanning 80° of arc, with incident X-rays of 15 keV ($\lambda = 0.8262$ Å). Data were collected at two detector positions and stitched together to cover the gaps between detector modules. The non-isothermal experiments were heated from ambient temperature using a Eurotherm hot air blower. For the isothermal experiments a hot air blower was heated to the temperature and then the sample was inserted and measurements begun. Data were collected in a continuous fashion with 30 s exposures (10 s exposures for the experiment conducted with a 50 K/min heating rate).

Full pattern fitting was performed using Topas 4.2 (Bruker). A 5$^{th}$ order Chebyshev polynomial was used, together with three broad peaks, to describe the
background scattering from the quartz capillary. The wavelength and beam shape parameters were determined using a LaB₆ standard (NIST). Al₂O₃ and TiO₂ structural parameters were as follows (at 500°C):

Al₂O₃, $R\bar{3}c$, $a = 4.774$ Å, $c = 13.037$ Å, Al (0, 0, 0.3523), O (0.3064, 0, 0.25)

TiO₂ (anatase), I4₁/amd, $a = 3.799$ Å, $c = 9.544$ Å, Ti (0, 0, 0), O (0, 0, 0.2078)

For Al₂O₃ the fitted parameters were wt.%, $a$, $c$, and Lorentzian crystallite size (4 parameters). For TiO₂, the fitted parameters were wt.% $a$, $c$, O occupancy, O z co-ordinate, O Bₚ, Lorentzian, Gaussian crystallite sizes and strains (10 parameters). The O occupancy did not deviate from 1. The effective crystallite size $D_{eff}$ reported in the main text was estimated numerically from

$$\frac{1}{D_{eff}} \approx 0.5346 \frac{D_L}{D_L^2} + \frac{1}{D_G^2}$$

Eq.3.1

where $D_L$ is the Lorentzian crystallite size and $D_G$ is the Gaussian crystallite size. The surface morphology was studied by a field emission scanning electron microscope (FEI Quanta 200F ESEM). To investigate the wetting properties of the specimens, water contact angles were measured on a goniometer (KSV CAM-101) at room temperature with 3.5 μl water droplets, and analyzed by the built-in program.

3.2.4 Crystallinity Calculation

The method for mass percentage calculation of the TiO₂ amorphous phase is based on an Al₂O₃ standard with known crystallinity (91.75 wt.%). The XRD samples are a mixture of TiO₂ and Al₂O₃, which is made up of up to four components: crystalline and amorphous standard Al₂O₃ (CSA and ASA) and crystalline and amorphous TiO₂ (CT and AT), as shown in Figure 3.1.
For each measurement, 205.3 mg standard Al₂O₃ was added to 575.9 mg as-synthesized anodic TiO₂. The weight percentage of standard Al₂O₃ is calculated as 26.28%. As the crystallinity of the Al₂O₃ standard does not change during annealing, the weight percentage of CSA is 24.11% (91.75%×26.28%). Topas gives the weight percentage of the crystalline phase. The weight percentage of CT (WCT) can be determined from:

\[
WCT = \frac{a \times b}{(1-a)}
\]  
Eq.3.2

where \(a\) is the percentage of crystalline TiO₂ given by Topas, and \(b\) is the weight percentage of CSA (24.11%).

Therefore, the weight percentage of AT (WAT) can be calculated from:

\[
WAT = 1 - 26.28\% - WCT
\]  
Eq.3.3

Finally, the degree of crystallinity of TiO₂ is

\[
\frac{WCT}{(WCT+WAT)} = \frac{WCT}{0.7372}
\]  
Eq.3.4

3.3 Results and discussion

3.3.1 Effect of post annealing on crystal structure

The as-synthesized TiO₂ displayed a tubular morphology with amorphous
structure (Figure. 3.2a). It crystallized to anatase after annealing. TEM images and selected area electron diffraction patterns indicated that heterogeneous TiO$_2$ nanocrystals formed during annealing (Figure 3.2b). While the outside surfaces formed crystals (covered by a thin disordered layer, Appendix Figure S1), the inner parts consisted of both crystalline and amorphous regions (Fig. 3.2c).

![TEM images of TiO$_2$ nanotubes](image)

Figure 3.2 TEM images of TiO$_2$ nanotubes: (a) before and (b) after annealing at 450°C for 1 hour. HRTEM images of (c) partially crystallized TiO$_2$.

The presence of both crystalline and amorphous regions was also reported for calcined titania nanoparticles that were annealed at different temperatures.$^{38}$ In our as-synthesized TiO$_2$, the Ti and O atoms lack any long-range order. Crystallization induced by heat treatment requires diffusion of atoms to the lattice positions, which strongly depends on the annealing conditions. In order to elucidate the influence of annealing on TiO$_2$ structures, real-time *in situ* synchrotron XRD was used to characterize the TiO$_2$ incomplete crystallization process (Appendix Figure S2). To determine the amount of amorphous phase present, an internal Al$_2$O$_3$ crystallinity standard was added in order to perform quantitative analysis using Rietveld refinement.

To determine the crystallization onset temperature, non-isothermal annealing experiments from 25°C to 700°C with two ramp rates (10 K/min and 50 K/min) were performed. For the slow ramp rate, the onset temperature was ~300°C, while for the fast
ramp rate, the onset temperature was ~330°C (Appendix Figure S3). In both cases, the
degree of crystallization increased rapidly above the onset temperature, and the
crystallization process was largely complete by around 350°C. Above this temperature,
the crystalline content increased slightly from 60 to ~70 wt.%. The grain size also
increased rapidly above the onset temperature, reaching a value of approximately 100
nm for 10 K/min ramp and 80 nm for the 50 K/min ramp (Appendix Figure S4).

The lattice parameters changed in a similar way during crystallization for both
ramp rates: the $a$ lattice parameter decreased between 300 and 500°C, then remained
stable until decreasing again at higher temperatures, while the $c$ parameter increased
systematically (Appendix Figure S5). The negative thermal expansion behaviour in the
$a$ direction is not observed in bulk anatase,$^{39}$ but has previously been observed in
anatase nanoparticles, which the authors attributed to surface effects.$^{40}$

Isothermal annealing was conducted at selected temperatures between 300 and
600°C (Figure 3.3a). Crystallization began immediately and was complete within 100 s
at or above 330°C and within 500 s at 300°C. The final degree of crystallinity increased
from 60 to 75 wt.% with increasing annealing temperature, with the exception of the
experiment performed at 300°C. In a similar manner to the non-isothermal experiments,
once the maximum degree of crystallinity was reached, the crystallite size stopped
change (Figure 3.3b). The final crystallite size was smaller at higher temperatures,
reducing systematically from 80 nm at 300°C to ~45 nm at 600°C.
Figure 3.3 Parameters extracted from Rietveld fitting of synchrotron XRD isothermal annealing experiments at various temperatures: (a) degree of crystallinity, (b) crystallite size.

The lattice parameters do not follow the same kinetics with crystallinity and crystal size at the various temperatures studied (Figure 3.4). They exhibit similar behaviour at 300, 330 and 390°C. Both $a$ and $c$ decrease over the first 2000 s, and then tend to be stable. In contrast, at 600°C the $c$ lattice parameter increases with time, while $a$ lattice parameter decreases. Of particular interest is the curve at 500°C, which initially followed the trends for the lower temperature experiments, but after 2500 s deviated towards the values obtained in the experiment performed at 600°C. This suggests that there is an energy barrier corresponding to a temperature of around 500°C, which may be related to the movement of grain boundaries, phase transition, and the stability of atomic defects (e.g. oxygen vacancies, interstitial sites, fluorine dopants), etc.
Figure 3.4 Lattice parameters of crystalline anatase for the isothermal annealing at various temperatures as indicated.

3.3.2 Hypothesis of incomplete crystallinity during post annealing

The crystallization of TiO$_2$ NTs involves nucleation and crystal growth processes, as illustrated in Figure 3.5. The final crystallite size and degree of crystallinity is expected to be limited by the behavior of the grain boundaries. At temperatures above 300°C there is sufficient thermal energy to induce nucleation of crystalline TiO$_2$ within the amorphous region. Zhang et al.\cite{41} and Exarhos et al.\cite{42} reported that the activation energies of anatase nucleation from the amorphous phase for nanoparticles and films are 147 kJ/mol and 142 kJ/mol, respectively. A modified Avrami model was used to understand the crystallization kinetics.\cite{43} The equation has the form:

$$y = M\left(1 - \exp\left(-\left(kt\right)^n\right)\right)$$

where \(y\) is the measured crystallinity, \(M\) is the maximum crystallinity that could be achieved, \(t\) is the time, \(k\) is a rate constant related to the activation energy and \(n\) is a kinetic constant corresponding to the growth mechanism.

The crystallinity wt.% vs. time data for the experiment performed at 300°C was fitted to this equation (Appendix Figure S6) and yielded \(n = 3.5 \pm 0.1\), which
corresponds to three-dimensional growth with a decreasing nucleation rate.\textsuperscript{43} Data from the experiments at higher temperatures could not be fitted using this model because the reaction proceeded too quickly compared to the data collection time.

At the crystalline-amorphous boundary, Ti and O atoms are reorganised and the crystallites grow, extending their boundaries (Figure 3.5). When two crystallites meet, the thermal energy even at 600°C is insufficient to allow further grain growth at the crystallite-crystallite grain boundaries, and so the crystallites stop growing due to the large energy barrier or constraints imposed by the tube wall.\textsuperscript{44}

At low temperatures (T < 390°C) the nucleation rate is a slow and continuous process. As crystallites are growing, new nuclei are being formed. This is supported by the Avrami model fitting described above. In contrast, at high temperatures the nucleation and growth rates are rapid, resulting in a large number of nuclei which then grow quickly. This results in a smaller average crystallite size for the experiments performed at higher temperature (Figure 3.5). The final crystallite size is then inversely proportional to the number of nuclei, which is proportional to the temperature. There are
regions between the crystallites which remain amorphous (Appendix Figure S7).

In addition to grain boundaries, we expect atomic defects to play an important role in the phase transformation of TiO$_2$, particularly oxygen vacancies ($V_o$) and fluoride ions ($F^-$). These both contribute to the heterogeneous strain, which is included in the Rietveld refinement as a fitted parameter (Appendix Figure S8).

The as-anodized TiO$_{2-x}$ is an intrinsic defective structure.$^{32}$ Diffusion of O atoms to lattice positions would result in the formation of localized crystalline anatase with a stoichiometric ratio when annealed. If no additional oxygen is added or removed, the remaining amorphous regions would have the formula TiO$_{2-y}$ where $y = x/(1-f)$ ($f$ is the fraction of formed crystalline TiO$_2$). In this case, the originally substoichiometric amorphous regions would become more oxygen-deficient. Fig. S1 illustrates that the amorphous layer, marked by the yellow dashed lines, was formed on the outside of the crystallized region, which indicates the centre was preferentially transformed. Similar results were reported by Varghese et al.$^{44}$ Tian et al. also observed core-shell TiO$_2$ nanoparticles obtained from out-diffusion of $V_o$ after annealing at 700°C, with the amorphous outer layer being sub-stoichiometric in oxygen (with Ti:O ratio approximately 1:1.5).$^{38}$

In our work, amorphous regions could also be observed trapped within crystallized cores (Fig. 3.2c). We hypothesize these are oxygen-deficient regions. The removal of more oxygen for the crystallization process will come at an increasingly higher energy cost, which, in addition to the energy barrier for further reorganisation at the grain boundaries, results in the crystallization ceasing. This is also supported by the result from the Avrami model fitting that the nucleation rate decreases with time.

$F^-$ is easily incorporated in TiO$_2$ during anodization due to the faster migration speed compared to oxygen ions and the flexibility of the amorphous structure.$^{45, 46}$ This
may contribute to the formation of oxygen vacancies, whose influence on crystallinity was mentioned above. F\(^-\) is also able to stabilise oxygen vacancies.\(^{47}\) Furthermore, the behaviour of F\(^-\) ions is temperature-dependent: it starts to be removed from TiO\(_2\) at temperatures above 300\(^\circ\)C, with complete removal at 600\(^\circ\)C in air after 6 hours.\(^{48}\) Previously reported thermogravimetric analysis (TGA) for fluoride-containing TiO\(_2\) shows an additional weight loss between 300-500 \(^\circ\)C that is not observed when fluoride is absent.\(^{49}\) We observed similar features in the TGA curves (Appendix Figure S9), with an associated rapid drop in F\(^-\) concentration determined by X-ray photoelectron spectroscopy (XPS) for samples annealed in the same temperature range, as listed in Table 3.1.

Fluorinated TiO\(_2\) has a larger unit cell than unfluorinated TiO\(_2\),\(^{50}\) while in oxygen-deficient black TiO\(_2\) the lattice parameters are contracted.\(^{51}\) These effects compete in our system, and may explain why \(a\) decreases while \(c\) increases. Our hypothesis is that the loss of F\(^-\) causes the difference in lattice parameter behavior between the low (300-390\(^\circ\)C) and high (600\(^\circ\)C) temperature experiments, and that removal of fluoride past a critical concentration is responsible for the change in unit cell behavior observed at 500\(^\circ\)C after 2500 s (Figure 3.4), and in the temperature ramps above this temperature (Appendix Figure S5).
Table 3.2 Concentration of F ions in atomic percent under different annealing temperature obtained from XPS results

<table>
<thead>
<tr>
<th>Annealing temperature (℃)</th>
<th>Annealing time (min)</th>
<th>Fluorine concentration (Atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>18.78</td>
</tr>
<tr>
<td>300</td>
<td>1</td>
<td>15.39</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>11.73</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10.37</td>
</tr>
<tr>
<td>400</td>
<td>1</td>
<td>7.28</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>6.00</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5.59</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>6.89</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.35</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.57</td>
</tr>
</tbody>
</table>

Atomic defects in TiO₂ have a significant effect on its physical and chemical properties. ³², ⁴⁷, ⁵² Partially crystallized TiO₂ contains disordered regions ³⁴, ⁵³ and exhibits distinct photocatalytic properties compared to pure anatase TiO₂. ²⁰ Lattice defects and grain size play important roles in determining the charge diffusion and electrical resistance. ⁵⁴-⁵⁶ The surface adsorption of small molecules and optical absorption properties can be enhanced by introducing V₀. ⁵⁷ Different concentrations of V₀ in the crystalline and amorphous regions were also found to influence the microwave absorption properties due to an interfacial electric field. ³⁵ In this work, we have shown that different degrees of crystallinity in anodic TiO₂ can be obtained through controlling the annealing treatment, which provides an effective way for engineering atomic defects to obtain specific physical properties.

For example, to form larger grains, lower temperatures (e.g. 300-400°C) are
required during the initial nucleation and growth stage. To remove $F^-$, temperatures greater than 500°C are required; but if the grain structure has already been controlled through a low temperature hold, this would be maintained. Such control of the atomic and grain structure of TiO$_2$ would be useful for tailoring its physical properties and expand functional applications related to environmental and energy technologies.

3.4 Conclusions

In summary, the degree of crystallinity and the crystal size of anodic TiO$_2$ NTs increase rapidly and then remain constant within a short time after annealing. However, the lattice parameters take a longer time to stabilise. There are three main factors controlling the crystallization process: the limitation on crystallite coarsening due to the insufficient thermal energy and spatial constraints imposed by the tube walls, non-stoichiometric TiO$_2$ phases produced by diffusion of oxygen vacancies and the effect of fluoride ions on oxygen vacancy formation and the lattice structure. All of these factors govern the degree of crystallinity and contribute to incomplete crystallization. This work highlights the importance of the entire annealing protocol – not just the temperature – for controlling the defect density, grain size and degree of crystallinity in anodic TiO$_2$. The concept of partial crystallization of amorphous TiO$_2$ may be used to develop new properties of other semiconducting oxides.
CHAPTER 4

Effect of anodic TiO₂ crystallinity on the Ni electroplating behaviour

Based on the understanding of post annealing treatment (Chapter 3), this chapter continues to discuss the effect of crystallinity on the platability of TiO₂ NTs and proves the electroplating technique is a feasible method to modify TiO₂ NTs with metals. The as-anodized TiO₂ (amorphous phase) and the annealed TiO₂ NTs (anatase phase) were adopted as the substrates for Ni electroplating. The formation mechanism of the different deposited Ni nanostructure was discussed. The hybrid Ni-TiO₂ nanocomposites could also be used as a catalyst for oxygen production.

* This chapter is based on a journal paper under submission to Electrochimica Acta: J. Dong, F. Hou, X. Yue, Y. Wang, C. Goode, W. Gao. “Effect of thermal annealing on the platability of anodic TiO₂ substrate and the oxygen evolution performance of Ni-TiO₂ hybrid nanocomposites”
CHAPTER ABSTRACT

Development and modification of common and versatile titanium dioxide (TiO₂) is of enormous significance due to its wide application to energy, environmental and electric device fields. Electroplating is a simple and cost-effective way to introduce various conductive materials into TiO₂ which has the ability to expand the industrial application of these films. In the present work, the platability of anodic TiO₂ nanotube substrate before and after thermal treatment is investigated using Ni electroplating. The results reveal that the deposited Ni grows inside the nanotube on annealed TiO₂ substrate, while it only forms a compact layer on the top of as-anodized. It was found that different electrodeposition behaviour is closely related to the electric resistivity and wettability of the TiO₂ substrate. The resultant Ni-TiO₂ nanocomposite on annealed TiO₂ substrates exhibited better oxygen evolution performance than on amorphous substrates in terms of low overpotential at a current density of 10 mA/cm² and small Tafel slope. This work may provide guidance for fabricating hybrid nanocomposites via electroplating and support material preparation for oxygen evolution reaction catalysts.

4.1 Introduction

Titanium dioxide (TiO₂) is a common and widely used transition metal oxide. One-dimensional nanotube structure endow TiO₂ with large surface area and short transfer path, which improves its performance in solar cells and photo-electro devices. Following the successful precedent on anodic aluminium oxide (AAO) template, hybrid nanocomposites have been developed on anodic TiO₂ nanotube arrays (NTs), incorporating metals, metal oxides and even polymers, with the extended applications in supercapacitor, light detector, magnetic storage, and photovoltaic device. The electrodeposition technique is a simple, fast and versatile method to obtain these
structures. Unlike the AAO with its electrical insulating properties, an $n$-type TiO$_2$ layer is easily polarized, in a biased state, and has current leakage problems under negative potential. This weaknesses leads to the deposition occurring around the tube mouth; blocking the tubular structure, and reducing the effective TiO$_2$ NTs surface.

The idea of opening TiO$_2$ tube bottom and applying an Ag layer instead to assist metal growth inside was proposed by D. Fang et al. However, the freestanding hybrid coating layer is not appropriate as an integrated electrode. Selectively reducing TiO$_2$ nanotube endcap through the electrochemical self-doping showed the similar deposition behaviour without requiring the oxide layer to be peeling off, however the reaction time needs to be precisely controlled to preserve the conductivity difference between tube wall and bottom.

In recent years, the combination of annealing treatment and current pulse technique attracts great attention and has been proven to be an effective method to fill the TiO$_2$ NTs. The pulse loading plays an important role in the homogeneous nucleation of deposited material and formation of dense nanowires all over the inner tube wall. F. Liang et al. and C. Wang et al. stated that the post annealing treatment has a significant impact on the Ni filling behaviour into TiO$_2$ NTs, however, the influence mechanism of annealing treatment has rarely been discussed.

Water splitting is a promising method to produce sustainable energy, but the oxygen evolution reaction (OER) that requires large external potentials limits its practical application. OER electrocatalysts, such as ruthenium, Iridium and their oxide, work to increase the electrolysis efficiency. However, the high cost and low stability pose great obstacles to their development, which may be addressed by employing catalyst support. On one hand, support materials help reduce the required amount of expensive catalysts; on the other hand, it also provides large surface area for electrolyte
adsorption and catalysts dispersion.

Conductive carbon materials are normally used to provide support, however they lack of durability at high potentials which may cause the agglomeration of catalysts.\textsuperscript{21} Due to good chemical stability and tuneable conductivity, TiO\textsubscript{2} may be a good alternative support. The enhanced OER activity and stability of IrO\textsubscript{2} on TiO\textsubscript{2} support was also reported.\textsuperscript{22} The bimetallic catalysts supported on anatase TiO\textsubscript{2} even exhibited 53\% higher current than unsupported nanoparticles with same compositions.\textsuperscript{23}

In this Chapter, both as-synthesized and annealed TiO\textsubscript{2} NTs prepared by electrochemical anodization were adopted as plating substrates to fabricate Ni-TiO\textsubscript{2} nanocomposites via electrodeposition. The crystallinity and wettability of the different substrates were characterized to reveal the effect of thermal annealing on the platability. The OER performance of the hybrid nanocomposites was also studied to understand the influence of substrate crystallinity and develop good support material for oxygen production catalysts.

4.2 Experimental

4.2.1 Materials preparation

The highly ordered anodic TiO\textsubscript{2} NTs were prepared through two-step electrochemical anodization. Mechanically polished Ti foil (> 99.6\% Ti, 40×25×0.5 mm\textsuperscript{3}) was used as anode and Ti mesh as cathode in a two-electrode system. The first anodization was performed in the electrolyte composed of ethylene glycol, 0.25 wt.% ammonium fluoride and 2 vol.% DI water at 60 V for 25 h. The obtained oxide layer was then removed by strong ultrasonic cleaning. The second anodization was conducted on the treated Ti foil in the same electrolyte at 80 V for 10 min. The as-anodized TiO\textsubscript{2} NTs was cleaned in ethanol and dried at ambient air. For comparison, some of the TiO\textsubscript{2} NTs were calcinated at 450°C for 1 h in the ambient atmosphere.
A galvanostatic electroplating approach was used to prepare Ni-TiO₂ hybrid nanocomposite. The TiO₂ NTs samples were washed in sodium hydroxide solution and dilute hydrofluoric acid for 5 min and 1 min, respectively before electrodeposition. A typical two-electrode cell was utilized with TiO₂ NTs as working electrode and Ni foil as counter electrode. The Ni electroplating was performed in aqueous solution consisted of 0.96 M nickel sulphate, 0.25 M nickel chloride and 0.65 M boric acid at 5 mA/cm² with air agitation and temperature of 55 °C. After that, the as-synthesized samples were washed with DI water and dried under an air atmosphere.

4.2.2 Materials characterization

The morphologies of surface and cross-sectional areas were characterized by field emission scanning electron microscopy (FE-SEM, Philips XL-30S). Energy-dispersive X-ray spectrometer (EDS) equipped with FE-SEM and X-ray photoelectron spectroscopy (XPS, PHI Quantera-II SXM) were employed to analyse the chemical composition. The binding energy obtained from XPS was calibrated via C 1s peak at 284.8 eV. The phase structure analysis was executed using X-ray powder diffraction (XRD, Bruker D2-Phaser) with Cu Kα1 radiation (λ = 1.5406 Å) between 2θ range of 20°–80°. Mass change during thermal annealing was recorded by Thermogravimetric analyser system (TGA, Shimadzu TGA-50) and bonding structure was investigated by Fourier Transform Infrared spectroscopy (FTIR, Spectrum 100, Perkin-Elmer). The TiO₂ NTs resistivity was measured using a 2-point measurement system comprising a micromanipulator (ZEISS-Stemi 2000 C) and an Agilent B2901A analyser unit at potentials ranging from +2 to -2V with a sweep speed of 20 mV/s with a thin Ag layer deposited on surface of TiO₂ NTs by magnetron sputtering as the working electrode. Contact angle goniometer (KSV CAM-101) was used to measure the water contact angles at room temperature.
The electrochemical measurements were performed using CHI604D electrochemical workstation (Chenhua, China) in a conventional three-electrode system. The Ni-TiO$_2$ nanocomposites were used as the working electrode and potentials were referred to Ag/AgCl (in saturated KCl) reference electrode with a piece of Pt foil as counter electrode. The electrocatalytic performance in oxygen evolution were characterised through potential polarization curves in 1 M KOH electrolyte at room temperature with a scan rate of 50 mV/s. All the recorded potentials referred to Ag/AgCl reference electrode were calibrated to the potential reversible hydrogen electrode (RHE) for Tafel plots analysis.

### 4.3 Results and discussion

#### 4.3.1 Effect of TiO$_2$ crystallinity on the electroplating behaviour

Two-step anodization was conducted to produce a well-defined self-assembly NTs without bundling and precipitation (Appendix Figure S10). Unlike the TiO$_2$ NTs with voids between neighbouring tubes prepared using one-step anodization, the parallel NTs produced by double anodization, reported in this paper, created a thin nanoporous layer with a pore size of ~80 nm. This structure facilitates the deposition inside the tubes as the intertubular voids were reported to have faster ion diffusion and better conductivity than tube cavity. The tubular structures did not change significantly after annealing at 450 °C except for the roughening tube walls, which is consistent with former research. The different Ni electrodeposition behaviour between as-anodized and annealed TiO$_2$ substrate could be found in Figure 4.1.

It can be seen that the deposited Ni agglomerated into large clusters and stayed on the top of as-synthesized TiO$_2$ substrate (Figure 4.1a), however, there is no trace of Ni inside the tubes. At the interface, the Ni layer base has numerous extrusions, which may insert into tube mouth with shallow depth as shown in Appendix Figure S11a. This
phenomenon could be attributed to surface tension caused by the trapped air inside nanotubes or capillary effect.\textsuperscript{25, 26} In contrast, Ni almost filled the annealed TiO\textsubscript{2} nanotubes from bottom to top and formed vertically aligned nanowires with the width of ~58 nm.

As shown in Figure 4.1b, the nanowires grew out of tubes, tangled each other, and turned into dense Ni layer on the top when the deposition time is prolonged. The integrated nanowires create a tight joint with Ni layer, however the connections at the edge appear to break down when cross-section samples are prepared (marked by dashed line in Appendix Figure S11b). EDS analysis shows the high Ni concentration across the cross-section area, and the backscattered electron image reveals that the Ni nanowires uniformly distributed along the tube length (Appendix Figure S12).

Figure 4.1 SEM images of cross-sectional view of Ni-TiO\textsubscript{2} nanocomposite: (a) as-anodized TiO\textsubscript{2}, (b) annealed TiO\textsubscript{2} at 450 °C under the air atmosphere

The bases of Ni-TiO\textsubscript{2} nanocomposites on both as-synthesized TiO\textsubscript{2} (Ni-AS-TiO\textsubscript{2}) and annealed TiO\textsubscript{2} (Ni-AN-TiO\textsubscript{2}) substrate were characterized to verify the Ni deposition. As shown in Figure 4.2a, Ni-AS-TiO\textsubscript{2} had the typical hexagonal shape and each hexagon corresponds to one nanotube. According to the EDS result, it can be inferred that few Ni locates around the tube bottom, which is consistent with the
findings in Figure 4.1a. However, the Ni-AN-TiO₂ exhibited two distinct layers (inner shell and outer shell) after thermal annealing (Figure 4.2b), which is common for anodic TiO₂ with heat treatment due to the loss of carbon and fluoride species.²⁷ The Ni concentration around the bottom of Ni-AN-TiO₂ nanocomposites is 19.4 at.%, which is nearly 20 times higher than that of Ni-AS-TiO₂, indicating the full filling of Ni inside the annealed TiO₂ tubes.

Figure 4.2 SEM images of bottom of (a) Ni-AS-TiO₂, and (b) Ni-AN-TiO₂. Inset images are the EDS analysis of each sample.

Post thermal annealing normally has great influence on the morphology, crystallinity, physical and chemical properties of anodic TiO₂ NTs.²⁸ In this chapter, TiO₂ NTs did not exhibit obvious diffraction peaks of crystalline TiO₂ after 250°C annealing (Figure 4.3a). The sharp peaks of anatase phase were found after annealing at 350°C and above, and apparent rutile phase appeared at 550°C. Another noticeable change induced by heat treatment is fluorine ion (F⁻) concentration. It can be seen in Figure 4.3b, the F⁻ decreased with the annealing temperature and the steep drop could be observed around 250°C, but it remained nearly constant at temperature above 450°C, which is also supported by the mass change of anodic TiO₂ during non-isothermal annealing process (inset in Figure 4.3b). Although these features did not have direct
relationship with Ni electrodeposition behaviour, they may affect the conductivity and wettability of TiO₂ substrate, resulting in the improved distribution of Ni.

Figure 4.3 (a) XRD patterns of anodized TiO₂ NTs after annealing at different temperatures (A: anatase TiO₂, R: rutile TiO₂, Ti: titanium substrate); (b) High resolution XPS spectra of F 1s of anodized TiO₂ NTs before and after annealing at different temperature. Inset is the TGA curve during non-isothermal heat treatment of anodized TiO₂ NTs.

Due to their amorphous structure, the anodic TiO₂ NTs had a high electrical resistivity of $10^9 - 10^{10}$ Ω cm. However, the conductivity improved by several magnitudes after thermal annealing as shown in Figure 4.4. The resistivity of TiO₂ decreased with the annealing temperature before rising again at temperatures higher than 350°C under ambient atmosphere. The decreased resistivity below 350°C could be attributed to the initiation of crystallization and the increased crystallinity, which is consistent with the XRD results. The different trend of conductivity at high temperature might be due to the formation of rutile phase at the NTs-Ti interface.

It is reported that the transition from anatase to rutile was promoted in oxygen-rich atmosphere and the presence of rutile could deteriorate the electrical conductivity. Therefore, compared to the as-anodized NTs, crystalline TiO₂ with low electrical resistivity provided fast track for movement of electrons along tube length, where they could take part in the redox reaction of deposited Ni ions.
The diffusion rate of ions also plays a significant role in the deposition reactions, especially for TiO$_2$ NTs with high length to width ratio.$^{35}$ As shown in Figure 4.4, the wettability of TiO$_2$ could be adjusted through thermal annealing, which promotes diffusion and compensation of Ni ions during the electrodeposition. The water contact angle (WCA) decreased significantly from 95° to 10.4° with increasing annealing temperature, indicating that the TiO$_2$ surface gradually became hydrophilic. The steep fall of WCA happened below 250°C, and then it remained the same between 250°C and 350°C following by a sharp drop at 450°C. At last the WCA decreased slightly to 10.4° at 550°C.

The reason for this phenomenon could be the combined effect of F$^-$ and TiO$_2$ crystallinity. The low temperature (≤250 °C) annealing would not trigger the phase transition revealed by XRD results (Figure 4.3a), while the F$^-$ concentration reduced dramatically from 10.33 at.% to 1.94 at.%. The sudden change of the F$^-$ eliminates the superhydrophobic terminal group (-CF$_3$) $^{36}$ and results in the increased wettability. Although the F$^-$ level remained almost constant after annealing at temperatures (>250°C), the crystallinity degree obviously improved, which might explain the increased hydrophilicity between 350°C and 450°C.$^{37}$

Another hypothesis for the enhanced wettability proposed by Simonsen et al. is the formation of hydroxyl groups on the surface,$^{38}$ but the concentration of hydroxyl groups (Ti-OH) revealed by deconvoluting O 1s peak did not change a lot with annealing temperatures (Appendix Figure S13a). Similar conclusion could also be made according to the FTIR spectroscopy shown in Appendix Figure S13b. Therefore, the TiO$_2$ annealed at 450°C in air were selected as the electrodeposition substrate from the perspective of reasonable conductivity and good wettability.
4.3.2 Electro catalytic property of Ni-TiO₂ hybrid nanostructures

Although TiO₂ is an inactive catalyst of oxygen production due to the high overpotential, the deposited Ni exhibits the prominent electrocatalytic activity towards OER. It can be seen in Appendix Figure S14 that both Ni-AS-TiO₂ and Ni-AN-TiO₂ exhibited typical anodic and cathodic peaks of Ni, which illustrates the redox conversion between Ni(OH)₂ and NiOOH. Following the oxidation of Ni (II) to Ni (III), the current rises sharply at ~0.61 V (Ag/AgCl), indicating the initiation of oxygen generation. The linear sweep voltammetry and Tafel slope were plotted to understand the electrocatalytic OER process quantitatively.

As shown in Figure 4.5a, both the amorphous and crystalline TiO₂ did not show catalytic activity as expected with almost no exchange current density (CD). However, the CD increase sharply with both the Ni deposition and TiO₂ phase transition. Normally, the overpotential at 10 mA/cm² was adopted to evaluate the catalyst ability, consequently only the Ni-AN-TiO₂ and Ni-AS-TiO₂ with 10 min Ni coating exhibited the acceptable catalytic activity (dot dash line). It can be seen in Figure 4.5b, the Tafel
slope of Ni-AN-TiO₂ was lower than that of Ni-AS-TiO₂, and the annealed TiO₂ with 3 min Ni coating shows the lowest value, indicating their favourable OER activity.

Tong et al.⁴³ concluded that two different enhancement mechanisms of OER process, geometric enhancement and electronic enhancement, could be revealed by the CD and Tafel slope, respectively. Due to the intrinsic low resistivity of annealed TiO₂ and the Ni nanorods formed inside nanotubes, Ni-AN-TiO₂ facilitate the catalytic-generated electrons transfer to the metallic conductive collector, which is responsible for the high CD in Figure 4.5a and low Tafel slope in Figure 4.5b compared to Ni-AS-TiO₂. As for the annealed TiO₂ with different Ni coating, the CD increased with Ni deposition time, resulting from the production and participant of more NiOOH in the electrocatalytic reaction or the roughened surface with large surface area.⁴⁰

On the other hand, as the transformation from Ni(OH)₂ to NiOOH is a diffusion-controlled process,⁴⁴ it might be suppressed when the deposited Ni formed a thick and compact layer with the increase of Ni coating time. The untransformed Ni(OH)₂, a p-type semiconductor, may act as barrier layer for electron transport and elevate the Tafel slope. Therefore, 5 min Ni deposition time and annealed TiO₂ substrate could be the optimized conditions for preparing the OER catalyst with moderate overpotential and large kinetics.

Figure 4.5 (a) Polarization curves and (b) Tafel plots of Ni-TiO₂ nanocomposites with different Ni coating in 1 M KOH.
4.4 Conclusions

In summary, electrodeposited Ni stacked and covered the top of as-anodized TiO₂ nanotube substrate forming a compact Ni layer. However, electrodeposited Ni exhibited the “bottom to top” growth manner and formed the nanowires inside the nanotubes post annealing. The change of crystallinity and fluoride ion concentration induced by thermal treatment could account for the changed Ni deposition behaviour as the improved conductivity facilitates electron transport and the enhanced wettability promotes ions diffusion and replenishment. Although both the as-anodized and annealed TiO₂ nanotube do not show catalytic activity towards oxygen evolution in isolation, the anatase TiO₂ substrate helps decrease the overpotential and increase the kinetics of OER for Ni-TiO₂ hybrid nanocomposites. However, the electrocatalytic performance of nanocomposite on annealed TiO₂ substrate also deteriorated with abundant Ni deposition. These findings demonstrated that the annealed TiO₂ nanotube could act as not only the electrodeposition substrate but also the OER catalyst support in the future.
CHAPTER 5

Photocatalytic activities of TiO$_2$ modified by Cu nanoparticles

The Chapter 4 illustrates it is possible to decorate TiO$_2$ NTs with metals through electrochemical method. In this chapter, a novel method of modifying TiO$_2$ NTs with Cu through physical process was proposed. The Cu was deposited on the TiO$_2$ NTs by the Magnetron Sputtering technique. With the help of an additional heat treatment called “thermal dewetting”. A Cu layer could be transformed to uniform Cu nanoparticles. The modified Cu-TiO$_2$ nanocomposites exhibit 4-fold photocatalytic activity more than the TiO$_2$ NTs.

CHAPTER ABSTRACT

The modification of titanium dioxide (TiO\textsubscript{2}) using noble metal nanoparticles is considered as a promising technique to make electrode with outstanding photocatalytic performance. In this chapter, self-organized anodic TiO\textsubscript{2} nanotube arrays were decorated with well-distributed small Cu nanoparticles through a novel technique that combines magnetron sputtering and thermal dewetting. The obtained nanocomposite catalyst exhibited 4-fold increase in the photodegradation rate of methylene blue aqueous solution under simulated solar light irradiation than anatase TiO\textsubscript{2} prepared with same anodization conditions. The enhanced photocatalytic activity was attributed to the synergistic effect of Schottky barrier and surface plasmon resonance. The influence of post annealing process, sputtering time and thermal dewetting temperature on photocatalytic performance was studied; and the optimal preparation conditions were proposed. The results of this study may provide a new strategy to improve photocatalytic efficiency of TiO\textsubscript{2} without using high-cost noble metals.

5.1 Introduction

Titanium dioxide (TiO\textsubscript{2}) has been exploited as multifunctional semiconductors in environmental treatment, gas sensing, energy conversion and photovoltaic cells for decades due to its stable and excellent properties.\textsuperscript{1-3} As one of the leading photocatalyst candidates, it exhibits great potential since Fujishima and Honda first reported its marvelous hydrogen production ability.\textsuperscript{4} The photocatalytic properties of TiO\textsubscript{2} depend on its morphologies; and the one dimensional TiO\textsubscript{2} nanotube arrays (NTs) shows much better photocatalytic properties than other topography because of large specific surface area, short carrier diffusion length and easy recycling character.\textsuperscript{5-8}

However, TiO\textsubscript{2} has a large energy band gap (~3.2 eV) and only works under UV
irradiation that can excite electrons from valance band \((VB)\) to conduction band \((CB)\). Various attempts have been adopted to extend the range of response spectrum and improve the visible light photocatalytic performance, for example, narrowing the band gap via non-metal\(^{10,11} \) and transition metal ions doping\(^{12,13} \) and shifting band gap by coupling another semiconductor to form hetero junction\(^{14,15} \). Recently, nanocomposites of TiO\(_2\) decorated with noble metal nanoparticles have attracted great attention due to their enhanced photocatalytic performance arising from good visible light absorption and reduced photo-excited charge carriers recombination\(^{16,17} \).

Several research groups have reported that TiO\(_2\) decorated with platinum\(^{18,19} \), gold\(^{20,21} \), and silver\(^{22,23} \) have improved photocatalytic performance. Au nanoparticles on TiO\(_2\) substrate exhibits obvious photocurrent peak in the visible light region\(^{24} \). Sobana \textit{et al.} prepared Ag doped TiO\(_2\) composite, in which Ag nanoparticles act as traps to enhance electron-hole separation\(^{25} \). The photocatalytic activity of Ag loaded TiO\(_2\) nanocomposites has a 2.7-fold improvement than that of pure TiO\(_2\)\(^{22} \). They also exhibit higher photocatalytic degradation rate under solar light and \textit{UV} \ light irradiation than Pt/TiO\(_2\), while similar photocatalytic properties with Au/TiO\(_2\)\(^{26} \).

As another conventional metal, Cu has proper work function and reasonable cost\(^{27,28} \). TiO\(_2\) can be sensitized with Cu to have extended light absorption and higher photocatalytic properties\(^{29} \). The carbon dioxide was reported to be reduced to methane and ethylene using Cu loaded TiO\(_2\) powders at ambient temperature under Xe lamp irradiation\(^{30} \). TiO\(_2\) deposited with Cu particles via wetness impregnation technique also showed significant improvement in photocatalytic hydrogen production\(^{31} \). Cu doped TiO\(_2\) colloids yield 55 percentage degradation of paraquat under visible light for 240 min\(^{32} \). Even compared with Ag or Au doped TiO\(_2\), Cu/TiO\(_2\) hybrid composite has higher photocatalytic activity\(^{33,34} \).
A number of methods have been reported to modify semiconductor with noble nanoparticles. Photochemical reduction is one of the common methods to decorate TiO$_2$ nanotube arrays (NTs) with noble metals. However, it is hard to achieve uniform nanoparticle size and good distribution, even by using ultrasonic aiding technique. Magnetron sputtering has been reported as an effective way to achieve good adhesion and uniform metal particle distribution. The plasma deposition process can be accurately controlled by sputtering power and gas pressure to determine the deposition density.

As the deposited metal layer covers most TiO$_2$ substrate, subsequent heat treatment named as thermal dewetting is conducted to avoid surface shading and improve the adhesion between metal particles and TiO$_2$ NTs substrate. The dewetting behavior on flat substrates has been well studied, but the effect of dewetting conditions on the photocatalytic properties are not well investigated.

In this chapter, well-dispersed Cu nanoparticles on the self-organized TiO$_2$ NTs were achieved through a novel technique combining with magnetron sputtering and thermal dewetting. The photocatalytic properties of Cu/TiO$_2$ nanocomposite were evaluated by photodegradation of methylene blue under solar light irradiation and further optimized through adjusting preparation conditions. Furthermore, mechanism of the enhanced photocatalytic performance was discussed.

5.2 Materials and Methods

5.2.1 Preparation of TiO$_2$ NTs

The highly aligned TiO$_2$ NTs were prepared by two-step electrochemical anodization on thin titanium foil (>99.6%Ti, 40×25×0.5 mm). The substrate preparation includes mechanically polishing and ultrasonically cleaning. Anodization reaction was conducted in a two-electrode system with Ti foil as the anode and Ti mesh as the
The first anodization was carried out in ethylene glycol based solution containing 0.25 wt.% NH_4F and 2 vol.% DI water at 60 V for 25 h. The obtained TiO_2 nanotube layer was removed by ultrasonication in DI water. The second anodization was performed on the concaved Ti foil left by first anodization in the same electrolyte at 80 V for different duration followed by washing and drying at ambient air.

5.2.2 Synthesis of Cu loaded TiO_2 NTs composite

The deposition of Cu on TiO_2 NTs was carried out in a Direct Current (DC) reactive sputtering system (Kurt J. Lesker Nano 36) with Cu target (99.99%Cu). The TiO_2 nanotube films were allocated on a plate substrate, and 300 mm away from the target. Afterwards the chamber was evacuated to below 1.0×10^{-5} Torr, argon (Ar) gas with pressure of 10 mTorr was filled. The deposition was performed at a DC power of 100 W with 1 W/s ramp rate to excite plasma. The sputtering time were varied to control the quantity of Cu deposited on the TiO_2 NTs array. Dewetting of TiO_2 NTs with Cu layer was performed in Ar atmosphere at different temperatures for 1 h. For comparison, some specimens were calcined in Ar at 400°C for 1 h before sputtering process to become anatase TiO_2. The detailed experimental conditions are listed in Table 5.1.
Table. 5.1 Summary for preparation conditions of Cu loaded TiO$_2$ samples

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Scheme name</th>
<th>Composition</th>
<th>Post annealing</th>
<th>Sputtering time (s)</th>
<th>Dewetting Temperature ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>N-annealing, sputtering, N-dewetting</td>
<td>Amorphous TiO$_2$ + Cu film</td>
<td>N/A</td>
<td>40</td>
<td>N/A</td>
</tr>
<tr>
<td>S2</td>
<td>Annealing, sputtering, N-dewetting</td>
<td>Anatase TiO$_2$ + Cu film</td>
<td>Yes</td>
<td>40</td>
<td>N/A</td>
</tr>
<tr>
<td>S3</td>
<td>Annealing, N-sputtering, N-dewetting</td>
<td>Anatase TiO$_2$</td>
<td>Yes</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>S4</td>
<td>N-annealing, sputtering, dewetting</td>
<td>Anatase TiO$_2$ + Cu nanoparticles</td>
<td>N/A</td>
<td>40</td>
<td>400</td>
</tr>
<tr>
<td>S5</td>
<td>Annealing, Sputtering, dewetting</td>
<td>Anatase TiO$_2$ + Cu nanoparticles</td>
<td>Yes</td>
<td>40</td>
<td>400</td>
</tr>
<tr>
<td>S6</td>
<td>N/A</td>
<td>Anatase TiO$_2$ + Cu nanoparticles</td>
<td>N/A</td>
<td>20</td>
<td>400</td>
</tr>
<tr>
<td>S7</td>
<td>N/A</td>
<td>Anatase TiO$_2$ + Cu nanoparticles</td>
<td>N/A</td>
<td>80</td>
<td>400</td>
</tr>
<tr>
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<td>Yes</td>
<td>40</td>
<td>200</td>
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<tr>
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<tr>
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<td>Yes</td>
<td>40</td>
<td>500</td>
</tr>
</tbody>
</table>

5.2.3 Characterization

Surface and cross-sectional morphologies of Cu-loaded TiO$_2$ NTs were characterized by field-emission scanning electron microscopes (FESEM, Philips XL-30S) operating at 5 kV. The chemical composition was qualitatively analysed through energy-dispersive X-ray spectrometer (EDS) on FESEM. High-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F20, 200 kV) was used to characterize the morphology and lattice structure of TiO$_2$ NTs and Cu decorated samples. The polycrystalline structure was studied through X-ray powder diffraction (XRD, Bruker D2-Phaser) with Cu K$_{\alpha1}$ radiation ($\lambda = 1.5406$ Å) between 2$\theta$ range of 20° to 80°.
chemical states were determined by X-ray photoelectron spectroscopy (XPS, PHI Quantera-II SXM) using a pass energy of 20 eV. C 1s peak with 284.8 eV was used for calibration of binding energy. The optical absorption of films was tested on Shimadzu UV-2550 UV-Visible spectrometer. The absorption spectra of dye solution were recorded on an UV-vis spectrophotometer (Perkin Elmer Lambda 35).

5.2.4 Photocatalytic property measurement

The photocatalytic activity of Cu loaded TiO$_2$ NTs was evaluated by decomposition of methylene blue (MB) under simulated solar light. MB aqueous solution is considered as the standard contaminant to test photocatalytic activity which is hard to degrade by semiconductor-mediated system under visible light.$^{44}$ Before the test, Cu-TiO$_2$ catalyst films were immersed into 40 mL MB solution with concentration of 5 ppm and magnetic stirring in dark for 1 h to establish adsorption/desorption equilibrium. The films were then irradiated with 300 W high-pressure lamp (Ultra vitalux 230 V E27, light intensity distribution shown in Figure 5.1) for 4 h to decompose the pollutant.

1 mL solution samples were taken out at certain intervals and measured using UV-vis spectrophotometer with wavelength ranging from 400 to 800 nm. The concentration of MB is in linear relationship with the absorbance peak intensity at wavelength of 664 nm. As the photodegradation of MB follows first order reaction kinetics, the reaction can be expressed as $\ln(C_0/C) = kt$. Where $C_0$ is the initial concentration after dark adsorption, $C$ is concentration at sampling time, $k$ is degradation rate, and $t$ is reaction time.
5.3 Results and discussion

5.3.1 Characterization of Cu-TiO₂ nanocomposite

The schematic of Cu/TiO₂ NTs synthesis process is shown in Figure 5.2. Cu layer was deposited on surface of anodic TiO₂ NTs through magnetron sputtering and then transformed to Cu nanoparticles by thermal dewetting. For comparison purpose, some anodic amorphous TiO₂ NTs were calcined to form anatase phase before sputtering process, and then magnetron sputtering and thermal dewetting were conducted under the same conditions. The preparation conditions were listed below and the samples have codes listed in Table 5.1.
Surface morphologies of TiO$_2$ NTs before and after sputtering and dewetting are shown in Figure 5.3. Well-aligned anodic TiO$_2$ NTs with length of $\sim$4.7 $\mu$m and pore size of $\sim$120 nm was obtained via electrochemical anodization (Figure 5.3a). The surface is smooth without any protrusion, an ideal substrate for particle deposition. Figure 5.3b shows the surface after Cu sputtering. The glossy surface was roughened by Cu deposition that covers entire surface of TiO$_2$ NTs. The deposited Cu even agglomerates into small clusters in certain regions as the shining bright dots. The detailed image is given in cross-sectional view (Figure 5.3c), illustrating Cu layer lies on the top of TiO$_2$ NTs like a “cap”.

Obvious Cu peak appears according to the EDS spectra shown in (Appendix Figure S15), indicating the coarse layer on TiO$_2$ NTs surface is Cu. The thin Cu layer turns into well-dispersed nanoparticles after thermal dewetting as shown in Figure 5.3d. They allocate on the top or attach near the mouth of TiO$_2$ NTs with average size of 48 nm in diameter (Appendix Figure S16).
Figure 5.3 SEM images of: (a) as-synthesized TiO$_2$; (b) and (c) surface and cross-sectional of Cu film+Amorphous TiO$_2$; (d) Cu nanoparticles+anatase TiO$_2$.

TEM image in Figure 5.4a demonstrates the as-synthesized TiO$_2$ NTs have clear tube walls and inner channel. Two nanoparticles appear around the tube mouth after Cu sputtering and thermal dewetting with size of 55 nm and 27 nm, respectively (Figure 5.4b). The HRTEM of large particle surface was shown in Figure 5.4c, which exhibits two parts with obviously different lattice structure marked by yellow and orange lines. The top region is identified as CuO (111) based on interplanar distance, and bottom part with smaller interplanar spacing is Cu (200). The chemical composition was discussed further through XPS result in the following section.
Figure 5.4 TEM images of: (a) as-synthesized TiO$_2$; (b) Cu nanoparticles+anatase TiO$_2$; (c) HRTEM images of particle in Figure 5.4b.

XRD patterns of TiO$_2$ before and after Cu sputtering and thermal dewetting are shown in Figure 5.5. The anodic TiO$_2$ NTs only have Ti substrate diffraction peaks due to the amorphous structure of TiO$_2$ obtained via anodization. Anatase diffraction peaks appear as expected with post annealing. Although obvious Cu peaks are displayed in EDS spectrum after sputtering, no Cu or copper oxide peaks appear after dewetting. This is because of the low content and poor crystallinity of Cu nanoparticles. Similar results were also reported in TiO$_2$ nanoparticles decorated with Pt, Au and Ag particles.$^{31, 45}$

With regard to the anatase phase diffraction, peaks with similar intensity and full width at half maximum can be observed before and after sputtering and thermal dewetting, indicating that sputtering and dewetting treatment had little influence on the crystalline structure of TiO$_2$. 
Figure 5.5 XRD patterns of different samples.

The chemical composition of Cu-loaded TiO2 NTs was further characterized by XPS analysis. Figure 5.6a shows the indexed peaks can be ascribed to C, O, Cu and Ti elements. The inset shows the Cu 2p core level spectrum with Cu (2p1/2) and Cu (2p3/2) peaks centred at 932.5 eV and 952.5 eV, respectively, evidence of the existence of Cu. However, there are no shake-up satellite peaks between two Cu 2p peaks.

In order to identify the chemical valence of Cu, Cu 2p3/2 peak was fitted using Gaussian function shown in Figure 5.6b. It is consisted of two peaks for S1. The major peak positioned at 932.48 eV was identified as metallic Cu, indicating the successful deposition of Cu on TiO2 NTs. The other peak located at 934.80 eV can be attributed to Cu(OH)2 or CuCO3, which may arise from impurities that formed with carbon dioxide or water in the atmosphere, and can be ignored due to the low quantity.

Compared with Cu 2p3/2 spectrum of S4, a new additional peak appears at 933.6 eV corresponding to CuO after dewetting. Although dewetting process was conducted in Ar atmosphere, it is inevitable to have a small amount of CuO formed when exposed to air. Another explanation on the existence of CuO is the by-product of Cu(OH)2 or
CuCO₃ decomposition under elevated temperature. Therefore, it is believed that co-catalyst after sputtering and thermal dewetting are made up of metallic Cu, a small quantity of CuO and base substrate TiO₂ NTs.

![Figure 5.6](image)

**Figure 5.6** (a) XPS survey spectra of Cu nanoparticles+anatase TiO₂; (b) high resolution Cu 2p₃/₂ spectra of Cu film+Amorphous TiO₂ (S1) and Cu nanoparticles+anatase TiO₂ (S4).

The **UV-Vis** absorbance spectra of Cu loaded TiO₂ NTs are shown in Figure 5.7. The as-synthesized TiO₂ NTs exhibits an absorption maximum around 350 nm, which can be attributed to the trapped holes⁴⁸ or charge transfer between **VB** and **CB**⁴⁹. The absorption spectrum of S1 shows a slight decrease in full light absorbance spectrum due to the good reflectivity of metallic Cu. However, S4 has apparent visible light absorption ability with a broad absorption peak centered at 540 nm due to the surface plasmon resonance (SPR) effect of Cu nanoparticles. Similar absorption band of Cu was also reported by Masoud⁵⁰ and Sangpour³³. Compared with sharp peak produced by Cu nanoparticles with size of 8 nm in reference, the broad absorption band can be attributed to the large and inhomogeneous particle size (Appendix Figure S16).⁵¹,⁵²
5.3.2 Influence of Cu shape on the Photocatalytic property

The photocatalytic activities of Cu-loaded TiO₂ NTs were evaluated through the degradation of MB in aqueous solution under solar light irradiation as shown in Figure 5.8a. For comparison, dye solution without catalyst was conducted under the same conditions. The blank MB solution showed negligible self-degradation under solar light irradiation. After 240 min irradiation, the concentration of MB was reduced by only 5% for S2 (blue triangle), which is similar to that of S1 (Red dots). However, S3 (green stars) decomposed 37% of MB during the same duration.

As the pristine amorphous TiO₂ NTs has a large number of defects acting as the recombination center that deteriorates the photocatalytic performance, S1 is expected to have the low degradation efficiency. The photodegradation efficiency of S3 had much improvement because anatase TiO₂ could utilize UV light to excite electron-hole pairs. However, the photocatalytic ability of S2 decreased after Cu layer deposition on S3,
because the active sites of anatase TiO$_2$ being blocked by Cu layer.$^{43}$

These results indicate that only Cu sputtering will decrease photocatalytic properties. If thermal dewetting process was performed after Cu sputtering, degradation percentage of S4 could reach up to more than 70% as shown by brown pentagon lines. This decomposition rate of MB is also a bit higher than reported Cu-TiO$_2$ catalyst prepared by different method.$^{53,54}$ Therefore, it can be concluded that the sputtering and dewetting processes need to work together to improve the photocatalytic performance.

The enhanced photocatalytic performance of S4 can be attributed to the synergistic effect of Schottky barrier and SPR effect from TiO$_2$ NT and Cu nanoparticles shown in Figure 5.8b. Moreover, the small amount of CuO may also contribute to the improved photocatalytic performance due to the heterojunction between CuO and TiO$_2$. As the Cu has higher work function than that of TiO$_2$ (3.9 eV),$^{28}$ electrons tend to migrate from conduction band of TiO$_2$ to metallic Cu favorably until new quasi-Fermi level ($E_f$) achieved.$^{55}$ The bands of TiO$_2$ bend to space charge region at the boundaries, leading to the formation of Schottky barrier that acts as electrons trap and improves the charge separation.$^{56,57}$ Under the $UV$ part of solar light, photoexcited electrons jump from $VB$ to $CB$ of TiO$_2$ and then quickly transfer to Cu nanoparticles due to the formed Schottky barrier.

The fast delivery of electrons prolongs the lifetime of electron and hole pairs, which subsequently react with molecular oxygen and water respectively to form highly reactive radicals for photodegradation.$^{58-61}$ Therefore, photocatalytic activity of S4 under $UV$ irradiation is a charge separation rate determined reaction. Not only Cu but also other noble metals that have suitable electron affinity share the similar mechanism.$^{62}$
On the other hand, Cu nanoparticles also help expand absorption light spectra to longer region, which is clearly displayed in Figure 5.7. The broad absorption band of co-catalyst system is ascribed to SPR effect of Cu. The light that has proper frequency introduces magnified electric field around Cu nanoparticles, which induce the collective oscillation of conductive electrons. As a result, the boosted electrons with enough energy are driven to interface, overcome Schottky barrier and injected back to CB of TiO₂. It is believed that the fast and efficient migration of electrons to TiO₂ contributes to the reverse transfer back to CB rather than to adsorbed oxygen. The whole process only takes less than 240 fs. Moreover, abundant vacant electron trap states distributed on the conduction band are also beneficial for the electron injection. This electron transport mode can also be verified by photocurrent in response to plasmon band. Under visible part of solar light, photon-excited electrons around Cu nanoparticles inject into the CB of TiO₂ due to SPR effect (red color ball in Figure 5.8b). Subsequently adsorbed oxygen molecule can trap these energetic electrons to form superoxide radicals, leading to charge separation and enhancement of dye degradation.
Zheng et al. also found the same process that dissolved oxygen was reduced on the surface of TiO$_2$ in the metal-semiconductor co-catalyst.\textsuperscript{65} Simultaneously, the transferred electrons of Cu nanoparticles can be compensated from dyes molecules,\textsuperscript{72} which is similar to the dye-sensitized solar cell.\textsuperscript{38} For visible light irradiation, TiO$_2$ acts as mediator for electrons injected from Cu nanoparticles. The dominant role is the SPR effect of Cu, which promotes the amount of surface electron and interfacial charge transfer.

5.3.3 Influence of post annealing on photocatalytic property

Annealing process has a great influence on the photocatalytic performance of TiO$_2$ NTs.\textsuperscript{73} The amorphous TiO$_2$ NTs has poor photocatalytic behavior. However, the situation improves a lot when annealed at above 300°C. It can also influence the deposition behavior of particles reported by Chang et al.\textsuperscript{74}. They found that Pd nanoparticles agglomerated on amorphous TiO$_2$ NTs but distributed uniformly on anatase TiO$_2$.

As for the thermal dewetting of noble metal layer, the situation is different depending on the type of metal deposited. Amorphous TiO$_2$ decorated with Au layer can be transformed into crystalline TiO$_2$ with Au nanoparticles simply by annealing in air at 450°C, which exhibits good hydrogen production properties\textsuperscript{75}. However, Pt layer requires multiple calcination to have adequate catalytic ability\textsuperscript{76}. Therefore, the post annealing process for Cu loaded TiO$_2$ NTs was investigated.

As shown in Appendix Figure S17, XRD patterns of all samples with and without post annealing process can be indexed to metallic Ti and anatase TiO$_2$. Their peak intensities of samples with the same anodization duration are nearly the same, which indicates that post annealing treatment does not have significant influence on the crystallinity of TiO$_2$ NTs. Three sets of Cu loaded TiO$_2$ NTs with different anodization
time (30, 60 and 120 min) were studied to further understanding the effect of post annealing process on photocatalytic properties.

The photocatalytic degradation rates shown in Figure 5.9 illustrate that the sample with post annealing has weaker photocatalytic activity than that without post annealing, indicating that the post annealing treatment is not necessary for photocatalytic degradation application. The possible reason is that Cu atoms can insert into anatase TiO$_2$ lattice structure during the thermal dewetting process, where the recombination center would be created. Another possibility is that the post annealing may roughen the surface, which could be against uniform Cu nanoparticle deposition. Moreover, the optimum thickness of TiO$_2$ NTs is around 4.7 µm with anodization time of 30 min (Figure 5.9). Due to the limited light penetration depth and long photo-excited carrier diffusion distance towards Cu particles, thick TiO$_2$ NTs produced by long anodization time have a declined photocatalytic degradation rate.

Figure 5.9 Photocatalytic degradation rate constant of MB under solar light irradiation of TiO$_2$ NTs prepared by different anodization duration with 40 s Cu sputtering and thermal dewetting at 400°C: (a) without post annealing; (b) with post annealing.

5.3.4 Optimization of Sputtering and Dewetting Conditions

Magnetron sputtering and thermal dewetting conditions were investigated to
further improve the photocatalytic performance. The sputtering time, applied DC power and Ar pressure are three dominant parameters that can be precisely controlled during the deposition process. The thickness of deposited metal layer is determined by sputtering time, while porosity is significantly affected by DC power and Ar pressure. In this study, the influence of thickness outweighs porosity on photocatalytic performance due to its close relationship with synthesized nanoparticle size induced by thermal dewetting. Different sputtering time, 20, 40 and 80 s, was employed to explore the optimal condition.

As shown in Figure 5.10a, the surface of S6 is completely flat without distinct trace of nanoparticles. It seems to be smoother than that of S1 (Figure 5.3b). The undetectable nanoparticles formed can be attributed to the low content of sputtered Cu. Similar result was reported by Nguyen et al. who found Pt nanoparticles size would be below 8 nm when the deposited Pt layer is thin. As a result, the synergistic effect between Cu and TiO2 NTs is not working effectively, leading to a low degradation rate but still higher than that of S3 (Figure 5.10c).

The photocatalytic activity is also hindered when the deposited Cu layer is too thick. Figure 5.10b shows the agglomeration of Cu nanoparticles on S7. It is believed that the surface shading of metal clusters would reduce the photon absorption by TiO2, and the TiO2 substrate has limited interfacial contact with Cu if the particle size is too large. Moreover, the high coverage of Cu particles would block the tube mouth and thus decrease the adsorption of MB molecules, resulting in the deterioration of photocatalytic performance.
Figure 5.10 SEM images of (a) 20s sputtering (S6) and (b) 80s sputtering (S7). (c) Photocatalytic degradation rate constant of Cu loaded TiO$_2$ with different sputtering time under solar light irradiation.

Thermal dewetting is a critical step to achieve high photocatalytic performance. Among different dewetting parameters, temperature is a significant factor affecting the size and density of nanoparticles. There are two specific temperature points that determine the mobility of atom during dewetting process: the Hüttig and Tamman temperatures. The state of metal will change from solid to liquid at the melting point. As for thermal dewetting, the driving force arises from minimizing surface energy that increases dramatically with decreasing film thickness. When the thickness of metal layer is around the nanoscale, it is possible for the metal atoms to travel at a temperature below the melting point. If the temperature is higher than Hüttig temperature, metal atoms at defects are capable of moving. As the temperature reaches to Tamman temperature, the rest of atoms will be mobile. As for copper, the Hüttig and Tamman temperature are 135°C and 406°C, respectively.

The morphologies of Cu loaded TiO$_2$ NTs with 40s Cu sputtering and thermal dewetting at different temperature were shown in Figures 5.11a-c. Before the sputtering process, all TiO$_2$ substrates changed from amorphous to anatase phase after annealing at 400°C for 1 h. Thermal dewetting at 200°C produces uniformly distributed tiny nanoparticles on the tube wall between neighbor pores as shown by white dots (rectangle area) in Figure 5.11a. As the temperature increased to 300°C, small nanoparticles merge into larger ones and agglomerate together in certain area (Figure
The nanotube wall looks smoother than that at 200°C due to the absence of tiny particles. When the temperature reaches 500°C, large particles appeared with diameter of ~200 nm (Figure 5.11c), which may cover two adjacent pores in the view range. The TiO₂ NTs walls are as cleaned as that at 300°C.

The change of particle size is also proved by the UV-Vis absorbance spectrum of Cu-loaded TiO₂ NTs with different thermal dewetting treatment (Appendix Figure S18). 200°C gives rise to Cu nanoparticles that has a plasmonic absorbance band center at ~420 nm, while the absorption peak at higher temperature exhibits red shift due to the larger particle size. Similar relationship between Ag nanoparticle size and corresponding plasmon resonance peak was reported by Oldenburg ⁸¹. Therefore, it can be concluded that particle size after the thermal dewetting increases with the temperature, while the particle distribution density decreases ⁸².

The photocatalytic activity coincides with the particle size and density change, and shows decrease trend with increasing dewetting temperature (Figure 5.11d). This is because small Cu nanoparticles have sufficient interfacial contact with TiO₂, and will not retard light absorbance of TiO₂ NTs substrate, resulting in high plasmonic excitation and efficient photoexcited electrons formation. The five consecutive photodegradation tests of S8 were conducted and the results are shown in Appendix Figure S19. Although the final MB removal percentage decreased over long-time reaction, no obvious deterioration of degradation rate was found. The deactivation of photocatalytic performance can be ascribed to the possibility of oxidation during photocatalytic reaction, resulting in the absence of SPR and low electron transfer ability ⁶⁶, ⁸³. It can be concluded that the Cu loaded TiO₂ is stable and will not lose effectiveness for repeated use.
5.4 Conclusions

In summary, we report first time the synthesis of well dispersed Cu nanoparticles on anodic TiO$_2$ nanotube arrays (NTs) by physical preparation technique. Cu loaded TiO$_2$ NTs were prepared by a two-step electrochemical anodization, followed by magnetron sputtering and thermal dewetting. The decorated Cu nanoparticles exhibit remarkable visible light absorption due to the surface plasmon resonance. In the meantime, the Schottky barrier formed in the space charge region between TiO$_2$ and Cu promote photo-excited electron-hole separation, which is beneficial to efficient utilization of photons. The synergistic effect of co-catalyst system contributes to a four-time higher photodegradation rate than that of anatase TiO$_2$ under solar light irradiation. The morphology of Cu/TiO$_2$ with the highest photocatalytic efficiency is small Cu nanoparticles dispersed on surface of nanotube walls, which is synthesized by 20 s of
Cu sputtering and thermal dewetting at 200°C. Although post annealing treatment does not improve the photocatalytic performance, it is essential to transform the amorphous TiO$_2$ to anatase phase for the low temperature dewetting process.
CHAPTER 6

Self-assembly porous WO₃ prepared by electrochemical anodization

The experience learned from Ti anodization (from Chapter 2 to Chapter 5) encourages the exploration of the anodization technique for other transition metals. In this chapter, the comprehensive studies about tungsten (W) anodization were conducted to understand the effect of various anodization conditions on the WO₃ morphology. The anodic nanoporous WO₃ were annealed and modified with Ag nanoparticles through magnetron sputtering and thermal dewetting similar to Cu nanoparticles preparation methods in Chapter 5. The as-synthesized Ag-WO₃ nanocomposites work as an efficient SERS substrate for organic pollutant detection with a large enhancement factor.

* This chapter is based on a journal paper under submission to Journal of Materials Chemistry A:
Surface-enhanced Raman spectroscopy (SERS) has been employed as a powerful and non-destructive technique for molecule detection mainly based on metal or dielectric substrate. A new design for hybrid nanoporous WO$_3$ loaded with Ag nanoparticles was introduced as a stable and sensitive SERS-active substrate. Regular self-organized nanoporous WO$_3$ acted as a template and was prepared through anodization in the electrolyte containing ethylene glycol, ammonium fluoride and DI water. The effect of anodization parameters on the morphology was investigated and optimized. The uniformly distributed Ag nanoparticles on nanoporous WO$_3$ was obtained by magnetron sputtering and subsequent thermal dewetting. Rhodamine B was then used as the Raman probe for SERS measurement. The results showed that large enhancement factor of $\sim 2.1 \times 10^7$ and a low detection limit of $\sim 1 \times 10^{-6}$ M were achieved for the hybrid Ag/WO$_3$ substrate. The visible light responding behaviour of WO$_3$, synergistic interaction between Ag nanoparticles and the WO$_3$ substrate, and the plasmonic behaviour of Ag collectively contribute to the enhanced Raman scattering. Fabrication of the hybrid nanostructured material as SERS substrate is proven to be a simple and effective technique that may be extended to other semiconductors and metals.

6.1 Introduction

Tungsten trioxide (WO$_3$) is a versatile transition metal oxide with applications, such as electrochromic devices, solar cells, photocatalysts and sensors. Nanostructuring endows it with large surface to volume ratio, adjustable bonding structure and quantum size effect, leading to the enhanced performance compared to bulk WO$_3$. There are several ways to synthesize WO$_3$ nanostructure, including physical vapour deposition and liquid phase technique. Electrochemical anodization is a facile
and cost-effective way to produce self-assembly metal oxide nanostructures on a solid substrate.\textsuperscript{10}

Ever since Grimes \textit{et al.}\textsuperscript{11} first produced nanoporous WO$_3$ through anodization in oxalic acid, different electrolytes have been tried to increase the uniformity and thickness of WO$_3$ layer. Berger \textit{et al.}\textsuperscript{12} fabricated regular nanoporous WO$_3$ using an aqueous solution containing H$_2$SO$_4$ and NaF. Three-dimensional porous WO$_3$ layer was obtained in the organic electrolyte composed of ethylene glycol and NH$_4$F.\textsuperscript{13, 14} In addition to the electrolyte composition, the effects of anodization voltage and time on the morphology have also been investigated.\textsuperscript{15, 16}

Due to the solubility of WO$_3$ in the electrolyte, these conditions have to be precisely controlled to avoid inadequate or excessive dissolution during anodization.\textsuperscript{17} Temperature is another critical influence factor in anodization.\textsuperscript{18} Recently, elevated electrolyte temperature has been found to notably improve the morphology of anodic WO$_3$. For the phosphoric electrolyte, high-temperature of $\sim$100$^\circ$C was necessary to produce mesoporous or nanochannel WO$_3$.\textsuperscript{19, 20} Lee \textit{et al.}\textsuperscript{21} reported that preheating procedure is essential to produce mesoporous WO$_3$, and the layer thickness increases with electrolyte temperature.

Surface-enhanced Raman spectroscopy (SERS) is a fast, sensitive and informative method for detecting and identifying molecules at low concentrations. It is widely used in analytical chemistry for biomolecular detection and security protection.\textsuperscript{22} The amplified signal is achieved by combining several resonances, such as surface plasmon, charge transfer, molecular or excitonic resonances, depending on the SERS substrate adopted.\textsuperscript{23}

Generally speaking, two mechanisms lie behind the enhanced Raman scattering: electromagnetic enhancement (EM) and chemical enhancement (CM).\textsuperscript{24} EM is well
known as the dominant contribution to SERS caused by intensive electromagnetic field, which leads to signal enhancement on the order of $10^4$-$10^6$. On top of that, CM has a further enhancement of $\sim 10$-$10^2$, which could be attributed to charge-transfer (CT) resonances between SERS substrate and adsorbed analyte. Noble metal nanostructures are commonly used as SERS substrate with high sensitivity due to the enhanced localized electromagnetic field derived from surface plasmon resonance (SPR). However, the active SERS area is only restricted to the “hot spots” region, which strongly depends on the morphology and spacing of metal nanostructure. The rigorous fabrication conditions, low controllability and poor stability limit their practical applications.

Semiconductors have been proven to be a good alternative to conventional noble metal. They show better stability and reproducibility because of their intrinsic physical and chemical properties, and high regular nanostructure synthesized. Moreover, semiconductor could also have self-cleaning and tuneable electrical properties, which significantly extends their applications. But the fatal weakness of semiconductor substrates is the low sensitivities, because CM with limited enhancement effect is mainly responsible for their SERS.

In recent years, incorporating oxygen vacancy ($V_o$) defect is commonly used to improve the effectiveness of semiconductor substrates. The introduced $V_o$ creates associated energy levels below the conduction band, which promotes the photo-induced charge carriers separation and CT efficiency between the semiconductor and adsorbed molecules, thus significantly amplify SERS signals. Zheng et al. produced sub-stoichiometry metal oxide with high SERS sensitivities through ion irradiation technique. Non-stoichiometric W$_{18}$O$_{49}$ nanowire was reported to significantly magnify Raman spectroscopy and reduce the detection limit to $10^{-7}$ M.
The photo-induced enhancement of Raman spectroscopy (PIERS) assisted by $V_o$ exhibited significant advantage for various molecules with low Raman cross-section. Nevertheless, the $V_o$ distributes shallowly and might be easily oxidized in the air atmosphere. Compared to defect engineering, functionalizing the proper semiconductor with noble metal could provide similar benefits. The decorated metal not only acts as the electron sink to decrease the recombination rate of carriers and promote CT, but also served as SPR sites to amplify the electromagnetic field. Jiang et al. reported that TiO$_2$ nanoparticles loaded with Au showed improved SERS enhancements compared to pure TiO$_2$. On the other hand, the conventional laser wavelength for Raman detection falls in the visible light region, which could not excite semiconductor with wide band gap. WO$_3$ has suitable band positions and might be a good candidate for SERS substrate.

In this Chapter, we report a novel SERS-active substrate that is composed of nanoporous WO$_3$ and Ag nanoparticles (NPs). The hybrid Ag/WO$_3$ nanocomposite overcomes the shortcomings of each component and exhibits the synergistic effect. The nanoporous WO$_3$ was prepared through simple electrochemical anodization and its morphology was further optimized based on the understanding of anodization conditions influence. The uniform deposition of Ag NPs was achieved through magnetron sputtering and thermal dewetting technique previously used for our Cu/TiO$_2$ system. The high SERS sensitivity of hybrid substrates were measured and the possible mechanism was proposed. The hybrid Ag/WO$_3$ nanostructure will be further studied as a reusable substrate, and extend to other semiconductors and metals in the future.

6.2 Experimental section

6.2.1 Fabrication of nanoporous WO$_3$
Pure tungsten (W) foil (purity >99.8%, 20 mm×10 mm×0.3 mm) was mechanically polished and ultrasonically cleaned in DI water, acetone and ethanol for 5 minutes, respectively. The electrochemical anodization was performed in a two-electrode cell with the cleaned tungsten foil as the anode and titanium mesh as the cathode. The rectangle area of W foil (15 mm×10 mm) was exposed to the electrolyte with the composition of ethylene glycol (99% anhydrous, ECP Ltd.), ammonium fluoride (NH₄F, 98% purity, Sigma-Aldrich) and DI water. Different concentrations of NH₄F and water, external potentials, duration time and electrolyte temperature were used to optimize anodic WO₃ morphology (as listed in Table 6.1). In the meantime, the transition current was recorded by the thermocouple data logger (pico technology, USB TC-08). The obtained WO₃ film was then washed in ethanol and fully dried at ambient air. Thermal annealing was conducted on WO₃ film at 500°C for 2 h under argon protection and gradually cooled down in the furnace.

Table 6.1. Summary for W electrochemical anodization parameters

<table>
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<tr>
<th>Sample Code</th>
<th>Ice Bath</th>
<th>Electrolyte</th>
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<th>Time (h)</th>
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<td></td>
<td>Water (vol.%)</td>
<td>NH₄F (wt.%)</td>
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<td></td>
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<tr>
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<td>0</td>
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</table>

6.2.2 Synthesis of Ag NPs loaded nanoporous WO₃

Evaporation of the Ag film was conducted using a Direct Current (DC) reactive
magnetron sputtering system (Kurt J. Lesker Nano 36). The working chamber pressure was set at $1.0 \times 10^{-5}$ Torr during deposition procedure. When the target pressure was achieved, 10 mTorr argon gas and 100 W power were used to excite the plasma. The deposition process was performed for 20 s under an argon atmosphere with a pressure of 3 mTorr. The as-synthesized nanocomposite was then thermally dewetted at 250°C for 1 h in argon. For comparison, annealed WO$_3$ with Ag sputtering and as-anodized WO$_3$ with Ag sputtering and dewetting were also prepared.

6.2.3 Raman spectra measurement

Raman spectra were measured on a Renishaw RM1000 Raman microprobe system equipped with a Leitz microscope. A ×50 objective with 0.95 NA was used which allows 1 – 2 µm laser spot size on the surface. An air-cooled argon ion 488 nm blue laser was used as the excitation source. The detector is a thermoelectrically cooled CCD. The spectrometer was equipped with a 2400 g/mm holographic grating and a HNF to remove Rayleigh scattered light, and the entrance slit was 50 µm.

Different concentration of Rhodamine B (RhB) was selected as the Raman probe. For each test, 3 µL of RhB solution was dropped onto the SERS substrate using a 20 µL pipette and dried in the air for 5 min before conducting the Raman measurement. The spectra were collected with an acquisition time of 60 s and 3 accumulations. To improve reproducibility of the test, Raman spectra were recorded from three different spatial positions and averaged. The obtained spectra were analysed by using the GRAMS 32 spectroscopic software.

6.2.4 Characterization

The morphology was characterized by field-emission scanning electron microscopy (FE-SEM, Philips XL-30S). The crystal structure was identified through X-ray powder diffraction (XRD, Bruker D2-Phaser) with Cu K$_\alpha$ radiation between 2θ from
20°-80°, and a high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G² F20, 200 kV). The chemical composition was determined by energy dispersive spectroscopy (EDS) equipped on FESEM.

X-ray photoelectron spectroscopy (XPS, PHI Quantera- II SXM) with pass energy of 20 eV was used for the surface analysis. All XPS spectra were calibrated by the interstitial carbon C 1s peak with an energy of 284.8 eV. The optical properties were recorded by Shimadzu UV-2500 UV-Visible spectrophotometer.

6.3 Results and discussion

6.3.1 Fabrication of nanoporous WO₃

Prior to this report, poor control of reaction rates and a lack of long-range ordered morphology hindered the application of WO₃. In order to produce regular WO₃ nanostructures, an ice-bath was adopted rather than a heated electrolyte. The optimal conditions for obtaining the regular morphology were decided as follows:

- Anodization was performed at a constant voltage of 40V,
- The ethylene glycol based electrolyte contains 1.8 wt.% NH₄F and 2 vol.% DI water, and
- Anodization time was 2 h.

As shown in Figure 6.1a, the as-prepared WO₃ nanostructure is uniform all over the surface, similar to the highly ordered TiO₂ or Al₂O₃ structure. The structure is made up of independent pores with inner diameter of ~230 nm (Figure 6.1b); and the WO₃ layer is around 200 nm thick (Figure 6.1c). Although the maximum thickness of WO₃ film did not improve a lot, it has the largest pore size reported to-date, which is desirable for sensing properties and is an ideal support for the next-step Ag deposition.⁴⁵, ⁴⁶
The chemical composition of the anodic WO$_3$ layer was examined through XPS and EDS analysis. As shown in the XPS survey spectra (Appendix Figure S20a), the distinct peaks can be attributed to the W, O and C element, which is consistent with EDS results (Appendix Figures S20b and S20c). The EDS mapping analysis also indicates that WO$_3$ was uniformly distributed across the whole surface. Compared to anodic WO$_3$, there is no obvious shift of W 4f$_{7/2}$ (35.93 eV) and W 4f$_{5/2}$ (38.12 eV) peaks after annealing (Appendix Figure S21), which are the characteristic binding energy of the W$^{6+}$ doublet. While two small peaks with lower binding energy of 31.26 eV and 33.4 eV that represent metallic W disappears. Generally the amorphous structure produced by anodization is detrimental to performance, so subsequent heat treatment is always required.

The core level spectra of W 4f after annealing were fitted based on Gaussian
functions (Figure 6.2a). The strong peaks centred at 35.95 eV (W 4f7/2) and 38.11 eV (W 4f5/2) illustrate the formation of fully oxidized WO3. Meanwhile, the existence of two broad peaks (34.86 eV for W 4f7/2 and 37.07 eV for W 4f5/2) reveals the formation of oxygen deficient tungsten oxide (WO3-x).49 However, the atomic percentage of W5+ is less than 9%, which is far less than that needed (> 20.9%) for SERS enhancement reported by Zheng et al.26 As shown in Figure 6.2b, the asymmetric O 1s peak could be resolved into two components, lattice oxygen (O lattice at 530.7 eV) and adsorbed oxygen (O adsorbed at 531.83 eV). While the former one is related to the W-O bond, the later corresponds to surface hydroxyl groups.50

Figure 6.2 High resolution XPS spectra of (a) W 4f and (b) O 1s after annealing

Figure 6.3a illustrates the XRD patterns of anodic WO3 film before and after annealing. It is clear that anodic WO3 only shared the same diffraction peaks with the metallic W substrate due to the amorphous structure produced. The small peak at ~43° might be ascribed to the formation of sub-stoichiometric WO3. However, two clear diffraction peaks appeared at 23.2° and 33° after annealing, which could be attributed to the (002) and (022) crystal facet of monoclinic WO3.20, 51

The TEM lattice fringes of annealed WO3 also verify the phase change after
annealing with the interplanar distance of 0.384 nm and 0.271 nm that corresponds to (002) and (022) plane, respectively (Figure 6.3b). Furthermore, as shown in Appendix Figure S22, the Raman spectra of anodic WO₃ has two broad Raman bands at ~790 and 920 cm⁻¹ possibly due to the formation of hydrated WO₃.⁵² New sharp peaks were observed at 271, 713, and 807 cm⁻¹ after heat treatment, which could be assigned to bending and stretching mode between W and O atoms of monoclinic WO₃.⁵³

Figure 6.3 (a) XRD patterns of WO₃ nanoporous before and after annealing; (b) HRTEM image of annealed WO₃.

6.3.2 Effect of anodization conditions on morphology

It is well known that the nanostructure obtained through anodization reflects the interactive effects of field-assisted oxidation, field-assisted dissolution and chemical dissolution; the contributions of these processes can be controlled by tuning preparation conditions.⁵⁴ The influence of anodization parameters on TiO₂ and Al₂O₃ nanostructure has been well studied.⁵⁵, ⁵⁶ Compared to the regular tubular or porous nanostructure of TiO₂ and Al₂O₃, anodic WO₃ nanostructure seems to be highly sensitive to the conditions and systematic analysis of different parameters is limited. In this study, their influence was elucidated according to the SEM figures and transient currents recorded (Figure 6.4).
For some transition metal oxides, the critical anodization temperature for regular morphology fabrication was reported to be below zero. Low temperature anodization of W was attempted from this perspective. As shown in Appendix Figure S23a and S23b, W1 exhibits the well-aligned and uniform surface topography with porous structure. However, the W2 prepared in No-ice bath only has breakdown oxide layers with micron sized holes and aggregated nanoparticles (Appendix Figures 23c and 23d). As for W1, the current density (CD) shows a sharp decrease at the beginning and gradually increases to a steady state (Figure 6.4a), which could be attributed to the dominated oxidation reaction in the initial stage and subsequent dynamic equilibrium between formation and dissolution. It is very similar to the typical CD curve of Ti and Al anodization. The continued increase in the CD of S2 illustrates that the dissolution overcomes the oxidation, but it also shows a slight decay afterward due to the formation of oxide layer. A similar trend was also found in W anodization under 15 V. It could be concluded that electrolyte temperature is the determinant factor in synthesizing nanoporous WO₃ layer.

Water is another key factor in anodization, which not only acts as the oxygen source during anodization, but also increases the conductivity of electrolyte and promotes the diffusion of etching ions. It can be seen in Appendix Figure S24a that only a portion of W3 surface turns into the nanopores with other parts remain as a compact layer. Compared to CD curve of W1, W3 does not show the obvious increase in DC after an initial drop (Figure 6.4b), indicating that the dissolution process might be suppressed due to the limited water content. When water content increased above 5 wt.%, no trace of nanoporous structure could be found except for the cracked oxide layer as shown in Appendix Figures S24c and S24d. W4 seems to be thicker and less etched than W5, which might be attributed to the enhanced dissolution with increased
water. The hypothesis could be verified by the lower CD of W4 than that of W5 (Figure 6.4b). In our anodization system, the water content has a more pronounced effect on the dissolution rate than oxidation rate.

The nanoporous WO₃ were reported to be obtained by anodization at 60 V in aqueous or organic electrolyte. However, the situation is different in our case. As shown in Appendix Figure S25, 20 V only produces a thin compact WO₃ oxide layer, which could not even conceal the surface appearance (wrinkle) of the initial W metal substrate, while large cracks and holes were found at 60 V with the size of ~5 μm. Compared to low voltage anodization, CD at 60 V increases continuously with oscillation and then suddenly decreases to a low value (Figure 6.4c). This situation might be ascribed to the breakdown of the initial oxide layer formed caused by thermal stress and the re-anodization of newly exposed W substrate.

The concentration of NH₄F is directly related to the dissolution of the WO₃ layer formed. As shown in Appendix Figures S26a-d, the distribution of the nanopores gradually spread from a small area to the whole surface with increasing NH₄F to 1.8 wt.% The regular nanopores were etched severely and only concave left with increasing NH₄F concentration (2.1 wt.%). These processes are vividly reflected in Figure 6.4d, in which that CD values rise with the increase of NH₄F concentration. The continuous growth process of nanoporous WO₃ under optimized conditions was captured as shown in Appendix Figure S27. The compact oxide layer was etched gradually and excessive dissolution started to disrupt the regular porous structure after 2 h.
Figure 6.4 Current density versus time curves during anodization of (a) W1 and W2; (b) W1, W3-W5; (c) W1, W6 and W7; (d) W1, W11-W13.

6.3.3 Synthesis of Ag/WO3 hybrid nanostructure SERS substrate

Compared with the conventional metal loading techniques, such as photochemical reduction\textsuperscript{63} and electro-deposition\textsuperscript{64}, a combination of magnetron sputtering and thermal dewetting has been proved as an effective way to achieve uniform distribution of NPs in our previous work.\textsuperscript{44} In this chapter, the optimized sputtering and dewetting conditions were determined through trial and error according to the distribution and shape of Ag NPs formed. As shown in Figure 6.5a, the surface of WO\textsubscript{3} was roughened along with the narrowed pores after sputtering due to the deposition of the Ag layer. The rough surface spontaneously transformed into a hybrid structure composed of well-defined Ag NPs and nanoporous WO\textsubscript{3} after dewetting (Figure 6.5b). The Ag NPs were uniformly distributed around pore mouth with a mean size of \textasciitilde35 nm (shown in Appendix Figure S28). Some of them even attached to the wall or sank onto the bottom, which might be
beneficial to increase the contact area between Ag and WO₃. Meanwhile, the pores look the same as that of as-anodized WO₃.

Figure 6.5 SEM images of annealed W1 with 20 s Ag sputtering: (a) no thermal dewetting and (b) thermal dewetting at 250 °C for 1 h.

The chemical composition of deposited Ag was also determined by Gaussian functions fitting as shown in Figure 6.6a. The Ag 3d spectra could be deconvoluted into four peaks, which are centred at 367.36 and 368.16 eV for Ag 3d₅/₂ and 373.37 and 374.17 eV for Ag 3d₃/₂. The doublet peak with larger binding energy could be attributed to the metallic Ag (Ag⁰) and predominant in the Ag NPs formed, and the other two peaks belong to the silver oxide.⁶⁵, ⁶⁶

To further confirm the valence of Ag, Ag MNN Auger peak was analysed based on the kinetic energy (Figure 6.6b). The Auger peak could also be resolved into four individual peaks, 349.1 eV, 352.5 eV, 354.7 eV and 358.1 eV, respectively, which represent the chemical state of Ag⁰ and oxidation state (Ag¹⁺).⁶⁷, ⁶⁸ indicating the existence of metallic particles and Ag₂O after sputtering and thermal dewetting. The AgN-WO₃ hybrid nanocomposite exhibits strong absorption both in the UV and visible light region (Appendix Figure S29). The enhanced optical properties might be attributed to the SPR effect of Ag NPs with small plasmon peak at ~450 nm,⁶⁹ while electrons transition between WO₃ substrate and Ag NPs might explain the additional new
absorbance over the 350-420 nm region.\textsuperscript{70, 71}

Figure 6.6 (a) High resolution XPS spectra of Ag 3d and (b) Ag MNN Auger spectrum. Inset is Ag MVV spectrum.

6.3.4 SERS effect of AgN-WO\textsubscript{3}

The RhB dye solution with a concentration of $1 \times 10^{-5}$ M was used as the Raman probe molecule on different synthesized substrates. As shown in Figure 6.7a, there is no signal detected on the annealed WO\textsubscript{3} substrate, while a small but sharp RhB characteristic peaks show up at 1648 cm\textsuperscript{-1} after Ag sputtering. Another two broad peaks that centred at around 1350 and 1580 cm\textsuperscript{-1} could not be assigned to RhB because they also existed on AgN-WO\textsubscript{3} substrate without dyes (Appendix Figure S30). They may come from the Raman band of carbon impurities.\textsuperscript{72} The SERS activity of annealed WO\textsubscript{3} seems to be reinforced after Ag film deposition even though it is not very apparent.

When the thin Ag film was transformed to Ag NPs after thermal dewetting, the SERS sensitivity of RhB improved dramatically with many characteristic RhB peaks emerging.\textsuperscript{73} It can be concluded that the morphology of Ag has a significant influence on the efficiency of SERS enhancement and Ag NPs turn out to be effective shape for that.\textsuperscript{74} Moreover, the detection accuracy of AgN-WO\textsubscript{3} substrate could be lowered to $1 \times
$10^{-6}$ M as shown in Appendix Figure S30. There are several obvious signals (marked by red circles) detected with $1 \times 10^{-6}$ M, while no trace of RhB peaks was found with $1 \times 10^{-7}$ M. The SERS effect of amorphous anodic WO$_3$ loaded with Ag NPs was also conducted to measure SERS induced by Ag NPs and reveal the importance of crystalline WO$_3$. As shown in Figure 6.7b, the intensity of SERS signals introduced by the Ag NPs was much lower than that of AgN-WO$_3$. However, it maintained the features of RhB peaks as shown in inset figure compared to the normal Raman spectra (Figure 6.7b).

![Figure 6.7 Raman spectra of RhB ($1 \times 10^{-5}$ M) on different substrates: (a) Annealed WO$_3$ with different Ag morphology; (b) Normal Raman spectra without substrate (Non-SERS), amorphous WO$_3$ with Ag NPs (SERS-Ag NPs) and AgN-WO$_3$.](image)

Based on the enhancement factor (EF) measurement equation,$^{38}$ the average EF was calculated for AgN-WO$_3$ and Ag NPs as $2.1 \times 10^7$ and $4.8 \times 10^5$, respectively. The average enhancement factor of different substrate was calculated according to the equation as following:

$$EF = \frac{I_{SERS} \times C_{RS}}{I_{RS} \times C_{SERS}}$$  \hspace{1cm} \text{Eq. 6.1}

Where $I_{SERS}$ and $I_{RS}$ are the intensities of the Raman probe obtained from SERS-active substrate and ordinary Raman, respectively. Correspondingly the $C_{SERS}$ and $C_{RS}$ are the
concentrations of the Raman probe for each test.

The Raman peak shift, intensity and calculated enhancement factor are listed in Table 6.2. Therefore, the annealed nanoporous WO₃ and particular Ag NPs are considered as the essential conditions to achieve the high SERS sensitivity.

Table 6.2. Calculated enhancement factor of SERS-Ag NPs and SERS-AgN-WO₃

<table>
<thead>
<tr>
<th>Probe</th>
<th>Raman shift (cm⁻¹)</th>
<th>Intensity (a.u.)</th>
<th>SERS-Ag NPs shift (cm⁻¹)</th>
<th>Intensity (a.u.)</th>
<th>EF</th>
<th>SERS-AgN-WO₃ shift (cm⁻¹)</th>
<th>Intensity (a.u.)</th>
<th>EF</th>
</tr>
</thead>
<tbody>
<tr>
<td>RhB</td>
<td>1195</td>
<td>807</td>
<td>1196</td>
<td>260.4</td>
<td>5.12×10⁵</td>
<td>1197</td>
<td>7717.8</td>
<td>2.03×10⁷</td>
</tr>
<tr>
<td></td>
<td>1282</td>
<td>429</td>
<td>1285</td>
<td>161.2</td>
<td>4.79×10⁵</td>
<td>1281</td>
<td>9640.5</td>
<td>2.06×10⁷</td>
</tr>
<tr>
<td></td>
<td>1363</td>
<td>1580</td>
<td>1360</td>
<td>436.0</td>
<td>5.77×10⁵</td>
<td>1359</td>
<td>20523.2</td>
<td>2.39×10⁷</td>
</tr>
<tr>
<td></td>
<td>1507</td>
<td>1202</td>
<td>1508</td>
<td>498.3</td>
<td>3.84×10⁵</td>
<td>1507</td>
<td>20670.6</td>
<td>1.80×10⁷</td>
</tr>
<tr>
<td></td>
<td>1565</td>
<td>1719</td>
<td>1565</td>
<td>593.0</td>
<td>5.24×10⁵</td>
<td>1564</td>
<td>25446.3</td>
<td>3.13×10⁷</td>
</tr>
<tr>
<td></td>
<td>1646</td>
<td>2897</td>
<td>1649</td>
<td>1066.0</td>
<td>4.49×10⁵</td>
<td>1647</td>
<td>42300.8</td>
<td>1.33×10⁷</td>
</tr>
</tbody>
</table>

It is well known that the SERS derives from EM and/or CM through electromagnetic field amplification or CT between adsorbed probe and active substrate.⁷⁵ Due to the lack of SPR, the SERS happened on semiconductor substrate can be attributed to the charge-transfer process, relying on molecular resonance within the probe, exciton resonance within semiconductor and charge-transfer resonance between them.²³, ²⁴ The annealed WO₃ in our work has the absorption edges around 496 nm with band gap of 2.51 eV (Appendix Figure S30), indicating its ability to use the visible Raman laser light to produce electron-hole pairs. However, the additional production of electrons did not much improve the RhB signal intensity (Figure 6.7a), which might be ascribed to the high recombination rate of the photo-induced charge pairs.

As for metal nanoparticles, the SPR, molecular transition and CT contribute to the SERS collectively. The amorphous WO₃ decorated with well-defined Ag NPs yielded high SERS activity with EF of 4.8×10⁵ (Figure 6.7b), which has the same order as that
of the solo metal. It can be speculated that the augmented electric field induced by SPR of Ag NPs along with charge-transfer resonance (between Ag and probe) could be responsible for the enhanced intensity because the amorphous WO$_3$ has the wide band gap and might easily block CT process within WO$_3$.

The hybrid SERS-active substrate AgN-WO$_3$ combines the advantages of both semiconductor and metal NPs. A 40-fold increase in the intensity of AgN-WO$_3$ than that of pure Ag NPs might be ascribed to the promotion of CT process between WO$_3$ and Ag NPs as shown in Figure 6.8. As the work function of WO$_3$ is larger than that of Ag, electrons thermodynamically flow from Ag to the conduction band (CB) of WO$_3$ after direct contact until a new quasi-Fermi level ($E_f$) is formed. When irradiated by the Raman laser light, photo-excited electrons jump to $CB$ and then migrate to Ag NPs due to the higher energy level of $CB$ than the equilibrium Fermi level. The Schottky barrier formed in the space charge region reduce the recombination rate of charge carriers and increase the electron density around Ag NPs.

This hypothesis could be supported by the additional peak position in UV-vis absorbance spectra (Appendix Figure S30). The plasma wavelength is inversely proportional to the electron density of metal. Normally the Ag NPs with size larger than 30 nm have plasma absorbance peak at wavelength longer than 400 nm. However, Ag NPs absorbance peak exhibits a blue shift in our system, centred at ~374 nm. This behaviour might be explained by the increasing electron density caused by electron transition from WO$_3$. The shift of W4f spectra also illustrates the electrons migration between annealed WO$_3$ and Ag. Similar results were reported for WO$_3$ nanodomes embedded by Au NPs. The high density electrons of Ag NPs trigger the enhanced local electric field through SPR and thus increase the Raman scattering. The final chemical charge transfer step between the Ag and Rhodamine B though is still not fully
resolved. Further studies are underway involving time-resolved transient absorption spectroscopy to understand the nature of the final step.

Figure 6.8 Schematic illustration of charge transfer process of AgN-WO₃.

6.4 Conclusions

In summary, highly aligned nanoporous WO₃ with pore size of ~230 nm and thickness of ~200 nm was produced via anodization of W. The optimized anodization conditions are ethylene glycol based electrolyte (containing 1.8 wt.% NH₄F and 2 vol.% DI water) under 40 V for 2 h in ice bath. The porous morphology is very sensitive to the change of electrolyte temperature, applied voltage and water content, while the influence of ammonium fluoride concentration and duration time is less critical.

Anodic nanoporous structures provide an ideal template for Ag deposition, resulting in Ag nanoparticles formation with size ~35 nm and uniformly distribution around the mouth of pores. Compared to the annealed WO₃ and Ag nanoparticles decorated amorphous WO₃, the AgN-WO₃ exhibits increased Raman intensity by orders of magnitude with the enhancement factor of $2.1 \times 10^7$. The high SERS activity could be attributed to extra electrons, charge transfer and plasmon resonance, resulting from
photo-induced charge pairs produced within WO₃, reduced recombination rate due to
the Schottky barrier, and the plasmonic effect of Ag nanoparticles. Therefore, hybrid
AgN-WO₃ substrates combine the advantage of semiconductors with low band gap,
uniform metal nanoparticles and heterojunctions to provide significantly enhanced
Raman signals. This methodology could also be extended to other combinations of
suitable semiconductors and noble metal nanoparticles.
CHAPTER 7

Self-organized ZnO nanorods prepared by electrochemical anodization

This chapter is a parallel study with the tungsten anodization and discusses about the possibility of preparing 1D ZnO nanostructure. Compared to TiO$_2$ and WO$_3$, ZnO is a special transition metal oxide with low chemical stability. In other words, there is a narrow process window for Zn anodization due to the severe dissolution process during the reaction. In this chapter, the aqueous NaOH solution was used as the electrolyte. Different electrolyte concentration and voltages were tried to find the optimal conditions. In addition, the optical properties of anodized ZnO nanorod were tested as the dark color appearance was present in the anodization under low voltage.

CHAPTER ABSTRACT

A new type of self-assembled Zinc oxide (ZnO) nanostructure has been prepared by electrochemical anodization of Zinc foil in NaOH aqueous electrolyte. Under optimized anodization conditions, well defined nanorods were obtained with stacking nanoparticle layer on the top and straight cellular structures underneath. The relationships between morphology of nanostructures and anodization parameters were studied in detail through field-emission scanning electron microscopes (FESEM), X-ray powder diffraction (XRD) and energy-dispersive X-ray spectrometer (EDS). The experimental results indicate that the primary factor affecting anodic nanostructure is the applied voltage, while anodization time and electrolyte concentration also play significant roles in tailoring nanorod morphology.

7.1 Introduction

Due to the direct wide band gap (around 3.4 eV), large exciton binding energy (60 meV) and high electron mobility\(^1\), zinc oxide (ZnO) has attracted great attention over past decades and found potential applications in light emission\(^2\), photocatalysis\(^3\), optoelectronic and sensor devices\(^4\), \(^5\). A wide range of ZnO nanostructures can be obtained through different techniques, such as hydrothermal processes\(^6\), chemical vapour deposition (CVD)\(^7\) and template-directed method\(^8\). Apart from these methods, electrochemical anodization appears to be an efficient, highly controllable and cost effective approach to fabricate ZnO\(^9\).

Unlike titanium and other valve metal that have been successfully anodized with regular nanoporous or nanotubular structure\(^10\), \(^11\), amphoteric anodic ZnO is hard to form with similar ordered morphology due to its instability in both acidic and alkaline electrolytes. However, various ZnO nanostructures can be prepared through anodization
Nanosheet and nanoflower morphologies are usually present in acidic electrolytes anodization. While nanoparticle and nanowire shapes are prone to appear in alkaline solution. It is interesting that even nanoporous ZnO can be synthesized in DI water through anodization.

Among different morphologies, highly ordered nanoporous and nanotubular oxide with large surface-volume ratio have wide potential applications. Therefore, much effort has been made to tailor anodic ZnO into tubular shape through changing experimental conditions, such as anodizing Zn foil in sulphides based electrolyte or at extremely low temperature. Recently, Ono et al. reported a method for fabricating anodic ZnO with porous structure in NaOH solution. However, little attention has been paid to the morphology evolution during anodization process.

In this chapter we present a facile approach to produce anodic ZnO nanorods in NaOH electrolyte and report a progress in understanding formation mechanism and morphology control of this anodization system. At the beginning we prepared well-defined nanorods for the first time by electrochemical anodization and then studied the mechanism of nanorods formation. We investigated the effect of experimental conditions on the morphology evolution and proposed optimization of reaction conditions. These results may provide information to design well-aligned one-dimensional ZnO nanostructures for various applications.

7.2 Experimental procedure

7.2.1 Preparation of anodic nanostructures

Cold-worked Zn foils (99.99% purity) of 0.2 mm thick were cut into specimens with size of 30×25×0.2 mm. Surface of foils were mechanically polished to mirror-like finishing by 3 μm diamond suspension prior to anodization. Subsequently, they were ultrasonically cleaned successively in acetone, ethanol and distilled water, and placed in
a nitrogen stream for drying. Zn foils were used as the anode in a two-electrode cell, while titanium mesh placed at a distance of 3 cm as the cathode. The anodization process was performed in NaOH aqueous electrolyte with constant stirring at ambient temperature. Different DC voltages (5-40 V), anodization time (0.5-1.5 h) and concentrations of NaOH electrolytes (0.05 M to 0.2 M) were employed. The resulted anodized foils were then cleaned in distilled water to remove remaining electrolyte and immersed in ethanol for 12 h at room temperature. Finally, they were dried and stored in a desiccator for characterization.

7.2.2 Characterization of anodic nanostructures

The surface and cross-section morphologies of anodized Zn sheet were observed with an field-emission scanning electron microscopes (FESEM, Philips XL-30S) operating at 5 KV. Their crystal structures were studied through X-ray powder diffraction (XRD, D2-Phaser, Bruker, Germany) with Cu Kα radiation (λ = 1.5406 Å). XRD patterns were recorded at a 2θ range of 20 to 80°. The chemical composition was characterized using energy-dispersive X-ray spectrometer (EDS). The UV-Vis absorbance spectrum were recorded on Agilent 8453 UV-Vis spectrophotometer over the wavelength range of 400-800 nm.

7.3 Results and discussion

7.3.1 Formation of regular nanorods ZnO

From cross-sectional view in Figure 7.1a, anodic film is composed of a thin compacted layer on the surface and vertically ordered cellular structure underneath. The top view in Figure 7.1b shows surface layer is densely arranged and piled up nanoparticles. XRD was employed to confirm crystal structure of synthesized film. As shown in Figure 7.1c, the pronounced diffraction peaks with green diamonds can be indexed as ZnO although most obvious peaks marked by blue dots belong to the Zn
substrate. These ZnO diffraction peaks correspond to (100), (002) and (101) lattice planes, indicating polycrystalline nature of anodic ZnO film. In addition, XRD patterns of the anodic films after annealing (Appendix Figure S31) only show the narrowing full width at half maximum (FWHM) of ZnO peaks, illustrating larger grain size and better crystallization with increasing annealing temperature.

Normally, the anodic film with amorphous structure can be fabricated through electrochemical anodization\textsuperscript{25-27} or converted to crystalline phase with post annealing\textsuperscript{28}. The ZnO with hexagonal wurtzite structure fabricated directly by anodization without annealing can be attributed to the unique regular cellular structure, which provides a pathway for ionic conduction and promote the growth of crystallized ZnO\textsuperscript{29}. The composition of anodic film was characterized through EDS, which also confirms the formation of ZnO\textsuperscript{30}. It can be seen in Figure 7.1d that Zn and O account for the main elements and their atomic ratio is approximately 1. The elements composition of cross-sectional layer also refers to the ZnO nanostructure obtained (Appendix Figure S32).
Figure 7.1 FESEM images of (a) cross-sections and (b) surface of anodic film prepared in 0.1 M NaOH aqueous electrolytes with 12 V for 1 h; (c) XRD patterns and (d) area scanning EDS spectrum of (b)

The formation of anodic ZnO film can be attributed to dynamic competition between Zn oxidation, chemical etching and field-assisted dissolution. Under certain anodization conditions, oxidation rate and dissolution rate will reach a dynamic equilibrium at a steady state and oxide layer with a critical thickness can be obtained\(^3\)\(^1\). As shown in Figure 7.2, oxygen-containing anions, such as \(O^{2-}\) and \(OH^-\), migrate to substrate/oxide interface to form oxide layers as following\(^3\)\(^2\):

\[
Zn + O^{2-} \rightarrow ZnO + 2e^- \quad \text{Eq. 7.1}
\]

\[
Zn + OH^- \rightarrow ZnO + H^+ + 2e^- \quad \text{Eq. 7.2}
\]

Two dissolution processes simultaneously contribute to the final shape of anodic ZnO film. One is the chemical etching occurring on the top surface of oxide due to presence of \(H^+\) ions\(^3\)\(^3\). The other is electrochemical etching happening in the oxide/electrolyte interface at bottom of oxide layer. Their relevant chemical reactions are as following:

\[
ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O \quad \text{Eq. 7.3}
\]

\[
ZnO + OH^- \leftrightarrow ZnOOH^- \quad \text{Eq. 7.4}
\]
As for the formation of nanoparticles on surface (Figure 7.1b), it has a close relationship with the unevenly distributed partial corrosion. Newly formed ZnO layers should not be flat, resulting in inhomogeneous distribution of electric field. The amorphous oxides or convex parts tend to be etched preferentially with the help of chemical etching and anisotropic field-assisted dissolution following Eq. 7.3 and Eq. 7.4, leading to partially dissolved ZnO nanoparticles.

The detailed information about cellular morphology underneath is given in Figures 7.3a-c. The upper, middle and bottom parts have smooth and straight cellular shape with similar width (~80 nm). Formation of such kind of orderly nanostructure can be attributed to ions transportation under electric field as shown in Figure 7.3d. During anodization process, thickness-varying electric field $E$ is established through oxide layer under a constant voltage $U$. The generated $E$ can enhance the oxidation rate as well as dissolution rate.

According to Tafel’s law, inward oxygen-containing ionic current $j$, which determines oxidation rate, has exponential relationship with $E$. Under effective electric field, transition of oxygen-containing anions to substrate/oxide interface will be accelerated (marked by dark arrow in Figure 7.3d), leading to consecutive generation of ZnO following Eq. 7.1 and Eq. 7.2. On the other hand, $E$ can cause polarization and impairment of Zn-O bond, which facilitate the preferential dissolution effect of $OH^-$ following reaction Eq. 7.4 illustrated by blue arrow in Figure 7.3d. Finally, a dynamic balance between oxidation and dissolution is reached, leading to the formation of well-defined cellular structure and relatively thick ZnO layer.
Figure 7.3 FESEM cross-section images of different parts of anodic film prepared in 0.1M NaOH aqueous electrolytes at 12 V for 1 h: (a) upper part, (b) middle part, (c) bottom part. (d) Schematic illustration of cellular structure formation process.

This nanostructure was further investigated from sectional views. As shown in Figure 7.4, straight cellular arrays are closely packed and separate from each other marked by yellow dots from top section view. However, there are no pores inside the cellular structure from bottom section view, which is different from the nanotubes prepared by Ti anodization. Therefore, it can be assumed that the as-formed cell-like structures are nanorods rather than nanotubes.
7.3.2 Effect of anodization conditions on the nanostructure of ZnO

Generally, thick layers with rough structures can be obtained with high voltage, long anodizing duration and high temperature. We investigated the effects of applied voltage, anodization time and electrolyte concentration on the morphology evolution of anodic ZnO.

7.3.2.1 Effect of applied voltages

The effect of applied voltages on the morphology was studied in 0.1 M NaOH electrolyte for 1 h at different voltages ranging from 5 to 40 V. Nanoparticles appear on surface of all anodic ZnO films, which is similar to that with 12 V discussed above. However, their cross-sectional morphologies beneath the granular layer are quite different. Figures 7.5a-c show the porous morphology obtained with 5, 7 and 9 V having an average thickness of ~1.60 μm. When the applied voltage increases to 12 V, separate straight cells with thickness of 6-7 μm formed similar to Keller’s model of porous alumina (Figure 7.5d).
The formation of nanoporous structure can be attributed to insufficient supply of voltage ($U$). Electrical field ($E$) varies directly with $U$ and inversely with oxide thickness $d$, which can be written as following:\textsuperscript{28}:

$$E = \frac{U}{d}$$

Eq. 7.5

As the thickness of oxide layer increases with reaction progress, strength of $E$ weakens under constant $U$. When $U$ is lower than 9 V, corresponding $E$ is too weak to drive oxygen-containing ions through the oxide layers to form ZnO as marked by black line in Figure 7.6 and oxidation process will eventually stop. Therefore, the thickness of whole layers prepared under different voltages stays constant around 1.6 μm. Due to migration rate of anions reducing with increasing $d$, residual $OH^-$ ions tend to diffuse...
freely and attack the formed ZnO randomly as shown by blue arrow (Figure 7.6), resulting in porous nanostructures. When $U$ increases to 12 V, critical value of electric field $E_c$ and oxide layer thickness $d_c$ will become constant at a steady state, resulting in unchanged oxidation and dissolution rate $^{36}$. Consequently, dynamic balance will be reached, leading to production of regular nanorod arrays.

Figure 7.6 Schematic illustration of formation process of ZnO nanoporous structure

As the voltages increase to high values of 20, 30 and 40 V, ZnO layers become thicker (Appendix Figure S33). However, abnormal stacking and cracking take place on the cross-sectional area, as shown in Figure 7.7. Nanorod arrays still locate perpendicularly to the substrates with gaps or cracks between layers. Inside the gaps, numerous nanoparticles appear similar to the granular surface. This phenomenon was also reported in the anodization of tin (Sn) $^{37,38}$. The discontinuities of anodic layers can be attributed to the fast growth of layers and violent production of oxygen during anodization.

As anodization process is accelerated under high voltages, oxygen is supposed to release rapidly. Vigorous oxygen evolution may disturb local stresses of oxide/substrate
interface. Therefore, brittle nanorods arrays are apt to crack along horizontal direction, and long-range structural order is destroyed. As for the nanoparticles that are sandwiched between separate layers, their production derives from dissolution of synthesized nanorods through $OH^-$ etching. In addition, more gaps or cracks are present inside layers with increasing voltages (shown in Appendix Figure S33) due to the larger amount of oxygen liberations.

![Image of anodic film prepared in 0.1 M NaOH aqueous electrolytes for 1 h at 40 V. Inset is the image of gaps between broken layers.](image)

**Figure 7.7** FESEM cross-sectional image of anodic film prepared in 0.1 M NaOH aqueous electrolytes for 1 h at 40 V. Inset is the image of gaps between broken layers.

### 7.3.2.2 Effect of anodizing duration

The influence of anodization time on the development of nanorods was investigated in 0.1 M NaOH electrolyte at 12 V for different time length. The prepared ZnO films also have granular nanostructure on the surface. The unusual phenomenon is that initial oxide layer will be peeled off with prolong anodization time, and the secondary anodization happens on the newly exposed substrate. As shown in Appendix Figure S34a and S34b, anodic ZnO layers are fabricated and the substrate with smooth
surface marked by yellow rectangle can be found underneath oxide layer. However, initial oxide layers are partially replaced by small secondary ZnO layer when duration time extends to 1.5 h (Appendix Figure S34c). Besides for the stripping phenomenon, the internal appearance also changes with increasing anodization time.

As shown in Figure 7.8a, the anodic ZnO layer is composed of bulk-like morphology or rough nanorods. With increasing time, the shape of ZnO changes to regular nanorods (Figure 7.8b). As time extending to 1.5 h, the nanorods obtained are etched severely and lost rod-like characteristic gradually as shown in Figure 7.8c. At the beginning of anodization, oxide thickness $d$ is much thinner than the critical value $d_c$. According to Eq. 7.5, $E$ will be larger than $E_c$ at balanced state. Due to exponential relationship between $j$ and $E^{36}$, oxidation rate is greater than dissolution rate, resulting in formation of compact oxide layer.

As the oxide layer increases, oxidation rate decreases exponentially with $E$, the reducing speed is quicker than dissolution rate. A new dynamic equilibrium will be reached inevitably, causing production of regular nanorods. However, such equilibrium will be disrupted by long anodization time due to stripping of the initial layer. The remaining smooth initial nanorod arrays are severely etched by $OH^-$ ions, leading to deterioration of morphology.
Figure 7.8 FESEM cross-sectional morphologies with high magnification of anodic film prepared in 0.1 M NaOH aqueous electrolytes at 12 V for different time: (a) 0.5 h; (b) 1 h and (c) 1.5 h.

7.3.2.3 Effect of electrolyte concentration

The effect of NaOH concentration on the morphology has been studied with applied voltage of 12 V and duration time of 1 h, while concentration varied between 0.05 M and 0.2 M. Although there are densely arranged nanoparticles on the surface of all anodic films, their morphologies are not the same. With increase of NaOH concentration, fracturing phenomenon happens and even pores can be observed on the top (Appendix Figure S35). Moreover, cross-section nanostructures also have some striking difference. Only inconspicuous nanorods can be observed in 0.05 M NaOH solution (Figure 7.9a). By increasing concentration to 0.1 M, bulk-like nanostructure develops into well-aligned nanorods as shown in Figure 7.9b. However, high
concentration NaOH (0.2 M) cannot produce thicker and more regular ZnO layer. Nanorods with smooth surface are etched into granulated structure as illustrated in Figure 7.9c.

This phenomenon can be attributed to the amount of OH\(^-\) ions participating in the anodization process. In low concentration of NaOH electrolyte (0.05 M), insufficient supply of OH\(^-\) ions will produce thin oxide layer, whose thickness is thinner than \(d_c\). Thus corresponding \(E\) is higher than \(E_c\). Oxidation rate will surpass dissolution rate, thickening the obtained oxide layer and producing bulk-like nanostructure. With increase of concentration, more OH\(^-\) ions take part in reaction and hence strengthen both oxidation and dissolution rate according to Eq. 7.2 and Eq. 7.4. As oxidation process dominates in the beginning of anodization discussed in previous section, thickness of prepared ZnO will increase to \(d_c\), resulting in an equilibrium between oxidation and dissolution process. Therefore, bulk-like nanostructures are fully etched into smooth nanorods. However, growth rate of oxide layer is so quick in high concentration solution that \(d\) will exceed \(d_c\) easily, leading to dissolution process overweight oxidation process. Consequently, the thickness of oxide layer reduces and regular nanorods are deteriorated by redundant anions.
7.3.3 Optical properties of anodized ZnO

In order to study photocatalytic properties of ZnO films prepared through anodization, the optical properties need to be analyzed at first. As shown in Figure 7.10, colour of ZnO prepared in 0.1 M for 1 h faded with increase of voltages. ZnO film prepared under 5 V exhibited black colour and changed to dark blue under 7 V. The Zn foils covered by white and transparent film were obtained under high voltages, as shown in Figure 7.10c and d. This phenomenon is in agreement with results found by Hidehito \(^\text{39}\). Generally, colour variation was related to the defects \(^\text{40}\) or density\(^\text{13}\) of nanostructure obtained. Due to the insufficient oxygen-containing ions during anodization process, it is reasonable to presume that defective ZnO\(_{1-x}\) film with oxygen vacancy would account for the colour change. The exact reason needs further study.
The optical absorption spectra of as synthesized ZnO prepared under different voltages were presented in Figure 7.11a, as well as that of commercial ZnO powder. The dark-coloured specimens have large visible light absorption, while the order is disrupted in the UV region. As discussed above, the different colour may be due to the defective structure in the fabricated specimens, which also contributed to the absorption difference\(^{41}\). The oxygen-containing ions would be driven more deeply into the oxide layer under higher voltages, resulting in less defective ZnO\(_{1-x}\) production. For comparison, commercial ZnO powder without defects showed least visible light absorption. There is also a hypothesis about the colour change under different, which is related with the surface morphology or roughness conditions. Further research would be
carried out in the future.

As annealing is an effective way to tailor defective state of ZnO, post-annealing process were employed on the as-synthesize ZnO foils. The optical absorption spectrum after post-annealing was shown in Figure 7.11b. It shifted to high wavelength with increase of annealing temperature. However, the visible light absorption did not change a lot. In the inset, it could be found that the value of absorption rose slightly with the annealing temperature.

![Figure 7.11](image)

Figure 7.11 UV and visible light optical absorption spectra of: (a) anodic ZnO and (b) annealed ZnO anodised at 12 V.

Due to the obvious shift of absorption spectra in different temperature annealing, the band gap ($E_g$) were supposed to change and estimated by the following expression 42:

$$a h \nu = A (h \nu - E_g)^{1/2}$$  \hspace{1cm} Eq.7.6

Where $a$ is absorption coefficient, $h$ is Plank’s constant, $\nu$ is frequency of vibration and $A$ is a proportionality constant.

The optical bandgap was determined by extrapolating the linear and the results were shown in Figure 7.12. It was illustrated that bandgap under different voltages fluctuated around 3.2 eV. The bandgap value decreased gradually with the increase of
post annealing temperature, which is also reported by Sachiko ⁹.

![Figure 7.12](image)

Figure 7.12 (a) Plots of \((ahv)^2\) versus \(hv\) for synthesized sample under 12 V after annealing at 350°C, (b) bandgap energy of different specimens.

### 7.4 Conclusions

We have demonstrated a facile method to prepare a new type of self-assembled ZnO nanostructure. Well-aligned anodic ZnO nanorods have been fabricated by anodization Zn metal using the optimized conditions in 0.1 M NaOH aqueous electrolytes at 12 V for 1 h. The obtained ZnO layer is ~7 μm thick and composed of nanorods of ~80 nm width with compact granular morphology on the surface. Applied voltage plays a crucial role in determining the morphology of ZnO. While porous structures can be obtained at voltages below 12 V, nanorods ZnO layer are formed at higher voltages. However, cracking inside the layers happened at voltages over 20 V due to oxygen evolution.

Anodization time and electrolyte concentration make minor modification to the synthesized nanorods. Short time and low NaOH concentration give rise to bulk-like ZnO layer or poor rod-shape, while excessive time and high concentration produce
over-etching nanorods. As for the optical properties/colour, the low voltage anodization gives rise to the ZnO nanostructures with dark colour and large visible light absorption ability, but the band gap calculated illustrate ZnO obtained at 12 V has the relatively low band gap energy and the values decreases with the annealing temperature. These results may provide guidance to the preparation of ZnO with regular morphology and high photocatalytic performance.
CHAPTER 8

Conclusions and Future Work
8.1 Conclusion

This thesis aims to complement and explore the synthesis, modifications and applications of three typical transition metal oxides, TiO$_2$, WO$_3$ and ZnO.

**Synthesis:** The formation mechanism of hierarchical nanostructures of TiO$_2$ through two-step anodization was proposed. The comprehensive studies about the influence of anodization parameters on the morphology of WO$_3$ and ZnO were conducted.

**Modifications:** The dynamic crystallization process of TiO$_2$ during heat treatment was revealed through *in situ* synchrotron X-ray diffraction techniques. The modification of TiO$_2$ with Ni and Cu were achieved through electroplating (chemistry method) and magnetron sputtering (physical method), respectively. In addition, similar physical modification technique also applies to the WO$_3$.

**Applications:** The effect of the aging electrolyte on the mechanical properties of the synthesized TiO$_2$ provides the guidance to the future design of electrical or photoelectrical devices made up of the anodic TiO$_2$ nanotube arrays. Ni decorated TiO$_2$ exhibits good oxygen evolution performance, which may be used as the catalyst for water splitting applications. The Cu-TiO$_2$ hybrid nanocomposites have several times larger photocatalytic efficiency than undecorated TiO$_2$ and could be employed as the potential photocatalyst in water treatment field. The hybrid Ag-WO$_3$ nanostructures can be used as a SERS substrate to detect the organic pollutant with low concentration, which may also find other applications in biomolecular detection and security protection.

The main conclusions are concluded as follows:

(1) The pre-treatment of Ti foils before anodization has a significant influence on the anodic TiO$_2$ morphology. The two-step anodization works effectively to produce regular hierarchical nanostructures. The first anodization leaves the concaves on Ti foil,
in which the second anodization induces etching pits. These pits gradually grow into separate tubes and finally their walls are eliminated due to the chemical dissolution, resulting in the emerging of neighbor nanotubes. The aging electrolyte could be an alternative to improve the morphology because the dissolution rate is decreased by the reduced conductivity and consumed water and fluorine ions. Not only the topography but also the mechanical properties are improved in the electrolyte with appropriate aging time.

(2) The degree of crystallinity and the crystal size of anodic TiO$_2$ NTs increase rapidly and then remain constant within a short time (~500 s) after annealing. However, the annealed TiO$_2$ is not fully crystallized (crystallinity only ~70 wt.%), even when the annealing time was prolonged to 7000 s at an elevated temperature. The incomplete crystallization after heat treatment can be attributed to the insufficient thermal energy, spatial constraints imposed by the tube walls, diffusion of oxygen vacancies, and fluoride ions.

(3) The hybrid Ni-TiO$_2$ nanocomposites with Ni in nanowires shape are fabricated by electroplating technique. The special “bottom to top” growth manner of Ni can be ascribed to the crystallinity and fluoride ion change after annealing. Although the pure TiO$_2$ nanotubes do not exhibit electrocatalytic activity, the hybrid nanocomposites shows the good oxygen evolution performance. The annealed TiO$_2$ nanotube could act as not only the electrodeposition substrate but also the OER catalyst support in the future.

(4) The hybrid Cu-TiO$_2$ nanocomposites with Cu nanoparticles well dispersed on the surface are fabricated by the combined techniques of magnetron sputtering and thermal dewetting. The synergistic effect of the co-catalyst system contributes to a four-time higher photodegradation rate than that of anatase TiO$_2$ under solar light irradiation.
because of the surface plasmon resonance and the formed Schottky barrier.

(5) The highly aligned nanoporous WO$_3$ with pore size of ~230 nm and thickness of ~200 nm is produced via anodization. The morphology of anodic WO$_3$ is very sensitive to the change of electrolyte temperature, applied voltage and water content, while the influence of ammonium fluoride concentration and duration time is less critical. Similar to the fabrication of Cu-TiO$_2$, the hybrid Ag-WO$_3$ nanostructures are obtained. This hybrid nanocomposites show high SERS performance with the increased Raman intensity by orders of magnitude, resulting from the low band gap of WO$_3$, plasmonic effect of Ag nanoparticles and the formed Schottky barrier.

(6) Well-aligned anodic ZnO nanorods have been fabricated by anodization in 0.1 M NaOH aqueous electrolytes. The obtained ZnO layer is ~7 μm thick and composed of nanorods of ~80 nm width with compact granular morphology on the surface. The morphology of anodic ZnO is dependent on the voltage, anodization time and electrolyte concentration. Although the ZnO nanostructures synthesized at low voltage have large light absorption properties, the calculated band gap of ZnO nanorods at 12V is the lowest. The values of ZnO further decrease with increase of annealing temperature.

8.2 Future Work

(1) Based on the preliminary understanding of the electrochemical anodization of pure transition metals, the anodization of binary and ternary alloys could be explored to prepare metal self-doped oxides or heterojunction structure in one step.

(2) The mechanism of the deficient TiO$_2$ formation through annealing has been discussed in this thesis. It is interesting to find out whether this method applies to the anodic WO$_3$ or ZnO or not. It is also worth trying other methods to introduce oxygen vacancy into stoichiometric metal oxides, such as electrochemical reduction and ion
irradiation.

(3) The SERS substrate fabrication based on the transition metal oxide is a promising field due to its wide applications. The morphology of anodic WO$_3$ may be further improved at the anodization temperature below frozen point and the size distribution of Ag nanoparticles could be optimized regarding the sputtering time and power. The above possible improvement of Ag-WO$_3$ may lead to the enhanced SERS ability.
Appendices

Figure S1. HRTEM image of TiO$_2$ nanotube arrays after annealing at 450°C for 1 hour. Dashed yellow lines illustrate the extent of the outer amorphous region.

Figure S2. Limited angular region of real-time *in situ* synchrotron XRD for the as-anodized TiO$_2$ mixed with Al$_2$O$_3$ as an internal crystallinity standard at 300°C, showing the general behaviour of peaks from the Al$_2$O$_3$ and TiO$_2$ phases. Data were fitted over the full $2\theta$ range from 4-84°.
Figure S3. Degree of crystallinity calculated for nonisothermal annealing with two ramp rates. The inset shows an enlargement of the region from 250 to 450°C.

Figure S4. Development of crystallite size for nonisothermal annealing with two ramp rates.
Figure S5. Development of lattice parameters for nonisothermal annealing with two ramp rates. The inset shows the tetragonal structure of anatase TiO₂.

Figure S6. Degree of crystallinity at 300 °C fitted with the modified Avrami model.
Figure S7. HRTEM image of amorphous region between two crystallites after annealing at 450°C for 1 hour.

Figure S8. Development of strain in the isothermal experiments.
Figure S9. TGA showing weight loss over the temperature range of interest at different heating rates: (a) 10°C/min, and (b) 50°C/min. The weight loss beginning at around 300°C may be caused by residual ethylene glycol.

Figure S10. SEM image of surface morphology of TiO₂ NTs prepared by two-step anodization.
Figure S11. SEM images of Ni-TiO$_2$ nanocomposites on different substrate: (a) as-anodized TiO$_2$, (b) annealed TiO$_2$

Figure S12. (a) EDS analysis, (b) Backscattered electron analysis of cross-section area of Ni-TiO$_2$ nanocomposite
Figure S13. (a) High resolution XPS spectra of O 1s, (b) FTIR spectroscopy of anodized TiO$_2$ NTs before and after annealing at different temperature.

Figure S14. Cyclic voltammograms of Ni-TiO$_2$ nanocomposites with different Ni coating at a scan rate of 50 mV/s
Figure S15. EDS spectra of (a) as-synthesized TiO$_2$ and (b) Cu film+Amorphous TiO$_2$ (S1).

Figure S16. Size distribution of Cu nanoparticles on Cu nanoparticles+anatase TiO$_2$ (S4).
Figure S17. XRD patterns of TiO$_2$ NTs prepared by different anodization duration with 40 s Cu sputtering and thermal dewetting at 400°C: (a) without post annealing; (b) with post annealing.

Figure S18. $UV$-$vis$ absorbance spectra at different thermal dewetting temperature.
Figure S19. Five consecutive photocatalytic MB degradation of S8

Figure S20. (a) XPS survey spectra; (b) SEM-EDS spectra; (c) EDS elemental mapping of anodic WO3.
Figure S21. High resolution XPS spectra of W region before and after annealing.

Figure S22. Raman spectra of WO$_3$ before and after annealing.
Figure S23. SEM images of anodic WO$_3$ prepared in: (a) and (b) Ice bath (W1); (c) and (d) No ice bath (W2).

Figure S24. SEM images of anodic WO$_3$ prepared in electrolyte with different water content: (a) 0 wt.% (W3); (b) 2 wt.% (W1); (c) 5 wt.% (W4); (d) 10 wt.% (W5).
Figure S25. SEM images of anodic WO₃ prepared under different Voltage: (a) 20V (W6); (b) 40V (W1); (c) 60V (W7)

Figure S26. SEM images of anodic WO₃ prepared in different concentration of NH₄F: (a) 1.2 wt.% (W8); (b) 1.5 wt.% (W9); (c) 1.8 wt.% (W1); (d) 2.1 wt.% (W10).
Figure S27. SEM images of anodic WO$_3$ prepared for different time: (a) 1h (W11); (b) 2h (W1); (c) 4h (W12); (d) 6h (W13).

Figure S28. Size distribution of Ag NPs on S1 with 20s Ag sputtering and thermal dewetting at 250 ºC for 1h.
Figure S29. *UV*-vis absorbance spectra of anodic WO$_3$, annealed WO$_3$ and AgN-WO$_3$. Inset is the enlarged absorbance of AgN-WO$_3$.

Figure S30. Raman spectra of RhB with various concentrations on AgN-WO$_3$ substrate. Raman spectra of AgN-WO$_3$ was used as comparison entitled as “No Dyes”
Figure S31. XRD patterns of as-formed ZnO in 0.1M NaOH aqueous electrolytes at 12 V for 1h and after annealing at different temperature for 1h.

Figure S32. EDS spectra of anodized ZnO prepared in 0.1M NaOH aqueous electrolytes at 12 V for 1h: upper part, middle part and bottom part.
Figure S33. FESEM cross-sectional images of anodic film prepared in 0.1M NaOH aqueous electrolytes for 1h at various voltages: (a) 20V, (b) 30V and (c) 40V

Figure S34. FESEM images with low magnification of anodic film prepared in 0.1 M NaOH aqueous electrolytes at 12 V for different duration time: (a) 0.5 h; (b) 1 h and (c) 1.5 h

Figure S35. FESEM images of anodic films prepared at 12 V for 1 h in different concentrations of NaOH in electrolytes: (a) 0.05M, (b) 0.1M and (c) 0.2M
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