Nanostructured titanium dioxide-based materials for lithium-ion batteries

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**NANOSTRUCTURED TITANIUM DIOXIDE-BASED
MATERIALS FOR LITHIUM-ION BATTERIES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2015

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Abstract

Developing next-generation lithium-ion batteries (LIBs) for upcoming large-scale applications has attracted great interest and numerous efforts worldwide. To achieve this goal, nanostructured electrode materials with outstanding electrochemical performance hold great promise. A group of titanium dioxide (TiO_2)-based materials, including various polymorphs of TiO_2 and several titanates, has been widely studied as potential anode materials for next-generation LIBs. These materials have demonstrated many advantages, such as improved safety and long-term cycling stability, fast Li^+ insertion kinetics, environmental friendliness and low cost. However, to fully realize the above-mentioned merits, properly designed nanostructures are indispensable. This thesis focuses on the rational design and facile synthesis of nanostructured titanium oxide-based materials with superior electrochemical properties for high-performance LIBs.

A unique solvothermal system using mixture of N, N-dimethylformamide (DMF) and acetic acid (HAc) as solvent is first developed to prepare rod-like anatase TiO_2 nanocrystals with asymmetric shape and exposed high-index facets. The nanocrystals show an asymmetric bipyramidal shape, where the two sides are bound by (201) and (401) facets, respectively. To reduce the high surface energy of these high-index facets, these nanocrystals tend to assemble on the (401) facets and form a dandelion-like hierarchical structure. The morphology and structure are thoroughly characterized, and the formation process is also investigated and discussed. The

as-prepared TiO₂ hierarchical structure exhibits high specific capacity and good cycling performance. This work also provides an opportunity to further study the effects of high-index facets for various applications.

With the assistance of lithium salts, a modified solvothermal system using mixed DMF and HAc as solvent is employed for the direct synthesis of anatase TiO₂ nanowires (TNWs) in large quantity. The morphology of TNWs varies from hierarchical assemblies to freestanding form according to the volumetric ratio of DMF/HAc as the solvent in the synthesis. In general, the as-prepared TNWs exhibit a curve and flexible feature, and show a length of hundreds of nanometers and a small diameter below 20 nm. Due to the significantly reduced diffusion length for Li⁺ ions, the TNWs show good lithium storage performance.

Hierarchical spheres assembled from ultrathin layered hydrogen titanate (LHT) nanosheets (NSs) are synthesized via a solvothermal method with DMF and isopropyl alcohol (IPA) as solvents. These hierarchical spheres exhibit a porous structure with high specific surface area and good structural robustness, with tunable size and morphology. Besides, these LHT hierarchical spheres can be easily transformed into anatase TiO₂ hierarchical spheres with well retained porous structure. Depending on the calcination atmosphere of air or N₂, pure anatase TiO₂ hierarchical spheres or carbon-supported TiO₂ hierarchical spheres can be obtained, respectively. Remarkably, these two types of TiO₂ hierarchical spheres both manifest excellent cycling stability and rate capability, which are superior to the above-mentioned asymmetric nanocrystals and nanowires, when evaluated as anode materials for high-power LIBs.

In order to increase the conductivity of TiO_2 -based materials so as to further improve their LIB performance, a hybrid nanostructure based on TiO_2 NS building blocks and conductive carbon supports is rationally designed and synthesized. Hierarchical nanocables with TiO_2 NSs directly anchored on carbon nanotube backbones (denoted as $\text{CNT}@\text{TiO}_2\text{-NSs}$) are synthesized by growing LHT NSs on CNTs followed by a subsequent annealing process in N_2 . This unique core-shell structure possesses several structural advantages, including reduced Li^+ ion diffusion distance, improved electrical conductivity, and high structural robustness. As a result, $\text{CNT}@\text{TiO}_2\text{-NSs}$ nanocables demonstrate further improved cyclability and high rate capability as a promising anode material for next-generation LIBs.

In brief, this research project discovers several novel solvothermal systems that lead to the facile and controllable syntheses of various TiO_2 -based nanostructures. The potential applications of these nanostructures, including quasi one-dimensional (1D) rod-like bipyramidal nanocrystals, 1D nanowires, two-dimensional (2D) nanosheets and their derived nanocomposites, as promising candidates of anode materials for high-performance LIBs have been well demonstrated. It is shown that enhanced physicochemical properties of TiO_2 -based anodes can be achieved by properly designed and fabricated nanostructures, which paves the way towards low-cost, large-scale and environmentally friendly synthesis of advanced electrode materials with high power/energy density and long life for next-generation LIBs.

Table of Content

Acknowledgement.....	i
Abstract.....	ii
Table of Content	v
List of Abbreviations.....	viii
List of Figures	xi
Chapter 1. Introduction.....	1
1.1. Background.....	1
1.2. Motivation.....	3
1.3. Overall Objective	4
1.3.1 <i>Synthesis of TiO₂ nanostructures via solvothermal methods</i>	4
1.3.2 <i>Investigation of electrochemical properties of TiO₂ nanostructures</i>	5
1.3.3 <i>Rational design and fabrication of hybrid nanostructures based on low-dimensional TiO₂ building blocks and carbonaceous supports</i>	6
1.4. Organization.....	6
Chapter 2. Literature Review	8
2.1. Overview of Lithium-ion Battery and Metal Oxide-based Anodes.....	8
2.2. Lithium Storage Mechanisms of TiO ₂ and Titanate Materials	11
2.2.1. <i>TiO₂ polymorphs</i>	11
2.2.2. <i>Spinel Li₄Ti₅O₁₂</i>	15
2.2.3. <i>Layered hydrogen titanates</i>	15
2.3. Titanium dioxide-based anode materials with different nanostructures.....	17
2.3.1. <i>Nanoparticles</i>	17
2.3.2. <i>Nanowires, nanotubes and nanorods</i>	19
2.3.3. <i>Nanosheets</i>	22
2.3.4. <i>Three-dimensional/hierarchical nanostructures</i>	24
2.3.5. <i>Nanocomposites</i>	25
2.4. Summary	28

Chapter 3. Experimental Section	30
3.1. Materials Synthesis	30
3.2. Materials Characterizations.....	30
3.3. Electrochemical Measurements.....	31
Chapter 4. Asymmetric Anatase TiO ₂ Nanocrystals with Exposed High-index Facets and Their Lithium Storage Properties.....	32
4.1. Introduction.....	32
4.2. Materials Synthesis	34
4.3. Results and Discussion.....	34
4.3.1. Morphological and compositional characterizations.....	34
4.3.2. Formation mechanism	38
4.3.3. Electrochemical measurements.....	41
4.4. Summary	44
Chapter 5. Direct Synthesis of Anatase TiO ₂ Nanowires and Their Lithium Storage Properties	46
5.1. Introduction.....	46
5.2. Materials Synthesis	48
5.3. Results and Discussion.....	49
5.3.1. Morphological and compositional characterizations.....	49
5.3.2. Formation mechanism	53
5.3.3. Removal of surface contaminants by calcination	57
5.3.4. Electrochemical measurements.....	59
5.4. Summary	63
Chapter 6. Synthesis of Uniform Layered Hydrogen Titanate Hierarchical Spheres and Their Transformation to Anatase TiO ₂ for Lithium-ion Batteries	64
6.1. Introduction.....	64
6.2 Materials Synthesis	67
6.2.1. Synthesis of layered hydrogen titanate hierarchical spheres.....	67
6.2.2. Synthesis of TiO ₂ hierarchical spheres.....	67

6.3 Results and Discussion.....	68
6.3.1. <i>Morphological and compositional characterizations</i>	68
6.3.2. <i>Controlling the structure and morphology</i>	71
6.3.3. <i>Conversion of LHT to anatase TiO₂ spheres</i>	73
6.3.4. <i>Electrochemical measurements</i>	78
6.4 Summary	81
Chapter 7. TiO ₂ Nanosheets Hierarchically Assembled on Carbon Nanotubes as High-rate	
Anodes for Lithium-ion Batteries.....	83
7.1. Introduction.....	83
7.2. Materials Synthesis	85
7.3. Results and Discussion.....	86
7.3.1. <i>Morphological and compositional characterizations</i>	86
7.3.2. <i>Electrochemical measurements</i>	91
7.3.3. <i>Understanding the excellent electrochemical properties</i>	95
7.4. Summary	98
Chapter 8. Conclusions and Outlook.....	99
8.1. Conclusions.....	99
7.2. Outlook.....	103
Complete List of Publications	107
References.....	114

List of Abbreviations

LIBs: lithium-ion batteries

TiO₂: titanium dioxide

DMF: N, N-dimethylformamide

HAc: acetic acid

NW: nanowire

TNW: TiO₂ nanowire

LHT: layered hydrogen titanate

NS: nanosheet

IPA: isopropyl alcohol

N₂: nitrogen gas

CNT: carbon nanotube

CNT@LHT-NSs: LHT nanosheets on CNT

CNT@TiO₂-NSs: TiO₂ nanosheets on CNT

0D: zero-dimensional

1D: one-dimensional

2D: two-dimensional

3D: three-dimensional

Li⁺: lithium ion

LiCoO₂: lithium cobalt oxide

Li₄Ti₅O₁₂: spinel lithium titanium oxide

SnO₂: tin dioxide

SEI: solid-electrolyte-interface

TMO: transition metal oxide

MO: metal oxide

M: metal nanoparticle

HF: hydrofluoric acid

FESEM: field-emission scanning electron microscope

TEM: transmission electron microscope

XRD: X-ray diffraction

EDX: energy-dispersive X-ray spectroscopy

FTIR: Fourier transform infrared spectroscopy

TGA: Thermogravimetric analysis

PVDF: poly (vinylidene difluoride)

LiPF₆: Lithium hexafluorophosphate

CV: Cyclic voltammetry

F⁻: fluorine ions

NC: nanocrystal

TB: titanium butoxide

BET: Brunauer-Emmett-Teller

HRTEM: High-resolution transmission electron microscope

SAED: selected-area electron diffraction

FFT: fast Fourier transform

LiAc: lithium acetate

LiCl: lithium chloride

NaAc: sodium acetate

TIP: titanium(IV) isopropoxide

TNW-A: annealed TiO₂ nanowires

LTHS: layered hydrogen titanate hierarchical sphere

PTHS: porous titania hierarchical sphere

CTHS: carbon-supported titania hierarchical sphere

EIS: electrochemical impedance spectroscopy

List of Figures

Figure 2.1 Crystal structure of rutile TiO_2 . Li-ion diffusion path and vacant sites are also indicated. ^[10] Reproduced with permission from ref. 10. Copyright 2009 RSC.	13
Figure 2.2 Crystal structure of anatase TiO_2 . ^[10] Reproduced with permission from ref. 10. Copyright 2009 RSC.	13
Figure 2.3 Crystal structure of $\text{TiO}_2\text{-B}$. ^[10] Reproduced with permission from ref. 10. Copyright 2009 RSC.	14
Figure 2.4 Crystal structures of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$. ^[7] Reproduced with permission from ref. 7. Copyright 2010 Wiley.	15
Figure 2.5 Crystal structures of several members of the layered hydrogen titanate family. ^[49] Reproduced with permission from ref. 49. Copyright 1996 ACS.	16
Figure 2.6 Cycling performance and charge-discharge profiles of rutile nanoparticles with various sizes at 50 mA g ⁻¹ (R15, R30 and R300 denote nanoparticles with sizes of 15, 30 and 300 nm, respectively). ^[51] Reproduced with permission from ref. 51. Copyright 2007 ECS.	18
Figure 2.7 Charge-discharge profiles of anatase nanoparticles with size of (a) 6 and (b) 30 nm. ^[52] Reproduced with permission from ref. 52. Copyright 2007 Elsevier.....	19
Figure 2.8 $\text{TiO}_2\text{-B}$ (A) nanowires and (B) nanotubes. ^[5] Reproduced with permission from ref. 5. Copyright 2008 Wiley.	20
Figure 2.9 TiO_2 nanotube arrays with different diameter and length. ^[58] Reproduced with permission from ref. 58. Copyright 2006 Elsevier.	21
Figure 2.10 (A, B) Electron microscope images of TiO_2 nanosheets hierarchical spheres. Cycling performance at (C) constant and (D) various current rates. ^[62] Reproduced with permission from ref. 62. Copyright 2010 ACS.	23

Figure 2.11 (A, B) Electron microscope images of SnO ₂ @TiO ₂ -NSs hollow spheres using SiO ₂ spheres as template. ^[65] Reproduced with permission from ref. 65. Copyright 2010 RSC. (C, D) Electron microscope images of TiO ₂ -NSs hollow spheres using polystyrene hollow spheres as template. ^[77] Reproduced with permission from ref. 77. Copyright 2011 RSC.	25
Figure 2.12 (A, B) Electron microscope images of TiO ₂ /graphene nanocomposites. (C) Cycling performance at various current densities and (D) Nyquist plots of (a) TiO ₂ /graphene composites and (b) reference TiO ₂ . ^[88] Reproduced with permission from ref. 88. Copyright 2011 Wiley.	27
Figure 4.1 (A) XRD pattern and (B – C) FESEM images of as-synthesized dandelion-like TiO ₂ obtained at 200 °C for 10 h. (D) high-magnification FESEM image of the TiO ₂ needles from top view.	35
Figure 4.2 Nitrogen adsorption/desorption isotherm of dandelion-like TiO ₂ at 77K (inset: pore-size distributions calculated by the BJH method).	36
Figure 4.3 (A) TEM images of a bundle consisting of several TiO ₂ needles. (B) TEM image of an individual TiO ₂ needle (inset: corresponding SEAD pattern). (C, D) HRTEM images taken from the dotted circles I and II in (B) respectively. The insets in C and D show the fast Fourier transform patterns of the corresponding region. (E) Schematic illustration of an individual asymmetric TiO ₂ NC.	37
Figure 4.4 FESEM and TEM images of dandelion-like TiO ₂ with different reaction durations: (A, B) 3h, (C, D) 4h, (E, F) 6h, and (G, H) 10h.	39
Figure 4.5 XRD patterns of dandelion-like TiO ₂ with different reaction time.	39
Figure 4.6 FESEM images of dandelion-like TiO ₂ with different temperatures and reaction durations: 180°C for (A) 10h, (B) 24h, (C) 5d, and (D) 220°C for 10h.	40
Figure 4.7 Schematic illustrations of (A) the formation of dandelion-like TiO ₂ and (B) growth of individual TiO ₂ bipyramids along the [001] direction.	41
Figure 4.8 (A) Charge/discharge curves of the first, second and fifth cycles of the	

dandelion-like TiO ₂ at a charge/discharge rate of 0.5 C. (B) cycling performance and corresponding Coulombic efficiency of the dandelion-like TiO ₂ at a charge/discharge rate of 0.5 C.	42
Figure 4.9 Cycling performance of the dandelion-like TiO ₂ at current rate of 5 C.	43
Figure 5.1 FESEM and TEM images of TiO ₂ NWs (TNWs) prepared in organic solvents with different volumetric ratios of DMF/HAc: (A, B) 4/6, (C, D) 5/5, and (E, F) 6/4.	50
Figure 5.2 (A) XRD pattern, (B) TEM and (C) HRTEM images of TNWs prepared with a DMF/HAc volumetric ratio of 5/5. (D) Magnified HRTEM image taken from the dotted square in (C) and corresponding FFT pattern (inset). The asterisk in (A) indicates the possible impurity of brookite.	51
Figure 5.3 XRD patterns of TNWs prepared in organic solvents with DMF/HAc volumetric ratios of (I) 4/6 and (II) 6/4.	52
Figure 5.4 Nitrogen adsorption/desorption isotherm of TNWs at 77K (inset: pore-size distribution calculated by the BJH method).	53
Figure 5.5. Digital photo of 1.97 g TNWs prepared in 40 mL of solvent.	54
Figure 5.6 TEM images of TNWs obtained after reaction for (A) 2 h and (B) 4 h.	54
Figure 5.7 FESEM image of sample prepared with titanium isopropoxide (TIP) as the Ti precursor.	55
Figure 5.8 FESEM and TEM images of samples prepared without adding LiAc.	55
Figure 5.9 FESEM images of samples prepared with (A) LiCl and (B) NaAc.	56
Figure 5.10 TGA curve of TNWs under an air flow.	57
Figure 5.11 (A) XRD pattern, (B) FESEM, (C) TEM and (D) HRTEM images of TNWs after annealing (TNW-A).	58
Figure 5.12 Nitrogen adsorption/desorption isotherm of TNW-A at 77K (inset: pore-size distribution calculated by the BJH method).	58

Figure 5.13 Representative CV curves of TNWs at 0.5 mV s^{-1}	60
Figure 5.14 (A) Representative charge-discharge voltage profiles at various current rates, and (B) rate capability of TNWs.	61
Figure 5.15 Cycling performance at 2 and 5 C rate, respectively, and Coulombic efficiency at 5 C.	62
Figure 5.16 FESEM images (A) before and (B) after cycling at 5 C for 100 cycles....	62
Figure 6.1 Schematic illustration for the synthesis routes of layered hydrogen titanate hierarchical spheres (LTHSs) and the derived porous TiO_2 hierarchical spheres (PTHs) and carbon-supported TiO_2 hierarchical spheres (CTHSs).	66
Figure 6.2 (A) FESEM image, (B - D) TEM images, (E) HRTEM image (inset: magnified HRTEM image taken from the area marked by a square) and (F) XRD pattern of the as-synthesized LTHSs.	69
Figure 6.3 Nitrogen adsorption/desorption isotherm of the as-synthesized LTHSs (inset: pore size distributions calculated using the BJH method from both branches).	70
Figure 6.4 (A) EDX analysis of the as-synthesized LTHSs. (please note that the signal of Si comes from the substrate) (B) FT-IR spectrum of the as-synthesized LTHSs.	70
Figure 6.5 FESEM images of LTHSs prepared at different temperatures: (A) 180°C , (B) 200°C , and (C) 220°C . (insets: FESEM images of single hierarchical sphere from the corresponding sample)	71
Figure 6.6. LTHSs prepared with different DMF/IPA volume (mL/mL): (A) 6/34, (B) 14/26. LTHSs prepared with different amount of TB: (C) 0.4 mL, (D) 2.0 mL.	72
Figure 6.7 TGA curves of (A) as-synthesized LTHSs and (B) CTHSs.	73
Figure 6.8 XRD patterns of PTHs and CTHSs.	74
Figure 6.9 (A, B) TEM and (C) HRTEM images of PTHs. The inset in (A) is a digital photo of the as-synthesized PTHs).	75
Figure 6.10 Nitrogen adsorption/desorption isotherms of PTHs (insets: pore size	

distributions calculated using the BJH method from both branches).	76
Figure 6.11 (A, B) TEM and (C) HRTEM images of CTHSs. The inset in (A) is a digital photo of the as-synthesized CTHSs).	77
Figure 6.12 Nitrogen adsorption/desorption isotherms of CTHSs (insets: pore size distributions calculated using the BJH method from both branches).	77
Figure 6.13 (A) CVs of PTHSs at a scan rate of 0.5 mV s^{-1} between 1 and 3 V. (B) Cycling performance of PTHSs at constant current rates of 2 C and 5 C, and Coulombic efficiency at a current rate of 5 C.	79
Figure 6.14 (A) CVs of CTHSs at a scan rate of 0.5 mV s^{-1} between 1 and 3 V. (B) Cycling performance of CTHSs at constant current rates of 5 C.	80
Figure 6.15 Rate performances of PTHSs and CTHSs at various current rates from 1 to 10 C.	81
Figure 7.1 Schematic illustration of the synthesis route of CNT@TiO ₂ -NSs. The first step involves the growth of LHT NSs on the CNT backbone. The second step is a simple calcination in N ₂ to convert LHT to anatase TiO ₂	85
Figure 7.2 TEM image of pristine CNTs.	86
Figure 7.3 (A) FESEM and (B) TEM images of CNT@LHT-NSs.	86
Figure 7.4 (A, B) FESEM images, (C ~ E) TEM images and (F) elemental mapping of CNT@TiO ₂ -NSs.	87
Figure 7.5 HRTEM image of TiO ₂ NSs on the CNT@TiO ₂ -NSs.	88
Figure 7.6 Nitrogen adsorption/desorption isotherm of CNT@TiO ₂ -NSs (inset: pore size distributions calculated using the BJH method from both branches).	89
Figure 7.7 (A) XRD patterns of (I) CNTs, (II) CNT@LHT-NSs and (III) CNT@TiO ₂ -NSs. (B) TGA curves of (I) CNT@LHT-NSs and (II) CNT@TiO ₂ -NSs.	90
Figure 7.8 (A) Cyclic voltammograms of CNT@TiO ₂ -NSs at a scan rate of 0.5 mV s^{-1} .	

(B) Charge-discharge voltage profiles of CNT@TiO ₂ -NSs at a current rate of 1 C (170 mA g ⁻¹) for the first, second and fifth cycles.	93
Figure 7.9 Cycling performance of CNT@TiO ₂ -NSs at constant current rates of (A) 5 C, (B) 1 and 10 C.	95
Figure 7.10 Cycling performance of CNT@TiO ₂ -NSs at different current rates.	95
Figure 7.11 Nyquist plots of (A, B) CNT@TiO ₂ -NSs nanocables and PTHSs fresh cells, and (C, D) CNT@TiO ₂ -NSs nanocables before and after 200 cycles at 5 C.	96
Figure 7.12 FESEM images of (A, B) PTHSs and (C, D) CNT@TiO ₂ -NSs electrodes after 200 cycles at 5 C.	97
Figure 8.1 Comparison of (A) cycling performance and (B) rate capability from different TiO ₂ -based nanostructures in this thesis. Initial capacity in (A) and all the capacity in (B) are obtained from the second cycle at particular current rates.	101

Chapter 1. Introduction[†]

1.1. Background

The ever-growing energy consumption strongly demands highly efficient and advanced energy conversion and storage devices, such as rechargeable batteries which can store electrical energy in the form of chemical energy. Lithium-ion batteries (LIBs) have become one of the most popular rechargeable batteries with many outstanding features including high energy density, no memory effect, low maintenance, and little self-discharge. In the past 20 years since the first commercial products manufactured by Sony, LIBs have gained dominance as the power source for many portable electronic devices, and they are now showing great potential for the upcoming large-scale applications (e.g., electric cars and stationary energy backup systems). Meanwhile, the growing demands for better LIBs have never been greater, in terms of improved safety, longer lifetime, smaller size/lighter weight, and lower cost.^[1-3]

In a conventional LIB cell, lithium metal oxide (e.g., LiCoO_2) and graphite are used as cathode (positive electrode) and anode (negative electrode) materials, respectively. Two electrodes are separated by a porous membrane separator and soaked in a non-aqueous liquid electrolyte. During discharging, Li^+ ions de-intercalate from the anode, pass through the electrolyte and insert into the cathode, while electrons flow from the anode into the cathode through the external circuit and power the electronic

[†] Reproduced in part and modified from [H. B. Wu, J. S. Chen, H. H. Hng, X. W. Lou, *Nanoscale*, 4, 2526-2542 (2012)] by permission from *The Royal Society of Chemistry*. Copyright 2012.

devices. The process is reversed during charging when an external voltage is applied on the battery. Since LIBs function based on the reversible shuttling of Li^+ ions and the difference of electrochemical properties between the cathode and the anode, the inherent properties of the electrode materials would be a crucial factor that largely determines the overall performance of batteries.

A variety of metal oxides has been investigated as potential negative electrode materials for LIBs with superior properties over the commercialized graphite anode. Among the numerous metal oxides that have been studied, titanium dioxide (TiO_2 , titania) stands out as a low-cost and environmentally benign anode material. Besides the various polymorphs of TiO_2 such as anatase, rutile and $\text{TiO}_2\text{-B}$ that have been demonstrated as promising host materials for Li ions, titanate materials specially spinel lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) and layered hydrogen titanates (LHT) also draw considerable attention. The minimal volume expansion upon Li ions intercalation of these materials offers the great potential as high rate and long cycle life anodes. Since titanium oxide-based electrodes operate at higher voltage window ($> 1 \text{ V vs. Li}^+/\text{Li}$), the side reactions associating with electrolyte decomposition are also effectively reduced.

Although these titanium oxide-based anodes possess many attractive characteristics, achieving good electrochemical performance in practical applications still remains a great challenge. The major obstacles include the relatively low electronic and ionic conductivities, which are quite common for transition metal oxides. Consequently, traditional titanium oxide-based materials only result in poor cyclability

and low capacity.

1.2. Motivation

The rapid development of nano-science and -technology has provided a powerful tool to tailor the properties and improve the performance of conventional functional materials. It has been demonstrated by numerous examples that the performance of electrode materials can be significantly enhanced by designing and constructing proper nanostructures. Therefore, synthesis of nanostructured electrode materials has long been an attractive research area. Nanostructured titania- and titanate-based materials such as nanoparticles, nanotubes/wires and nanosheets have demonstrated many advantages over their bulk counterparts. However, the results achieved by nanomaterials so far are still not satisfying. There still remain some unsolved questions: what are the most desirable nanostructures for high-performance anodes? And how can we controllably synthesize these nanostructures in efficient and facile ways?

Due to the high reactivity and hydrolysis rate of most titanium precursors, such as titanium alkoxides, TiO_2 -based nanomaterials are commonly synthesized by controlling the hydrolysis of Ti-precursors in the presence of surfactants or other structure-directing agents. Solvothermal synthesis of TiO_2 using organic solvents as both the reaction mediates and structure-directing agents could be very promising and effective for preparing nanostructured TiO_2 , although this strategy has not yet been well studied. With the capability to controllably fabricate diverse nanostructured TiO_2 -based

anodes, the correlation between structure and electrochemical properties could be better understood. Therefore, great challenges as well as numerous opportunities lay in the synthesis of titanium oxide-based anodes with novel nanostructures and outstanding performance.

1.3. Overall Objective

The main objective of this research project is to develop novel solvothermal systems for the controllable syntheses of various TiO_2 -based nanostructures and to investigate their electrochemical properties. The crystal growth behavior of titania and titanate in the mixtures of several common organic solvents, such as N, N-dimethylformamide (DMF), acetic acid (HAc), and isopropyl alcohol (IPA), has been thoroughly studied. Products with unique morphologies, especially those assembled from low-dimensional building blocks are characterized and investigated as anode materials for LIBs. TiO_2 nanostructures with exceptional electrochemical properties would be identified and further used to construct hybrid nanostructures composed of these highly electrochemically active TiO_2 building blocks and various carbonaceous supports. Specifically, the objective of this project can be categorized into the following three aspects.

1.3.1 Synthesis of TiO_2 nanostructures via solvothermal methods

To prevent rapid hydrolysis of titanium precursors in aqueous solutions that leads

to irregular particles, several common organic liquids, such as DMF, HAc and IPA, are utilized as the solvents for the controllable growth of titania and titanate nanostructures. One major aim of this project is to discover several novel solvothermal systems that could produce TiO_2 -based nanostructures with potential applications in LIBs. The formation process and possible mechanism will be studied in order to shed some light to the controllable growth of TiO_2 -based nanostructures in organic solvents. Detailed characterizations will also be performed on these as-prepared materials to reveal their structural and compositional features.

1.3.2 Investigation of electrochemical properties of TiO_2 nanostructures

Due to the poor electrical and ionic conductivity, bulk TiO_2 typically exhibits low electrochemical activity. The lithium storage properties could be enhanced by reducing the size of the particles, which shortens the diffusion distance of charges. Electrochemical performance of the as-prepared TiO_2 nanostructures will be investigated in order to understand the effects of their structural characteristics, such as the exposed crystal facet, geometric shape of nanocrystals, surface area, porosity, and hierarchical architecture, on specific capacity, high-rate performance and long-term cycling stability. By comparing the lithium storage performance of different samples, the most promising TiO_2 nanostructures as anode materials will be identified and further optimized for high-performance LIBs.

1.3.3 Rational design and fabrication of hybrid nanostructures based on low-dimensional TiO₂ building blocks and carbonaceous supports

Carbon is widely used to improve the electrical conductivity of electrode materials. Fabrication of hybrid nanostructures that intimately integrate the electrochemically active metal oxides with carbon supports is expected to significantly prompt the electron transport. Therefore, the pristine solvothermal systems to synthesize TiO₂ nanostructures will be modified for the one-pot synthesis of nanocomposites based on low-dimensional TiO₂ building blocks and various carbon supports (e.g., carbon nanotubes (CNTs), graphene, carbon cloth, etc.). Detailed electrochemical measurements will be performed to evaluate the lithium storage properties of the as-prepared nanocomposites, and the origin of the exceptional performance of these hybrid nanostructures will be proposed and discussed.

1.4. Organization

The layout of this thesis is shown below:

In Chapter 1, a brief introduction of the study is provided, including the background information, motivation and objectives of the research project. After that, some recent advances in the synthesis of representative nanostructured titanium oxide-based materials and their application in LIBs are reviewed in Chapter 2. The general synthetic methodology, materials characterization techniques, and electrochemical measurement procedures applied in this project are summarized in

Chapter 3. For Chapter 4 to 6, three novel solvothermal systems are presented to produce different TiO_2 -based nanostructures, including rod-like asymmetric anatase TiO_2 nanocrystals with exposed high-index facets, ultrathin anatase TiO_2 nanowires, hierarchical spheres assembled from LHT nanosheets (NSs) and their derived anatase TiO_2 spheres. The electrochemical lithium storage properties of the as-prepared TiO_2 materials are also investigated and compared. In Chapter 7, a rationally designed and fabricated hybrid nanostructure is demonstrated by hierarchically assembling LHT-derived TiO_2 NSs on CNTs. The electrochemical properties of the as-prepared core-shell CNT@ TiO_2 -NSs nanocables is also studied, which show the great potential of the hybrid nanostructures for high-performance LIBs. Finally, the overall conclusion of the research project is drawn in Chapter 8, together with some prospects for future studies in this research area.

Chapter 2. Literature Review[†]

2.1. Overview of Lithium-ion Battery and Metal Oxide-based Anodes

Lithium-ion batteries (LIBs) have become the most popular types of rechargeable batteries with many remarkable advantages, including high energy density, no memory effect, low maintenance, and little self-discharge.^[1, 3] In a typical lithium-ion battery, LiCoO_2 and graphite are used as cathode (positive electrode) and anode (negative electrode) materials, respectively, separated by a porous membrane separator and soaking in a non-aqueous liquid electrolyte.^[4] Upon charging, Li^+ ions deintercalate from the layered LiCoO_2 , pass through the electrolyte and insert into the graphite layers. This process reverses during discharging. Before graphite is widely used in LIBs, the negative electrode was first constructed with Li metal, which was abandoned later and replaced by graphite because of safety issue.^[3] Such LIB system based on LiCoO_2 and graphite has gained dominance as power sources for portable electronic devices.

However, the performance of graphite anode is no longer satisfying when LIBs are expected to serve for large-scale applications such as hybrid or pure electric vehicles and grid energy storage, which require high power density, long cycle life and improved safety.^[5-8] Because of the low lithium insertion potential close to Li^+/Li ,

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graphite also suffers from safety problem related to the deposition of Li metal on the graphite surface, as well as some parasitic reactions associating with electrolyte decomposition. Increasing the kinetic or the rate capability of electrodes and batteries by using nanoparticles does not seem to be a plausible idea due to the serious side reactions, low density and severe aggregation that degrades the performance.^[5] Besides, the theoretical capacity of graphite anode (372 mA h g⁻¹) is now becoming the limitation to further increase the energy density of full cells. A variety of metal oxides have been discovered and intensively studied as novel anode materials in recent years, which reversibly store Li⁺ ions based on different mechanisms.^[6, 8-15]

For example, SnO₂ shows attractive lithium storage properties based on the following two reactions:^[16-18]

Reaction (2.1) is generally considered as irreversible, although it has been suggested partially reversible in some studies.^[17, 19] The alloying/dealloying reaction described by reaction (2.2) endows SnO₂ with the capability to accommodate maximally 4.4 Li per Sn, corresponding to a theoretical specific capacity of ~790 mA h g⁻¹. Two features are generally identified in SnO₂-based anodes. Specifically, the Coulombic efficiency is normally low in the first few charge/discharge cycle, which is caused by the occurrence of irreversible processes, including the reduction of SnO₂ into Sn and the formation of solid-electrolyte-interface (SEI) layer.^[20, 21] Secondly, rapid capacity fading still takes place in the subsequent cycles, making bulk SnO₂ unsuitable for the practical

application. The major cause of this fast capacity fading has been identified as the tremendous volume change of up to 200% upon full lithiation of metallic Sn, forming $\text{Li}_{4.4}\text{Sn}$ alloy.^[22] Consequently, the integrity of electrode is severely damaged due to the pulverization of electrodes after repeated charge/discharge.

Another intensively studied category of anode materials is transition metal oxides (TMOs), most of which exhibit a distinct lithium storage mechanism named conversion or displacement reaction. Generally, the electrochemical reactions could be summarized by the following equation:^[14]

This forward displacement redox reaction between MO and Li^+ is actually thermodynamically favorable, and the conversion of the metal oxides to the metallic state typically involves multiple-electron transfer per metal atom, leading to a high theoretical lithium storage capacity.^[9, 23] However, the reversed reaction of extracting Li^+ from Li_2O seems to be thermodynamically unachievable under normal conditions. It is argued that the formed metal nanoparticles (M) during the first discharge will facilitate the reversible formation and decomposition of the Li_2O matrix, and the use of nanostructured materials possessing large surface area, high surface energy and enhanced electrochemical reactivity can also facilitate the backward reaction.^[23] In another word, the conversion reaction is more facile and reversible in nanoscale. In addition to the above-mentioned thermodynamic restriction and possible kinetic limitation for the lithium diffusion, the structural reorganization and volumetric variation upon charge/discharge have also been identified as the main cause for the

cracking of active materials and rapid capacity fading.

Although the above two categories of metal oxides as novel anode materials show high specific capacity compared with traditional carbonaceous anodes, these materials are not suitable for high power and long lifespan applications due to quick capacity fading and poor kinetics.^[9, 24] Meanwhile, a group of titanium oxide-based anode materials has drawn considerable attention, including several polymorphs of pure TiO₂ (especially anatase, rutile and TiO₂-B), spinel lithium titanate (Li₄Ti₅O₁₂) and layered hydrogen titanates (LHT).^[6, 10, 11, 13, 25-29] The most significant characteristic of these titanium oxide-based materials (including both titanates and several polymorphs of TiO₂) is the great potential to achieve excellent cyclability and high rate capability. Although their gravimetric capacity is relatively low (e.g., ~ 300 mA h g⁻¹ for TiO₂-B, ~ 170 mA h g⁻¹ for anatase and Li₄Ti₅O₁₂), the volumetric capacity, which is actually more important in real applications, is comparable to graphite anode due to their higher density. Besides, the high cycling stability and improved safety, which far beyond other candidates, would also compensate their shortages. The Li storage mechanism and electrochemical performance of various titanium oxide-based nanostructured materials are reviewed and discussed in the following sections.

2.2. Lithium Storage Mechanisms of TiO₂ and Titanate Materials

2.2.1. TiO₂ polymorphs

Because of the low toxicity, environmental benignity and widespread availability,

TiO₂ has become one of the most extensively investigated metal oxides. Its potential applications have been identified in numerous areas including dye-sensitized solar cell, photocatalysis, gas sensing and LIBs.^[10, 30] TiO₂ has several polymorphs, among which several have been studied as electrode materials for LIBs including anatase, rutile and TiO₂-B.^[26, 31-33] Generally, the reversible reaction between Li and TiO₂ can be commonly expressed by the following equation:

This forward redox reaction typically takes place at around 1.7 V vs. Li⁺/Li. Li⁺ ions reversibly insert/extract into/from the interstitial vacancies of the TiO₂ framework. If x reaches 1, the capacity of TiO₂ would be about 335 mA h g⁻¹. In a practical situation, the lithium insertion coefficient (x in eqn. 2.4) depends on various factors, such as the intrinsic characteristics of different polymorphs, experimental conditions and the structure/composition of the materials.

As the most common and thermodynamically stable polymorph of titanium dioxide, rutile consists of edge-shared and corner-shared TiO₆ octahedra (Figure 2.1). During discharging, Li⁺ ions preferentially insert into the oxygen octahedral vacancies of the tetragonal crystal structure.^[34] It has been found that the diffusion of Li⁺ ions in rutile framework is highly anisotropic, with Li⁺ diffusion coefficient of around 10⁻⁶ cm² s⁻¹ along the c-axis and much smaller value of 10⁻¹⁵ cm² s⁻¹ in the ab-plane.^[35] Thus, Li⁺ ions mostly migrate through the channels in c-axis direction (Figure 2.1), but are difficult to reach the thermodynamically favorable sites. As a result, rutile TiO₂ with micrometer-size can only accommodate small amount of Li⁺ ions even at

very low current density.^[33] The kinetic rather than thermodynamic restriction of Li^+ insertion is further confirmed by another report, which revealed that full Li^+ insertion of rutile with $x = 1$ could happen at elevated temperature of 120 °C.^[35] However, the capacity is strongly hindered by kinetic restriction under normal conditions.

Figure 2.1 Crystal structure of rutile TiO_2 . Li-ion diffusion path and vacant sites are also indicated.^[10] Reproduced with permission from ref. 10. Copyright 2009 RSC.

Anatase is the most widely-studied polymorph of TiO_2 . The crystal structure of anatase TiO_2 can be regarded as stacking of one-dimensional zigzag chains with strongly disordered edge-sharing octahedral (Figure 2.2). Empty channels connecting the interstitial sites are formed in the framework, leading to easier Li^+ insertion compared with rutile.^[13] And it has also been found that the lithium diffusion along

Figure 2.2 Crystal structure of anatase TiO_2 .^[10] Reproduced with permission from ref. 10. Copyright 2009 RSC.

the c axis is more facile.^[36-38] However, full occupation of all the octahedral vacancies is still unlikely to happen. Further study revealed that tetragonal anatase phase splits into tetragonal $\text{Li}_{0.05}\text{TiO}_2$ and orthorhombic $\text{Li}_{0.5}\text{TiO}_2$, accompanied by a small increase (around 4%) of the volume.^[39] In real situation, it is most consistently reported that the maximum coefficient x in the lithiated Li_xTiO_2 is about 0.5,^[40] corresponding to a capacity of $\sim 167.5 \text{ mA h g}^{-1}$.

$\text{TiO}_2\text{-B}$ has lower density and more open structure compared with anatase and rutile. The three-dimensional framework of $\text{TiO}_2\text{-B}$ is constructed by corrugated layers of corner- and edge-shared TiO_6 octahedra (Figure 2.3).^[41] It is expected the infinite channels and voids in the $\text{TiO}_2\text{-B}$ crystal structure would greatly benefit Li^+ insertion. Relatively fewer studies have been reported on this polymorph, which is likely due to the much more difficulty to synthesize phase-pure $\text{TiO}_2\text{-B}$ compared to other phases. Some early studies have demonstrated the superior performance of $\text{TiO}_2\text{-B}$, with a maximum insertion of about 0.85 Li per TiO_2 at room temperature.^[42] Nevertheless, the lack of proper method for the facile and large-scale synthesis would be a practical and significant challenge for the implementation of this material.

Figure 2.3 Crystal structure of $\text{TiO}_2\text{-B}$.^[10] Reproduced with permission from ref. 10. Copyright 2009 RSC.

2.2.2. Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$

The most promising candidate among lithium titanates for anode application is the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$.^[6] The spinel structure allows accommodating three Li atoms per formula unit at about 1.5 V vs. Li^+/Li , leading to a theoretical capacity of 175 mA h g^{-1} . One important characteristic of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is that the spinel structure transfers to rocksalt $\text{Li}_7\text{Ti}_5\text{O}_{12}$ without volume change (Figure 2.4).^[7, 43] In another word, it is a “zero-strain” anode material and the integrity of the electrode is improved during extended cycling.^[28] Besides, Li^+ diffusion in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ framework is facilitated by the three-dimensional network of channels, and high Coulombic efficiency is usually achieved in experiments.^[6] However, the use of lithium salts increases the cost of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Besides, synthesis of phase-pure and highly crystalline ternary metal oxide is considered more difficult compared to that of binary titanium dioxides. The high-temperature annealing process typically involved in the synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ also introduces additional difficulties to obtain desirable nanostructures.

Figure 2.4 Crystal structures of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$.^[7] Reproduced with permission from ref. 7. Copyright 2010 Wiley.

2.2.3. Layered hydrogen titanates

Layered hydrogen titanates (LHTs) are considered as the layered forms of

titanium dioxide.^[44-47] The well-defined layered structures have typical interlayer spacing of around 0.9 nm, corresponding to the (200) diffraction in the XRD patterns. The host layers consist of edge- and corner-sharing octahedral TiO_6 units with protons accommodated within the interlayer spaces (Figure 2.5). Relatively little investigation has been done on the electrochemical properties of LHTs as LIB anodes.^[29, 48] Typically, Li^+ ions insert into the layered host at a wide voltage range of around 1~2.2 V vs. Li^+/Li . As a result, only large slope instead of well-defined plateau is found in the charge-discharge profile. It has been reported that a higher capacity over anatase TiO_2 can be achieved with ~ 0.71 Li insertion per Ti.^[29] However, the conventional synthetic method of LHTs is also quite tedious, and the protons within the framework would possibly trigger side reactions.

Figure 2.5 Crystal structures of several members of the layered hydrogen titanate family.^[49] Reproduced with permission from ref. 49. Copyright 1996 ACS.

2.3. Titanium dioxide-based anode materials with different nanostructures

According to the above discussion, titanium dioxides, especially anatase, are very promising candidates as anode materials for LIBs taking the overall performance, ease of synthesis and low cost into consideration. The poor Li^+ transport kinetics has been considered as the major drawback of TiO_2 -based anodes. Moreover, the relatively low electronic conductivity of TiO_2 , which is quite common for metal oxides, is also identified as a considerable limitation.^[50] It is believed that once proper nanostructures are adopted, TiO_2 -based materials could manifest excellent high-rate performance and long cycle life, which can hardly be matched by other anode materials. Two general strategies have been proposed to promote the lithium-ion and electron transportation. By synthesizing small nanoparticles or rationally tailoring the shape and surface of nanocrystals, fast Li^+ insertion/extraction could be achieved owing to short diffusion length and low energy barrier for diffusion. On the other hand, hybrid nanostructures with conductive agents are expected to effectively increase the electronic conductivity, which is important for high-power applications.

2.3.1. Nanoparticles

Zero-dimensional (0D) nanoparticles are commonly used as the simplest and most straightforward example to demonstrate the advantages of nanomaterials. The electrochemical properties of rutile nanoparticles with various sizes were investigated to evaluate the size effect.^[51] The smallest nanoparticles with size of 15 nm show

significantly higher reversible capacity ($\sim 264 \text{ mA h g}^{-1}$) compared with larger counterparts (Figure 2.6), corresponding to an insertion ratio of about 0.7 Li per TiO_2 . Similar research was also carried out for anatase TiO_2 . Consistent with the results from rutile, anatase TiO_2 with particle size of 6 nm manifests improved capacity especially at high current rates and better capacity retention over the 30 nm-size sample.^[52] Moreover, further analysis of the charge-discharge profiles (Figure 2.7) shows that the plateau region C_{bc} of A6 (size of 6 nm) corresponding to storage of Li in bulk anatase is shortened since fewer interstitial sites are available in small particles; yet the slope region C_{ab} in A6 is prolonged, indicating the increased surface Li storage due to the increased surface area. However, it should be noted that large amount of carbon black (over 40%) was used to prepare electrodes for these nanoparticles in order to obtain good electronic conductivity and prevent strong agglomeration. Further considering the low packing density of nanoparticles, they might not be ideal candidates for practical applications.

Figure 2.6 Cycling performance and charge-discharge profiles of rutile nanoparticles with various sizes at 50 mA g^{-1} (R15, R30 and R300 denote nanoparticles with sizes of 15, 30 and 300 nm, respectively).^[51] Reproduced with permission from ref. 51. Copyright 2007 ECS.

Figure 2.7 Charge-discharge profiles of anatase nanoparticles with size of (a) 6 and (b) 30 nm.^[52] Reproduced with permission from ref. 52. Copyright 2007 Elsevier.

2.3.2. Nanowires, nanotubes and nanorods

One-dimensional (1D) nanomaterials have attracted lots of attention due to their unique characteristics such as high aspect ratio and unique anisotropic properties. The most extensively studied 1D nanomaterials among the titanium oxide family is based on layered titanates.^[44, 45] Typical synthesis involves the hydrothermal treatment of Ti precursor (e.g., commercial TiO₂ particles) in a concentrated NaOH solution. The as-synthesized nanowires or nanotubes (the morphology depends on the particular condition) could be converted to LHT form through ion-exchange in acid solution. Lithium storage in LHT nanowires is found to be a pseudocapacitive Faradic process, and the 1D nanostructure might facilitate the lithium intercalation.^[29]

More commonly, these titanates nanomaterials are used as precursors to synthesize 1D nanostructures with other TiO₂ phases, such as anatase and TiO₂-B. Armstrong et al. reported the synthesis and electrochemical insertion of lithium of TiO₂-B nanowires/nanotubes, which are prepared from LHT nanowires/nanotubes by controlled heat treatment (Figure 2.8).^[25, 26, 42] The TiO₂-B nanowires/nanotubes

demonstrate higher lithium storage capacity ($\sim 300 \text{ mA h g}^{-1}$) than most of other TiO_2 materials. The excellent high rate performance is believed to be rendered by the unique 1D structure with good electronic transportation and facile Li^+ insertion. Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowires and nanorods have been reported with outstanding performance through complicated processes starting from 1D layered titanate nanostructures, although the 1D structure is not very uniform and well-defined due to high temperature annealing process in order to obtain high crystallinity.^[53, 54] Besides, anatase TiO_2 nanowires/nanorods have also been synthesized employing layered titanates nanowires/nanotubes as precursors.^[55-57] Their electrochemical properties were not reported in these studies. Nevertheless, the tedious synthetic procedures make them unsuitable for low-cost and large-scale production. The unique features of 1D nanostructure, such as electron transport along the longitudinal axis and Li^+ ion insertion across the lateral surface, are not yet fully understood.

Figure 2.8 TiO_2 -B (A) nanowires and (B) nanotubes.^[5] Reproduced with permission from ref. 5. Copyright 2008 Wiley.

Another important method to produce TiO_2 1D nanostructures is anodic oxidation

of Ti foils.^[58] This extensively studied approach can be used to fabricate highly ordered and uniform TiO₂ nanotubes arrays (Figure 2.9). The lithium storage properties of such nanotubes arrays as integrated electrodes have been reported.^[59] It is also found that the crystallinity of the nanotube arrays also have great impact on the electrochemical performance.^[60] The direct contact of 1D TiO₂ active materials on current collectors might facilitate the charge transport. On the other hand, the limitations of such nanotube array-based electrodes are also obvious, for example, the low productivity and high cost of the synthesis, relatively low areal capacity due to the limited thickness of the film, as well as the robustness of the array structure.

Figure 2.9 TiO₂ nanotube arrays with different diameter and length.^[58] Reproduced with permission from ref. 58. Copyright 2006 Elsevier.

2.3.3. Nanosheets

As discussed previously, theoretical studies have suggested that lithium ions mainly diffuse in anatase host along channels in the *c* direction.^[36-38] Therefore, anatase nanosheets with exposed high-energy (001) facets have been considered as promising candidates for high-power LIB anodes, due to the high exposure of active surface for fast Li⁺ diffusion and reduced distance in the *c* direction. The electrochemical Li storage property of anatase nanosheets prepared from HF-assisted hydrothermal method has been investigated.^[61] Fast and efficient Li insertion/extraction is observed, resulting in high reversible capacity of ~120 mA h g⁻¹ at 10 C. The exceptional advantages of nanosheet structure are further proven by another superior material: TiO₂ nanosheets hierarchical spheres with nearly 100% exposed (001) facets (Figure 2.10).^[62] A reversible capacity of 174 mA h g⁻¹ is obtained after 100 cycles at current density of 1 C. More remarkably, the TiO₂ hierarchical spheres demonstrate excellent high rate capability with a reversible capacity of ~90 mA h g⁻¹ at very high current density of 20 C. Further modifications of this system include constructing hollow spheres assembled from TiO₂ nanosheets and incorporating conductive matrix.^[63-65]

Very recently, TiO₂-B nanosheets have been synthesized with atomic thickness and exposed (010) facets by one-pot solvothermal synthesis, which might have great potential in LIB application.^[66] Rutile nanosheets with exposed (001) facets could be prepared by using amorphous molybdenum trioxide (MoO₃) as a stabilizing agent.^[67] Such an unusual MoO₃-stabilized rutile TiO₂ hybrid nanomaterial delivers a reversible capacity of ~180 mA h g⁻¹ after 100 cycles at 600 mA g⁻¹, obviously surpassing that of

pure rutile TiO₂ nanoparticles.

Figure 2.10 (A, B) Electron microscope images of TiO₂ nanosheets hierarchical spheres. Cycling performance at (C) constant and (D) various current rates.^[62] Reproduced with permission from ref. 62. Copyright 2010 ACS.

Despite the above advances, the synthesis of TiO₂ 2D nanostructures is still challenging. Typical bottom-up fabrication of TiO₂ nanosheets requires stabilizing a large amount of exposed surfaces during the course of crystal growth, which are generally highly active and tend to evolve to more stable surfaces.^[68] On the other hand, titanates with layered structures could be exfoliated into nanosheets via a top-down approach due to the weak interlayer binding, although the synthetic procedure is usually tedious and time-consuming.^[69, 70] Bottom-up synthesis of sheet-like layered titanates has been reported as well.^[71] Their easy conversion to TiO₂ phase could pave a new way to obtain 2D TiO₂ materials with exceptional electrochemical properties.^[72]

2.3.4. Three-dimensional/hierarchical nanostructures

One common drawback for nanomaterials in practical LIBs applications is the strong aggregation associating with the high surface energy of nanomaterials, which would block the electrolyte penetration and result in inferior performance.^[73] Besides, the electrode films composed of randomly aggregated particles would lose the integrity and electrical contact during repeated charge-discharge cycles. High external surface of conventional nanomaterials would also trigger severe parasitic reactions that results in low Coulombic efficiency and rapid capacity fading. To overcome these problems, building low-dimensional nanoscale building blocks into hierarchical structures or porous network is an effective solution.

The hierarchical sphere constructed from anatase TiO₂ nanosheets discussed in section 2.3.3 is a good example for hierarchical 3D nanostructure.^[62] Indeed, the formation of complex hierarchical structures composed of low-dimensional sub-units is quite common in many one-pot synthetic systems,^[74-76] which might be related to some inherent characteristics, e.g., self-assembling driven by the high surface energy and crystal growth behavior. Such secondary assembled structures, which are typically in sub-micro/micrometer scale, would also help to maintain the overall structure during electrochemical processes. On the other hand, constructing hierarchical structures by design is also widely practiced. For example, further modification of the previous system that produces solid hierarchical sphere with TiO₂ NSs could rationally design and synthesize various hollow spheres composed of TiO₂ NSs (Figure 2.11).^[65, 77]

Other feasible approaches include fabricating micro-sized particles or hollow

structures with high porosity. This approach can be regarded as 3D network of nanoparticles.^[78] The effectiveness of porous structures has been demonstrated by the comparison of porous and dense TiO₂ nanospheres.^[79] Mesoporous spheres or hollow nonspherical colloids of TiO₂ have been synthesized via various facile solvothermal and hydrothermal routes.^[40, 73, 80, 81] Compared with hierarchical structures building from nanorods and nanosheets, porous structures with nanosize crystallites might possess some advantages such as ease of fabrication.

Figure 2.11 (A, B) Electron microscope images of SnO₂@TiO₂-NSs hollow spheres using SiO₂ spheres as template.^[65] Reproduced with permission from ref. 65. Copyright 2010 RSC. (C, D) Electron microscope images of TiO₂-NSs hollow spheres using polystyrene hollow spheres as template.^[77] Reproduced with permission from ref. 77. Copyright 2011 RSC.

2.3.5. Nanocomposites

The above-mentioned materials, including 0D nanoparticles, 1D nanowires/rods,

2D nanosheets, and 3D hierarchical/porous particles, exclusively focus on tailoring the nanostructures to modify the electrochemical properties. At the meantime, the physicochemical properties could also be tuned by engineering the composition and forming hybrid materials. The secondary compositions that are introduced to form hybrid nanostructures with TiO_2 could be generally divided into two groups: electrochemically active metals or metal oxides (e.g., Sn or iron oxides),^[82, 83] and inert conducting or stabilizing agents (e.g., carbon coating, carbon nanotubes, graphene).^[31, 50, 63, 84] However, the rationality of the first group of compositions should be treated with special care, since most other metal or metal oxides show distinct electrochemical characteristics and working potentials compared to TiO_2 and titanates. The introduction of foreign materials could significantly alter the lithium storage properties of pristine TiO_2 and titanates, which would likely sacrifice their unique advantages. Meanwhile, nanocomposites based on TiO_2 /titanates and carbonaceous materials are more extensively studied. The carbonaceous components generally serve two roles: improving the electronic transport of the electrode materials, which are typically semiconductors, and stabilizing the nanostructures by preventing aggregation of nanoparticles and buffering volume variation.

Carbon coating has been extensively used to modify electrode materials.^[85] Amorphous carbon is commonly used to form conformal coating on nanostructured TiO_2 .^[63, 73] Similar strategy is also applied to spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$.^[54, 86] Recently, a simple synthesis method employed ionic liquids to fabricate porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated with N-doped carbon, which demonstrates significantly improved high-rate performance

compared with pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and that coated with conventional carbon.^[87]

Some advanced carbonaceous materials such as carbon nanotubes (CNTs) and graphene are more appealing to fabricate nanocomposites due to their superior electrical conductivity, high surface area and structural robustness. Coaxial nanocables with porous TiO_2 sheaths on CNT cores have been synthesized by directly growing TiO_2 on CNTs surface.^[50] A more complex hierarchical structures composed of TiO_2

Figure 2.12 (A, B) Electron microscope images of TiO_2 /graphene nanocomposites. (C) Cycling performance at various current densities and (D) Nyquist plots of (a) TiO_2 /graphene composites and (b) reference TiO_2 .^[88] Reproduced with permission from ref. 88. Copyright 2011 Wiley.

nanosheets on CNTs have also been developed.^[89] In these cases, the porous sheaths and conductive cores guarantee facile Li^+ and electron transportation, respectively.

Nanocomposites based on graphene and $\text{TiO}_2/\text{Li}_4\text{Ti}_5\text{O}_{12}$ have been studied as well.^[31, 88, 90, 91] Improvements of cycling performance and high rate capability are generally reported. For example, nanocomposites consisted of mesoporous TiO_2 nanospheres and graphene sheets have demonstrated excellent Li^+ insertion kinetics with capacity of $\sim 100 \text{ mA h g}^{-1}$ at 50°C (Figure 2.12).^[88] However, construction of complex hybrid nanostructures that fully utilize the benefits of structural and compositional engineering via cost-effective and general synthetic methods still remains challenging.

2.4. Summary

A detailed literature survey reveals that anatase TiO_2 is a promising anode material for high-performance LIBs in view of its unique electrochemical lithium storage characteristics. Specifically, anatase TiO_2 -based anodes show great potential to operate for remarkably long lifespan with high power output and improved safety. Engineering the structure and composition of the TiO_2 -based anode materials has been demonstrated as an effective and practically feasible approach to fully realize the excellent electrochemical properties of such fascinating material. In particular, TiO_2 -based materials with low-dimensional nanostructures, such as 1D nanowires and 2D nanosheets, and/or carbonaceous supports exhibit many attractive features as advanced anode materials for LIBs. Nevertheless, facile and controllable synthesis of TiO_2 -based nanostructures still remains a great challenge. Moreover, the correlation between the nanostructure and electrochemical properties is not yet fully understood.

Therefore, it is highly desirable to explore novel synthetic approach towards TiO₂-based nanostructures and to investigate their lithium storage properties. In the following chapters, the crystal growth behavior of TiO₂ in the mixtures of several common organic solvents is presented in details, which demonstrates the synthesis of distinct TiO₂-based nanostructures and their derived nanocomposites. The formation mechanism and electrochemical properties were also studied and discussed.

Chapter 3. Experimental Section

3.1. Materials Synthesis

In a typical solvothermal synthesis, a predetermined amount of Ti precursor (e.g., titanium butoxide) was added into a particular solvent, which was prepared by mixing two organic liquids (e.g., IPA, HAc, DMF). In some syntheses, additives such as lithium salts or carbonaceous materials were dissolved or dispersed in the solvent prior to the addition of Ti precursor. After thorough mixing, the solution or mixture was transferred and sealed in a Teflon-lined stainless steel autoclave, and heated in an oven. Finally, the product was collected by centrifugation, washed thoroughly with ethanol and dried at 60 °C overnight. The detailed synthetic methods and conditions for different materials are separately described in each following chapter.

3.2. Materials Characterizations

The morphologies and structures were characterized by field-emission scanning electron microscope (FESEM; JEOL, JSM-7600F/ JSM-6700F, 5 kV) and transmission electron microscope (TEM; JEOL, JEM-2010/JEM-2100F, 200 kV). X-ray diffraction (XRD) measurement was performed with a Bruker D8 Advance diffractometer and a Shimadzu XRD-6000 diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Elemental composition was analyzed with energy-dispersive X-ray spectroscopy (EDX) attached

to the FESEM, and elemental mapping was analyzed with EDX attached to the JEM-2100F. Fourier transform infrared (FTIR) spectrum was recorded with a Perkin Elmer FTIR Spectrum GX. The nitrogen adsorption-desorption isotherm was measured using a Micromeritics ASAP 2020 sorptometer. Thermogravimetric analysis (TGA) was performed with Mettler Toledo TGA/SDTA851e at a heating rate of $2\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $600\text{ }^{\circ}\text{C}$ under air flow.

3.3. Electrochemical Measurements

The working electrode was prepared with active material (nanostructured TiO_2), conductive agent (carbon black, Super-P-Li), and polymer binder [poly (vinylidene difluoride), PVDF, Aldrich] in a weight ratio of around 70:20:10 (for $\text{CNT@TiO}_2\text{-NSs}$ nanocomposite, the ratio is 80:10:10). Half-cells were assembled using two-electrode Swagelok cells in an Ar-filled glovebox, with lithium foil as both the counter and reference electrodes. The electrolyte was a solution of 1.0 M LiPF_6 in ethylene carbonate and diethyl carbonate (w/w=1:1). Cyclic voltammetry (CV) was carried out between 3.0 and 1.0 V at a scan rate of 0.5 mV s^{-1} using an electrochemical workstation (CHI 660D). The charge/discharge measurements were performed in a voltage window of $1.0 - 3.0\text{ V}$ at different current densities using a NEWARE battery tester. Electrochemical impedance measurements were conducted in a frequency range of 100 kHz to 0.01 Hz at the open circuit potential with ac perturbation of 5 mV .

Chapter 4. Asymmetric Anatase TiO₂ Nanocrystals with Exposed High-index Facets and Their Lithium Storage Properties[†]

4.1. Introduction

Crystal shape engineering is an important area in materials science. By designing nanocrystals with exposed high-energy facets, superior properties could be harvested for a myriad of applications.^[92-95] In this regard, anatase titanium dioxide (TiO₂) nanocrystals (NCs) with controlled geometric shape and exposed facets have recently received great research interests. With the assistance of fluorine ions (F⁻) as the surface capping agent, Yang et al. have synthesized anatase TiO₂ micro-sheets with 47% exposed (001) facets, which possess the highest surface energy among the low-index facets of anatase TiO₂.^[96] The F element plays a critical role during the synthetic process: by adsorbing on the (001) facets, F⁻ effectively lowers the surface energy and then stabilizes these (001) surfaces, thus preventing the diminishment of these facets during crystal growth.^[96] Because of the unusual physicochemical properties brought by the uniquely exposed facets, these NCs demonstrate superior performance in photocatalysis and lithium-ion batteries.^[62, 72, 97]

As summarized in Chapter 2 and some recent review articles,^[8, 97] even though

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numerous systems have been reported for the synthesis of anatase TiO₂ NCs with different morphologies and percentages of exposed high-energy facets, those exposed facets are generally low-index surfaces such as (001) or (100) facets.^[55] Recently the synthesis of anatase TiO₂ micron-sized crystals bounded by (105) or (107) high-index facets has been reported via a gas-phase oxidation route,^[98] which requires a relatively complicated set-up and a very high processing temperature. Thus, it still remains as an unmet challenge to facily synthesize anatase TiO₂ NCs bounded by high-index facets. In addition, despite the advances in controlling the shape of the TiO₂ NCs by many approaches,^[99, 100] symmetric shapes are always formed because of the high symmetry of its tetragonal crystal structure. Even though asymmetric nanostructures such as bimetallic^[101] or janus particles,^[102] have been intensively studied, they usually contain more than one crystal phase. The synthesis of asymmetric single-crystals has rarely been achieved, and thus presents a significant challenge in the field of crystal growth.

In this chapter, a simple solvothermal approach is presented for the synthesis of asymmetric anatase TiO₂ NCs bounded by high-index facets. By using titanium butoxide (TB) as the TiO₂ precursor in a mixed solvent containing acetic acid (HAc) and N, N-dimethylformamide (DMF), asymmetric bipyramidal TiO₂ NCs are formed via the anisotropic growth of the TiO₂ nuclei along the [001] direction. These TiO₂ NCs are bounded by (201) facets along the positive *c*-axis, and (401) facets along the negative *c*-axis, forming the lower and higher pyramids, respectively. This might be the first synthesis of asymmetric anatase TiO₂ NCs bounded by high-index facets.

Due to the high surface energy of the high-index (401) facets, these asymmetric NCs self-assemble to form a dandelion-like hierarchical structure,^[103] in order to minimize the exposure of these high-energy facets. At the same time, the (201) surfaces are exposed to the exterior, probably stabilized by the carboxylic acid group of HAc or amine group of DMF in the system.^[100]

4.2. Materials Synthesis

The organic solvent used in this work was prepared by mixing acetic acid (HAc; Merck, 100%) and N, N-dimethylformamide (DMF; Alfa Aesar, 99%) with a molar ratio (HAc:DMF) of 1:1.1. In a typical synthesis, 0.5 mL of titanium butoxide (TB; Fluka, $\geq 97\%$) was added to 20 mL of the mixed solvent. The solution was then transferred to a Teflon-lined stainless steel autoclave, and heated in an oven at 200 °C for 2 – 24 h. Finally, the product was collected by centrifugation, washed thoroughly with ethanol and dried at 60 °C overnight.

4.3. Results and Discussion

4.3.1. Morphological and compositional characterizations

The XRD pattern of the as-prepared sample is shown in Figure 4.1A. All the identified peaks can be perfectly assigned to anatase TiO₂ (JCPDS card no. 21-1272; S. G. *I4₁/amd*; $a = 3.7852 \text{ \AA}$, $c = 9.5139 \text{ \AA}$) with excellent crystallinity, indicated by

the relatively high peak intensities. The lattice parameters from Rietveld refinement are $a = 3.793 \text{ \AA}$ and $c = 9.529 \text{ \AA}$, which are close to the standard values and indicate the high quality of the anatase nanocrystals directly obtained from solvothermal synthesis. The low-magnification FESEM image (Figure 4.1B) shows that the sample consists of spherical particles with size of about $1 \text{ }\mu\text{m}$. A single particle in Figure 4.1C clearly shows that this spherical assembly is composed of rod-like subunits pointing radially outward, forming a dandelion-like hierarchical structure. A closer examination (Figure 4.1D) reveals a square-shaped projection of the rod-like subunits when viewed from the top (marked by the dotted square).^[55] Such an interesting

Figure 4.1 (A) XRD pattern and (B – C) FESEM images of as-synthesized dandelion-like TiO_2 obtained at $200 \text{ }^\circ\text{C}$ for 10 h. (D) high-magnification FESEM image of the TiO_2 needles from top view.

Figure 4.2 Nitrogen adsorption/desorption isotherm of dandelion-like TiO_2 at 77K (inset: pore-size distributions calculated by the BJH method).

structure gives a moderate Brunauer-Emmett-Teller (BET) specific surface area of $25 \text{ m}^2 \text{ g}^{-1}$ (N_2 adsorption-desorption isotherm is shown in Figure 4.2). Only some irregular nanopores are found according to the calculated pore-size distribution curve, possibly ascribed to the interspaces among the rod-like subunits (note that the sharp peak in the pore-size distribution curve from desorption branch is likely artificial).

Figure 4.3A shows a TEM image of a bundle of the subunits, which is part of the large spherical assemblies. Apparently, the rod-like subunits exhibit an elongated rhombic structure, with asymmetric apexes at the two ends. Such a unique structure is further confirmed by a TEM image of a single subunit (Figure 4.3B). It can thus be deduced that the square-shaped projection (see Figure 4.1D) is the equatorial plane (marked by the black dotted line) which divides these NCs into two parts: a short pyramid exposing to the exterior, and a long pyramid that is attached to the adjacent subunits. The inter-planar angles at two apexes are measured to be $\sim 23^\circ$ and $\sim 11^\circ$, respectively, further proving the asymmetric structure of the NCs. The selected-area

electron diffraction (SAED) pattern (Figure 4.3B, inset) reveals the single-crystal characteristic, and also indicates that the subunit is actually lying on the (010) plane.^[55] High-resolution (HR) TEM images of the regions I and II (marked by the white dotted circles in Figure 4.3B) are depicted in Figure 4.3C and D, respectively. Clearly, region I shows a set of visible lattice fringes with an inter-planar distance of

Figure 4.3 (A) TEM images of a bundle consisting of several TiO_2 needles. (B) TEM image of an individual TiO_2 needle (inset: corresponding SAED pattern). (C, D) HRTEM images taken from the dotted circles I and II in (B) respectively. The insets in C and D show the fast Fourier transform patterns of the corresponding region. (E) Schematic illustration of an individual asymmetric TiO_2 NC.

0.35 nm, matching the (101) plane of anatase TiO_2 . In region II, the inter-planar distance is measured to be 0.24 nm, corresponding to the (103) plane. Since both regions give identical fast Fourier transform (FFT) spot patterns as that of the entire crystal (Figure 4.3B, inset), together with the evidence provided by the inter-planar angles, it can be concluded that the longitudinal axis of the crystal is along the [001] direction, and the short pyramid is bounded by four (201) planes, and the tall pyramid is bounded by four (401) planes. Based on this information, a schematic drawing of the NC has been constructed as shown in Figure 4.3E, and the inter-planar angles are calculated to be 22.5° between two opposite (201) planes and 11.4° between two opposite (401) planes, which are consistent with the measurement in the TEM image.

4.3.2. Formation mechanism

Time serial analysis was conducted to understand the formation process of such unique TiO_2 NCs (Figure 4.4). When the reaction time is as short as 3 h, the structure of the product appears quite irregular under FESEM observation; nevertheless, the TEM analysis reveals that some bundles consisting of needle-like subunits are already formed. As the reaction time is extended to 4 h, the rod bundle becomes significantly thicker with an increased number of subunits, making structures more clearly identifiable. Further prolonging the reaction to 6 h will lead to the formation of more densely packed rod bundles with sharp tips pointing outwards, but the complete spherical dandelion-like assembly can only be formed after 10 h of solvothermal treatment. The corresponding XRD patterns (Figure 4.5) are in good agreement with

the morphological evolution, where the peak intensity increases substantially with the reaction time. The synthesis was also carried out at different reaction temperatures (Figure 4.6). It is found that at a lower temperature of 180 °C, such dandelion-like hierarchical structures cannot be formed even after 5 days of solvothermal treatment, while more subunits seem to be included in the formation of this large assembly at a higher temperature of 220 °C.

Figure 4.4 FESEM and TEM images of dandelion-like TiO_2 with different reaction durations: (A, B) 3h, (C, D) 4h, (E, F) 6h, and (G, H) 10h.

Figure 4.5 XRD patterns of dandelion-like TiO_2 with different reaction time.

Figure 4.6 FESEM images of dandelion-like TiO_2 with different temperatures and reaction durations: 180°C for (A) 10h, (B) 24h, (C) 5d, and (D) 220°C for 10h.

On the basis of the above observations, we propose a formation mechanism of the unique structure (Figure 4.7). At the beginning of the reaction, the TiO_2 precursor TB slowly hydrolyzes and perhaps crystallizes into symmetric rhombic crystals bounded entirely by (401) facets in the current synthesis system. However, due to the high surface energy of these high-index facets, the NCs tend to assemble on the (401) surfaces from the tall pyramid to minimize the free energy. As a result, the other set of exposed (401) facets is less stable in the current system. Thus, during the following anisotropic crystal growth process, they start to diminish and transform into lower-index crystal surfaces. When reaching the (201) facets that possess greatly reduced surface energy, they can probably be stabilized by the organic species, e.g., Ac^- , present in the system. Since all eight surfaces are now effectively stabilized, the subsequent anisotropic growth along the [001] direction will only lead to the increase in

the size of structure, giving rise to NCs with better defined facets and improved crystallinity (Figure 4.7B). As the reaction proceeds, more crystals will form in the assembly, and eventually leading to the formation of the dandelion-like hierarchical structure as illustrated in Figure 4.7A.

Figure 4.7 Schematic illustrations of (A) the formation of dandelion-like TiO₂ and (B) growth of individual TiO₂ bipyramids along the [001] direction.

4.3.3. Electrochemical measurements

We investigated the electrochemical properties of the as-prepared sample as the anode material for lithium-ion batteries. Figure 4.8A shows the charge-discharge voltage profiles for the 1st, 2nd, and 5th cycles at a current rate of 0.5 C (here 1 C = 170 mA g⁻¹). Consistent with previous observations,^[62] two dominant voltage plateaus can be clearly identified at ~1.75 V and ~2 V, during the discharge and charge processes, corresponding to the lithium insertion and deinsertion, respectively. A capacity of 214 mA h g⁻¹ can be delivered at the end of the first discharge. The corresponding charge

capacity is 182 mA h g^{-1} , implying an irreversible capacity loss of $\sim 15\%$. This is considered very low for anatase TiO_2 -based anodes, as the value is usually in the range of 30 – 50%.^[62] Such low irreversible capacity loss is comparable with previously reported anatase TiO_2 nanosheets with exposed (001) facets,^[61, 62] which might be partly attributed to the exposed high-index facets. The Coulombic efficiency quickly increases to 94% and 97% in the second and fifth cycles, respectively. The

Figure 4.8 (A) Charge/discharge curves of the first, second and fifth cycles of the dandelion-like TiO_2 at a charge/discharge rate of 0.5 C. (B) cycling performance and corresponding Coulombic efficiency of the dandelion-like TiO_2 at a charge/discharge rate of 0.5 C.

Figure 4.9 Cycling performance of the dandelion-like TiO_2 at current rate of 5 C.

irreversible capacity loss is mainly attributed to insertion of Li^+ ions into the irreversible sites of the anatase framework.^[73] During the first discharge process, Li^+ ions occupy most of the irreversible sites and remain after the following charge process. Therefore, the trapping of Li^+ ions inside the anatase framework is greatly depressed in the subsequent cycles, resulting in the rapid increase of Coulombic efficiency. The cycling performance of the sample is shown in Figure 4.8B. It is obvious that the as-prepared material demonstrates superior cyclic capacity retention during extended cycling. A reversible capacity of 153 mA h g^{-1} can be retained after 100 cycles, corresponding to 0.3% capacity loss per cycle. Cycling tests were also performed at a higher rate of 5 C as shown in Figure 4.9. The sample demonstrates a relatively good cyclic retention and delivers a reversible capacity of 70 mA h g^{-1} after 100 cycles at 5 C.

4.4. Summary

In summary, rod-like asymmetric anatase TiO_2 nanocrystals bounded by high-index facets are successfully synthesized. Using a solvothermal system, elongated bipyramidal TiO_2 nanocrystals with two asymmetric pyramids are formed via the anisotropic growth along the [001] direction: the short pyramid is bounded by four equivalent (201) facets, while the tall pyramid is bounded by four (401) high-index surfaces. By attaching these high-energy (401) planes while exposing the (201) facets, these nanocrystals self-assemble to form a dandelion-like hierarchical structure. When applied as an anode material for lithium-ion batteries, the as-prepared TiO_2 material manifests a very low initial irreversible capacity loss and superior cyclic capacity retention upon extended cycling. This work opens up a new avenue for the design of single-crystal asymmetric nanocrystals, which could represent a very important aspect in materials science for both theoretical studies and practical applications.

The remarkable electrochemical properties would be partly attributed to the quasi-1D rod-like nanostructure, where the lithium diffusion distance is largely reduced. However, the quasi-1D shape and assembled structure might limit the exposed lateral surface for fast lithium insertion. It would be highly desirable to synthesize and explore the electrochemical lithium storage of well-defined 1D TiO_2 nanostructure with high aspect ratio. In the next chapter, ultrathin and uniform anatase TiO_2 nanowires are prepared in a similar solvothermal system containing HAc and DMF as solvent, and additional lithium salts as additive to guide the anisotropic

growth of anatase TiO_2 nanocrystals. The lithium storage performance is also evaluated to reveal the feasibility of utilizing 1D TiO_2 nanostructures as anode materials for LIBs.

Chapter 5. Direct Synthesis of Anatase TiO₂ Nanowires and Their Lithium Storage Properties[†]

5.1. Introduction

As have been discussed in the previous chapters, nanostructured materials with controlled geometric shapes and architectures have drawn considerable attention for both fundamental research and practical applications.^[104-108] Particularly, 1D nanostructures such as nanowires, nanorods, and nanotubes have drawn considerable attention owing to their unique physicochemical properties that originate from the anisotropic structures.^[109-112] A wide variety of materials have been successfully synthesized into 1D nanostructures, such as carbons (e.g., carbon nanotubes^[113] and nanofibers^[114]), metals (e.g., Si^[115] and Ag^[116]), and metal oxides (e.g., ZnO^[117] and MoO₃^[118]). However, except for some materials with a highly anisotropic crystallographic structure, synthesis of 1D nanostructures in a facile and scalable manner has never been an easy task. For example, solution-phase approaches have been widely used to prepare nanostructured materials with relatively low cost and good scalability. Constructing 1D nanostructures in solution is typically achieved by facilitating the anisotropic crystal growth along a particular direction with the assistance of properly selected capping agents.^[112]

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It has been generally accepted that the geometric shape and surface property have tremendous effects on the physicochemical properties of TiO_2 .^[62, 119-122] Recent studies have demonstrated the enhanced performance of TiO_2 nanowires, nanorods, and nanobelts in photocatalysis, dye-sensitized solar cells, and lithium-ion batteries, which can be largely ascribed to the particular exposed facets and the unique anisotropic structure.^[25, 121, 123-127] However, according to the Wulff construction, anatase TiO_2 crystals will adopt the octahedral shape with the majority of the exposed surface being the energetically stable (101) facets under normal conditions. Direct formation of anatase 1D nanostructures is thus not favored. As a result, except some anatase TiO_2 nanorods with small aspect ratios, most 1D anatase TiO_2 materials reported so far are synthesized via tedious multi-step processes. For example, anatase TiO_2 nanowires/rods/belts could be prepared by hydrothermally treating or annealing protonated titanate nanowires/tubes that are typically synthesized by alkaline hydrothermal methods with subsequent acid washing.^[121, 123, 126] To the best of our knowledge, direct synthesis of 1D anatase TiO_2 nanowires with high quality and large quantity has not been achieved before.

In this chapter, a facile one-pot solvothermal approach is presented for the direct synthesis of anatase TiO_2 nanowires (TNWs) in gram-scale. The organic solvent system developed in this work containing DMF and HAc, which is similar to the solvothermal system in Chapter 4. Moreover, lithium acetate (LiAc) is used as an extra additive, together with a high concentration of TB as Ti precursor to produce TNWs. After the solvothermal reaction, a large quantity of white and mud-like

product is obtained because of the high productivity and yield. The morphology of TNWs can be tuned into hierarchical architectures or remain in freestanding form depending on the volumetric ratio of DMF/HAc as the solvent in the synthesis. Typically, the as-synthesized TNWs manifest a curve and flexible feature, with hundreds of nanometers in length and a small diameter less than 20 nm.

5.2. Materials Synthesis

In a typical synthesis, 0.2 g of lithium acetate dihydrate ($\text{LiAc} \cdot 2\text{H}_2\text{O}$; Sigma-Aldrich) was dissolved in 10 mL of organic solvent containing DMF and HAc. After addition of 2 mL of TB, the solution was transferred into a Teflon-lined stainless steel autoclave, and heated in an oven at 200 °C for 20 h. Finally, the product was collected and washed thoroughly with ethanol for several times, and finally dried in a vacuum oven at 60 °C overnight. Mixed solvents with different ratios of DMF/HAc (v/v) were used for the synthesis: 4/6, 5/5, and 6/4. To investigate the effects of agents, experiments were also performed without LiAc, replacing LiAc with lithium chloride (LiCl) and sodium acetate (NaAc), or using titanium(IV) isopropoxide (TIP; Sigma-Aldrich, 97%) as the Ti precursor. The as-synthesized TiO_2 nanowires (denoted as TNWs) were further annealed in air at 350 °C for 2 h to obtain the annealed TiO_2 nanowires (denoted as TNW-A).

5.3. Results and Discussion

5.3.1. Morphological and compositional characterizations

The as-prepared TNWs are first characterized by FESEM and TEM to reveal the morphology and structure. All of the three samples prepared with slightly different condition as presented in Figure 5.1 are composed of well-defined nanowires with high uniformity. Besides, the assembled structure of the nanowires is quite different depending on the volumetric ratio of DMF/HAc in the mixed solvent. Flower-like assemblies with a size of ca. 500 nm are obtained in the product (Figure 5.1A) when a DMF/HAc ratio (v/v) of 4/6 is used. The sample consists of thin nanowires with length of ca. 200 nm and diameter of a few nanometers as revealed by the TEM image of an individual assembly (Figure 5.1B). Interestingly, it is observed that the nanowires form small bundles first, and these bundles serve as subunits to further construct the hierarchical structure by attaching one head to the center. If the solvent is a mixture of equal volume of DMF and HAc, similar hierarchical assemblies are observed as well (Figure 5.1C). However, much fewer nanowires with slightly increased length and diameter are found in each assembly (Figure 5.1D). The surface energy of these ultrathin nanowires might be probably reduced by forming such hierarchical, thus increasing the stability. Further changing the DMF/HAc ratio to 6/4 results in freestanding nanowires without any assembled structure, which show an increased aspect ratio with typical length of several hundred nanometers and diameter of tens of nanometers (Figure 5.1E, F).

Figure 5.1 FESEM and TEM images of TiO_2 NWs (TNWs) prepared in organic solvents with different volumetric ratios of DMF/HAc: (A, B) 4/6, (C, D) 5/5, and (E, F) 6/4.

The crystallographic structure and phase composition of the TNWs were examined by powder XRD analysis. The XRD pattern of all the TNWs prepared with different DMF/HAc volumetric ratios are depicted in Figure 5.2A and 5.3. In particular, all diffraction peaks of the sample prepared with DMF/HAc ratios of 5/5 (Figure 5.2A) are perfectly assigned to anatase TiO_2 (tetragonal, *I41/amd*, JCPDS

card no. 21-1272) except for a small peak at around 31° as marked by an asterisk that might come from a trace amount of brookite. Meanwhile, the other two TNWs samples show obvious presence of impurities assigned to rutile and brookite, respectively (Figure 5.3). Thus, the anatase TNWs with the highest purity (sample prepared with a DMF/HAc ratio of 5/5, as shown in Figure 5.1C and D) are selected as the main sample for further characterization. Figure 5.2B clearly shows the curved 1D structure with good flexibility, and the diameter of TNWs typically ranges from 5 to 20 nm. Besides, some TNWs tend to easily attach to nearby ones and form a

Figure 5.2 (A) XRD pattern, (B) TEM and (C) HRTEM images of TNWs prepared with a DMF/HAc volumetric ratio of 5/5. (D) Magnified HRTEM image taken from the dotted square in (C) and corresponding FFT pattern (inset). The asterisk in (A) indicates the possible impurity of brookite.

Figure 5.3 XRD patterns of TNWs prepared in organic solvents with DMF/HAc volumetric ratios of (I) 4/6 and (II) 6/4.

bundle, which might be related to the high surface energy of the ultrathin nanowires. Figure 5.2C depicts a representative HRTEM image of a nanowire with clear and continuous lattice fringes. Therefore, each individual nanowire is likely to be single-crystalline. From the magnified HRTEM image (Figure 5.2D), two sets of lattice fringes with inter-plane spacings of 0.24 and 0.35 nm are identified and attributed to (004) and (101) planes of the anatase phase, respectively. Based on the indexed fast Fourier transform (FFT) pattern, the zone axis of this HRTEM image is determined to be along the [101] direction.^[123] The lattice fringes corresponding to (101) planes are parallel to the longitudinal axis of the nanowire. On the basis of the above observation and the crystallographic structure of anatase TiO₂, the growth direction, namely the longitudinal axis of the nanowires can be deduced to be the [101] direction. A moderate BET specific surface area of 67.2 m² g⁻¹ is obtained for

such a hierarchical structure with 1D building blocks, according to the Nitrogen adsorption/desorption isotherm given in Figure 5.4.

Figure 5.4 Nitrogen adsorption/desorption isotherm of TNWs at 77K (inset: pore-size distribution calculated by the BJH method).

5.3.2. Formation mechanism

The solvothermal system shown in this chapter is highly efficient in producing TNWs in large quantity. For example, with a laboratory setup and merely 40 mL of solvent, about 2 g of TNWs (Figure 5.5) can be synthesized with almost 100% yield and excellent reproducibility (note that the yield of the as-synthesized TNWs here is slightly over 100% due to some adsorbed organic species as discussed shortly). One-step synthesis of nanowires in solution-phase with such a high precursor concentration and yield is quite unusual. To elucidate the formation process of these TNWs, time series analysis has been performed by examining the products obtained

with different durations. Instead of direct crystallization and growth of TB precursor into crystalline nanowires, a gel-like intermediate is first formed after a short reaction duration of about 1 h. Poorly-defined nanowires start to appear when prolonging the reaction to 2 h, and they further evolve to well-defined nanowires after reacting for about 4 h (Figure 5.6). To investigate the key synthetic parameters for the formation of 1D nanostructure, a series of controlled experiments were performed. It is found

Figure 5.5. Digital photo of 1.97 g TNWs prepared in 40 mL of solvent.

Figure 5.6 TEM images of TNWs obtained after reaction for (A) 2 h and (B) 4 h.

that similar TNWs could be obtained by replacing TB with titanium(IV) isopropoxide as the precursor, suggesting the versatility of this system (Figure 5.7). However, only assemblies of polyhedral nanocrystals are produced without LiAc as the additive (Figure 5.8). Moreover, replacing LiAc with another soluble lithium salt, i.e., lithium chloride (LiCl) also results in hierarchically assembled nanowires with similar morphology, whereas other acetate salts such as sodium acetate (NaAc) fail to

Figure 5.7 FESEM image of sample prepared with titanium isopropoxide (TIP) as the Ti precursor.

Figure 5.8 FESEM and TEM images of samples prepared without adding LiAc.

Figure 5.9 FESEM images of samples prepared with (A) LiCl and (B) NaAc.

produce any 1D nanostructure (Figure 5.9). Therefore, the Li^+ ions in the solvent are crucial for the synthesis of TNWs in this solvothermal system. However, the exact mechanism is not fully understood at this moment. According to the above observations, a possible formation mechanism of the TNWs is thus proposed as follows. Firstly, the rapid gelation of high-concentration Ti precursor in the solvothermal system forms a gel-like intermediate. The intermediate is unstable under the reaction condition, which gradually dissolves and grows into crystalline anatase TiO_2 . During the crystallization process, the solvent molecules and Li^+ ions might assist the preferential growth of anatase TiO_2 nanocrystals along the [101] direction, and thus finally form the nanowires. At the meantime, the DMF/HAc ratio of the solvent also has a great impact on the hierarchical architecture of the nanowires. In the previous chapter, the synthesis of asymmetric anatase TiO_2 nanocrystals is performed in a similar organic solvent system without the addition of lithium salt and with a much lower concentration of Ti precursor.^[128] Therefore, the comparison between these two systems indicates that both the presence of metal cations and precursor concentration would significantly affect the crystal growth behavior, thus

resulting in products with morphology and structure. Thus, solvothermal method is expected to provide vast opportunities for the controllable synthesis of unusual nanostructures.

5.3.3. Removal of surface contaminants by calcination

As mentioned previously, the raw yield of the as-synthesized TNWs is slightly over 100% even after thorough wash with water and ethanol. TGA reveals that the as-synthesized TNWs show a total weight loss of ca. 5% below 350 °C (Figure 5.10). This weight loss is mainly due to the loss of surface adsorbed organic species, including solvent molecules and their derivatives, as a result of the strong interaction between solvent and crystal surface. However, these organic species covering the surface of TNWs might be problematic for some applications. Therefore, the as-synthesized TNWs are further annealed in air at 350 °C for 2h (denoted as TNW-A) in order to obtain clear surface. The crystallinity of the material remains

Figure 5.10 TGA curve of TNWs under an air flow.

Figure 5.11 (A) XRD pattern, (B) FESEM, (C) TEM and (D) HRTEM images of TNWs after annealing (TNW-A).

Figure 5.12 Nitrogen adsorption/desorption isotherm of TNW-A at 77K (inset: pore-size distribution calculated by the BJH method).

almost unchanged after the annealing as revealed by the XRD pattern (Figure 5.11A). Additionally, FESEM and TEM images shown in Figure 5.11B and C confirm the generally well retained morphology after removing the surface adsorbed species, except for being slightly shorter. More importantly, the continuous lattice fringes of anatase TiO₂ (101) planes are still well observed as shown in the HRTEM image (Figure 5.11D). The lattice fringes of (101) planes in the TNW-A sample are also parallel to the grow direction, which is in agreement with that of the as-prepared TNWs (Figure 5.2C) and suggests the perfect retention of the structure. A similar BET surface area of 72.2 m² g⁻¹ is obtained for TNW-A sample, again showing the intact structure after annealing (the nitrogen adsorption/desorption isotherm is given in Figure 5.12).

5.3.4. Electrochemical measurements

Recent studies have suggested that ultrathin 1D anatase TiO₂ nanostructures would possess unusual lithium storage properties with Li uptake approaching one per formula unit,^[129] which is obviously higher than most of the reported nanostructured anatase with around 0.5 Li uptake per TiO₂. Porous film assembled from TiO₂ nanocrystals also exhibits unusual pseudocapacitive behavior especially at high rates.^[130] Therefore, the ultrathin TNWs reported here might be promising as anode materials for LIBs. We further examine the electrochemical lithium storage properties of the TNWs. The CV curves (Figure 5.13) are generally consistent with that of

Figure 5.13 Representative CV curves of TNWs at 0.5 mV s^{-1} .

previously reported anatase TiO_2 with one pair of dominant redox peaks at ca. 1.6/2.3 V (cathodic/anodic). Moreover, a cathodic peak at ca. 1.3 V is observed in the first cycle, and a pair of much less pronounced shoulder peaks at ca. 1.4/1.8 V could be identified as well. These additional peaks could be related to the surface storage of Li or phase conversion that associating with extract Li insertion. However, some irreversible insertion of lithium is observed during the first cycle of sweep. The rate capability of the TNWs electrode is evaluated and shown in Figure 5.14. The representative charge-discharge profiles in Figure 5.14A are obtained from the second cycle of each current rate as depicted in Figure 5.14B. The TNWs show satisfactory capacity and small over potential at relatively low rates (0.5 – 2 C), whereas the capacity drops at higher rates with a significant increase of over potential due to the semiconducting nature of anatase TiO_2 . At a low rate of 0.5 C, TNWs deliver a reversible capacity of ca. 178 mA h g^{-1} , with a lithium insertion coefficient slightly

over 0.5 Li per TiO_2 . The value decreases to 124 mA h g^{-1} at 2 C and eventually to 34 mA h g^{-1} at a high rate of 10 C.

Figure 5.14 (A) Representative charge-discharge voltage profiles at various current rates, and (B) rate capability of TNWs.

At the meantime, cycling performance at both 2 and 5 C as given in Figure 5.15 shows the satisfactory stability of the electrode. It is noted that rapid capacity fading is observed within the first 30 cycles, and then the capacity remains much stable. Specifically, at the end of 300 cycles at 2 C, the electrode retains around 82% of the capacity in the 30th cycle, and this value increases to around 87.2% for a higher rate of

5 C. The capacity fading might be related to the relatively fragile TNWs with a very small thickness, although the morphology is generally retained after cycling at 5 C for 100 cycles (Figure 5.16). Meanwhile, the Coulombic efficiency quickly increases to about 100% in a few cycles and remains this high value afterwards, which is an indication of the excellent electrochemical reversibility. Therefore, the as-prepared TNWs demonstrate satisfactory lithium storage properties due to the significantly reduced diffusion distance for Li^+ ions, whereas further improvement and modification are expected to tackle the problems associated with the cycling stability and capacity retention at high current rates.

Figure 5.15 Cycling performance at 2 and 5 C rate, respectively, and Coulombic efficiency at 5 C.

Figure 5.16 FESEM images (A) before and (B) after cycling at 5 C for 100 cycles.

5.4. Summary

In summary, a facile one-pot solvothermal method has been developed to synthesize anatase TiO_2 nanowires (TNWs) with high productivity and yield. The curved nanowires can be controllably grown into freestanding nanowires or hierarchical assemblies. The TNWs are typically several hundred nanometers in length and less than 20 nm in diameter, with the longitudinal axis along the [101] direction. After removing the adsorbed organic species by annealing, the TNWs perfectly retain the 1D nanostructure. The TNWs show satisfactory lithium storage performance with prolonged cycling test up to 300 cycles. Further modifications to improve the structural stability and electronic transport are expected to fully utilize the potential of the as-prepared TNWs as anode materials for LIBs.

The relatively poor structural robustness could be a potential shortage of these TNWs, which is also likely an inherent character of ultrathin 1D nanostructure. Indeed, 1D structure is not the sole solution to reduce the diffusion distance of Li^+ ions. Porous or 2D nanostructures can also substantially shorten the migration path of ions in solid TiO_2 framework. Meanwhile, they might exhibit better structural stability compared with ultrathin nanowires, thus to improve the cycling performance. In the next chapter, hierarchical spheres composed of ultrathin LHT NSs are solvothermally synthesized and used as precursors to prepare anatase TiO_2 spheres. These TiO_2 hierarchical spheres composed of nanoscale building blocks might exhibit the benefits of both fast Li^+ ion transport and good structural robustness.

Chapter 6. Synthesis of Uniform Layered Hydrogen Titanate Hierarchical Spheres and Their Transformation to Anatase TiO₂ for Lithium-ion Batteries[†]

6.1. Introduction

As one of the most important metal oxides, TiO₂ exists in several polymorphs such as anatase, rutile and brookite.^[30, 58, 131, 132] Moreover, TiO₂ can also exist in layered structures which are more commonly known as protonated titanates or hydrogen titanates,^[44-47] which belong to a large family of layered inorganic compounds including many metal oxides/hydroxides/chalcogenides et al.^[133-137] Despite certain variety in their chemical compositions and crystal structures, layered hydrogen titanates (LHT) typically share some common features. For example, the materials exhibit well-defined layered structures with a typical interlayer spacing of ca. 0.9 nm, which corresponds to a strong (200) diffraction at a small angle in the XRD pattern. The host layers are constructed by edge- and corner-sharing octahedral TiO₆ units with protons between the interlayer spaces. Although LHTs have not been as extensively investigated as pure TiO₂, anatase and rutile phase in particular, some previous studies have shown their great potential in many applications such as adsorption, acid-based catalysis, intercalation capability, as well as photocatalysis,

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LIBs, and solar cells.^[29, 138-142] Additionally, in view of controllable synthesis of nanostructured materials, LHTs could serve as unique precursors for different TiO₂-based functional materials with unusual nanostructures that are not able to synthesize directly.^[53, 57]

Fabrication of LHTs in a facile one-pot method is rather challenging, with only few sporadic reports on solution-based synthesis of single or multiple layered LHT NSs.^[71, 141] A widely studied alkaline hydrothermal reaction typically results in alkali metal titanates with 1D structure, such as nanotubes, nanorods and nanobelts.^[143-145] An additional ion exchange process would be necessary to transform these alkali metal titanates into their protonated forms, namely LHTs. At the meantime, exfoliation of lamellar compounds into single or multiple layered NSs has been a classic topic in materials science,^[146-148] and there have been several reports on the fabrication of single layered titanate NSs through such “top-down” approach.^[69, 70] Nevertheless, assembling low-dimensional building blocks into complex hierarchical structures through a “bottom-up” approach still remains as a great challenge for LHTs.^[149-151] Therefore, it is highly desirable to investigate the direct synthesis of LHT materials with complex hierarchical structures that might offer remarkable properties for various applications.

In this chapter, a facile solvothermal system is presented for the direct synthesis of layered hydrogen titanate hierarchical spheres (LTHSs) constructed from ultrathin NSs. The size and hierarchical architecture can be controlled by the synthetic parameters. The conversion of as-synthesized LTHSs into anatase TiO₂ (titania) spheres by simple annealing method is also investigated, which results in porous titania hierarchical

spheres (PTHs) or carbon-supported titania hierarchical spheres (CTHs) depending on the annealing atmosphere. A schematic illustration of the synthesis routes is shown in Figure 6.1. As inspired by some recent studies on 3D hierarchical structures with low-dimensional building blocks,^[62, 152-154] these TiO₂ hierarchical spheres possess the advantages of high surface area and short diffusion length for chemical reaction, and high porosity and stability provided by the robust 3D architecture. Thus, the potential application of the TiO₂ hierarchical spheres as high-rate anode materials for LIBs is also investigated.

Figure 6.1 Schematic illustration for the synthesis routes of layered hydrogen titanate hierarchical spheres (LTHSs) and the derived porous TiO₂ hierarchical spheres (PTHs) and carbon-supported TiO₂ hierarchical spheres (CTHs).

6.2 Materials Synthesis

6.2.1. *Synthesis of layered hydrogen titanate hierarchical spheres*

The LTHSs were synthesized by a facile solvothermal method. In a typical synthesis, 10 mL of DMF and 30 mL of isopropyl alcohol (IPA, Fisher Scientific, HPLC grade) were mixed as the organic solvent. After that, 1.0 mL of TB was added to the mixed organic solvent. The solution was then transferred to a 60 mL Teflon-lined autoclave, and heated in an electric oven at 200 °C for 20 h. Finally, the products were collected by centrifugation, washed thoroughly with ethanol and dried at 60 °C overnight. To control the size and morphology of LTHSs, syntheses were also carried out at 180 and 220 °C keeping other conditions unchanged. Effects of solvent and amount of TB were also investigated by changing the volume ratio of DMF/IPA (mL/mL) to 6/34 and 14/26, and the amount of TB to 0.4 mL and 2.0 mL, respectively, while keeping other conditions unchanged.

6.2.2. *Synthesis of TiO₂ hierarchical spheres*

The titania hierarchical spheres were obtained by controlled calcination of as-synthesized LTHSs in air or nitrogen atmosphere. To obtain porous titania hierarchical spheres (PTHs), the as-synthesized LTHSs were calcined in air at 450 °C for 2 h with a heating rate of 1 °C min⁻¹. For the synthesis of carbon-supported titania hierarchical spheres (CTHs), the as-synthesized LTHSs were calcined in nitrogen with other parameters unchanged.

6.3 Results and Discussion

6.3.1. Morphological and compositional characterizations

Low-magnification FESEM and TEM images (Figure 6.2A, B) reveal that the as-prepared sample from the one-step solvothermal method consists of highly uniform spherical particles with a diameter of ca. 600 nm. A magnified TEM observation reveals the hierarchical structure of these spherical particles, which are assembled from curved NSs (Figure 6.2C). A single flat-lying NS on the edge of the hierarchical spheres is almost transparent as revealed by the TEM image (Figure 6.2D), indicating the ultrathin feature of the 2D building blocks. The thickness of the NSs is estimated from a HRTEM image taken from a perpendicularly lying NS (Figure 6.2E), which is around 5 nm. The layered structure with an interlayer distance of ca. 0.7 nm can be clearly observed from the inset of Figure 6.2E, corresponding to the (002) planes of hydrogen titanate. The interconnected NSs results in a highly porous framework of these LTHSs as revealed by N₂ adsorption/desorption isotherm (Figure 6.3), which could be classified as type IV with a type H3 hysteresis loop. Such a porous structure gives rise to a high BET specific surface area of 107 m² g⁻¹ and a total pore volume of 0.42 m³ g⁻¹.

The crystallographic structure of these LTHSs was confirmed by XRD analysis as shown in Figure 6.2F. The pattern shows a strong peak at $2\theta = 9.1^\circ$, suggesting the presence of a typical layered crystal structure. The XRD pattern can be satisfactorily assigned to H₂Ti₂O₅·H₂O.^[141, 155] Based on the (200) diffraction (i.e., the strongest peak at $2\theta = 9.1^\circ$), the interlayer spacing is calculated to be 0.97 nm, and the value is

Figure 6.2 (A) FESEM image, (B - D) TEM images, (E) HRTEM image (inset: magnified HRTEM image taken from the area marked by a square) and (F) XRD pattern of the as-synthesized LTHSs.

slightly larger than that estimated from HRTEM image in Figure 6.2E. Such difference between the results of TEM and XRD analysis could be ascribed to imperfect alignment between the electron beam and the layer planes, as well as possible contraction of the interlayer spacing under the irradiation of high-energy electron beam.^[141] EDX analysis

Figure 6.3 Nitrogen adsorption/desorption isotherm of the as-synthesized LTHSs (inset: pore size distributions calculated using the BJH method from both branches).

further confirms the chemical composition of the LTHSs as given in Figure 6.4A. Besides the obvious signal of Ti and O, it should be noted that C is also detected in the sample. The existence of organic components in the LTHSs is also confirmed by FTIR spectrum (Figure 6.4B). These organic species could be solvent molecules or their derivatives that both adsorbed on the surface and/or intercalated into the interlayer space. Specifically, surface adsorption of organic molecules is almost inevitable for the LTHSs that are synthesized in organic solvents and possess high surface area,^[62] which

Figure 6.4 (A) EDX analysis of the as-synthesized LTHSs. (please note that the signal of Si comes from the substrate) (B) FT-IR spectrum of the as-synthesized LTHSs.

is also observed in TNWs as reported in the previous chapter. Moreover, intercalation of small organic species into the interlayer space of layered materials is also highly possible.^[72]

6.3.2. Controlling the structure and morphology

The effects of synthetic parameters on the structure and morphology of the LTHSs are further investigated. It is found that controlling the size and morphology of the LTHSs could be easily realized by tuning the reaction temperature, solvent composition and concentration of TB precursor. Figure 6.5 depicts the FESEM images of LTHSs prepared at various reaction temperatures while keeping other conditions

Figure 6.5 FESEM images of LTHSs prepared at different temperatures: (A) 180 °C, (B) 200 °C, and (C) 220 °C. (insets: FESEM images of single hierarchical sphere from the corresponding sample)

unaltered. Specifically, all three samples exhibit a spherical morphological that are assembled from NSs. The LTHSs prepared at a lower temperature of 180 °C possess a larger size of around 800 nm, and more densely constructed by NSs (Figure 6.5A). Thus only some small openings and channels can be observed from the surface of the LTHSs. LTHSs fabricated at 200 °C, which is the same sample shown in Figure 6.2, have a diameter of around 600 nm and a medium assembling density of NSs as illustrated in Figure 6.5B. The NSs that constructed the hierarchical spheres could be more clearly observed compared to the sample synthesized at 180 °C. When the temperature was further increased to 220 °C, the size of LTHSs remains almost the same. However, the sample resembles more of a flower-like morphology due the fewer number of NSs in each hierarchical sphere (Figure 6.5C). Besides, the ratio of

Figure 6.6. LTHSs prepared with different DMF/IPA volume (mL/mL): (A) 6/34, (B) 14/26. LTHSs prepared with different amount of TB: (C) 0.4 mL, (D) 2.0 mL.

DMF/IPA in the solvent and the added amount of TB precursor also has great influence on the size of the as-prepared LTHSs as shown in Figure 6.6. Generally speaking, a higher DMF/IPA ratio of the solvent or a less amount of TB precursor results in larger LTHSs. Therefore, the present solvothermal system is highly tunable for the controllable synthesis of LTHSs with desirable size and morphology, thus offering possibility to further optimize the properties in applications.

6.3.3. Conversion of LHT to anatase TiO_2 spheres

LHT can be easily converted to TiO_2 by dehydration at elevated temperature. The dehydration process and transformation of LTHSs into TiO_2 upon heating was first studied by TGA as depicted in Figure 6.7A. A total weight loss of ca. 14.5% due to the loss of H_2O and organic species during the transformation of LHT to TiO_2 is observed between 100 and 500 $^\circ\text{C}$, while the weight loss below 100 $^\circ\text{C}$ might be attributed to surface adsorbed water. The major weight loss takes place below 450 $^\circ\text{C}$ according to

Figure 6.7 TGA curves of (A) as-synthesized LTHSs and (B) CTHSs.

the TGA curve. Therefore, the conversion of LTHSs into TiO_2 is carried out by annealing the sample at 450°C in either air or N_2 . Both of the annealed products are found to be pure anatase phase (JCPDS no. 21-1272) without other detectable impurity by XRD analysis (Figure 6.8). The diffraction peaks are prominent but also obviously broadened, suggesting the highly crystalline feature but with nanoscale crystallites of the samples. The crystallite sizes are estimated using (101) peaks as 11.4 and 10.5 nm for PTHSs and CTHSs, respectively. Moreover, the Rietveld refinement gives lattice parameters of PTHSs and CTHSs ($a = 3.785 \text{ \AA}$, $c = 9.515 \text{ \AA}$) that matches well with the standard value ($a = 3.785 \text{ \AA}$, $c = 9.514 \text{ \AA}$).

Figure 6.8 XRD patterns and Rietveld refinement of PTHSs and CTHSs.

The as-prepared LTHSs convert to PTHSs after calcination in air, which are obtained as a yellowish powder as depicted in the inset of Figure 6.9A. The spherical morphology is well retained as shown in a TEM image of a typical PTHS (Figure 6.9A). However, a closer observation on the edge of the sphere indicates that the NS structure is less discernible and shrinks into assembly of small nanocrystallites (Figure 6.9B).

The diminishment of the NS structure could be related to the re-crystallization process of LHT into anatase TiO_2 and the subsequent growth of nanocrystallites in the ultrathin

Figure 6.9 (A, B) TEM and (C) HRTEM images of PTHSs. The inset in (A) is a digital photo of the as-synthesized PTHSs).

NSs that are relatively fragile. Nevertheless, the highly porous structure remains in the PTHSs, probably due to the relatively stable hierarchical architecture. The small primary crystallites as well as the pores among them in the hierarchical spheres can be easily observed from the HRTEM image (Figure 6.9C). The highly porous structure is also confirmed by nitrogen adsorption/desorption isotherms (Figure 6.10), with a BET surface area of $86 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $0.39 \text{ cm}^3 \text{ g}^{-1}$ for these PTHSs.

Figure 6.10 Nitrogen adsorption/desorption isotherms of PTHSs (insets: pore size distributions calculated using the BJH method from both branches).

On the other hand, CTHSs is obtained by a similar calcination process carried out in an inert atmosphere of N_2 . The color of the sample is dark grey (inset of Figure 6.11A), suggesting the presence of carbonaceous component, which likely comes from the organic species in the pristine LTHSs. The carbon content is estimated to be ca. 4.5 wt% according to weight loss between 100 and 500 °C in the TGA analysis (Figure 6.7B). The spherical morphology is also perfectly retained for CTHSs as shown in Figure 6.11A. Remarkably, in contrast to PTHSs, the NS structure in CTHSs is completely preserved after the phase transformation as shown in Figure 6.11B although they become polycrystalline as shown by HRTEM image (Figure 6.11C). Due to the well preserved NS structure, these CTHSs exhibit a high BET surface area of $105 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $0.30 \text{ cm}^3 \text{ g}^{-1}$ (nitrogen adsorption/desorption isotherm is shown in Figure 6.12). The high stability of the NS structure in CTHSs is likely due to the formation of carbon component during the calcination, which covers the surface of NSs, and prevents the structure from collapsing.

Figure 6.11 (A, B) TEM and (C) HRTEM images of CTHSs. The inset in (A) is a digital photo of the as-synthesized CTHSs).

Figure 6.12 Nitrogen adsorption/desorption isotherms of CTHSs (insets: pore size distributions calculated using the BJH method from both branches).

6.3.4. Electrochemical measurements

As discussed in previous chapters, anatase TiO_2 has been considered as a promising anode material for high-rate LIBs.^[8, 10] An effective strategy to improve the electrochemical performance of TiO_2 is to design and synthesize nanostructured materials with reduced Li^+ ion diffusion length and high structural stability.^[62, 156, 157] Thus, in view of the nanoscale crystallites and porous structure, these TiO_2 hierarchical spheres should well fulfill the criteria. Electrochemical measurements were carried out to evaluate the lithium storage properties of both PTHSs and CTHSs. Figure 6.13A displays the CV curves of PTHSs at a scan rate of 0.5 mV s^{-1} . A pair of current peaks is observed in the first cycle at 1.4 and 2.3 V during the cathodic and anodic sweeps, respectively, which correspond to the typical insertion/deinsertion processes of Li^+ ions in the anatase TiO_2 framework. In the following cycles, the cathodic peak slightly shifts a higher potential of 1.6 V. Meanwhile the anodic peak shift to 2.2 V, accompanied by a gradual increase of the intensity. This indicates less trapping of lithium in the following cycles. CTHSs deliver similar CVs, except for the ascendant intensity of the cathodic peak, which might suggest an activation process for lithium insertion (Figure 6.14A). The cycling performance of PTHSs is evaluated at different constant current rates as shown in Figure 6.13B. Remarkably, the sample demonstrates excellent capacity retention at both 2 and 5 C rates. Specifically, after 200 cycles, reversible capacities of 160 mA h g^{-1} and 130 mA h g^{-1} were obtained at current rates of 2 and 5 C, respectively ($1 \text{ C} = 170 \text{ mA g}^{-1}$). Almost no capacity fading is observed over 200 cycles. Moreover, the first cycle irreversible capacity loss at 5 C is less than 20%, which is considered

Figure 6.13 (A) CVs of PTHSs at a scan rate of 0.5 mV s^{-1} between 1 and 3 V. (B) Cycling performance of PTHSs at constant current rates of 2 C and 5 C, and Coulombic efficiency at a current rate of 5 C.

quite low for TiO_2 based anodes.^[62, 158] As shown in Figure 6.13B, the Coulombic efficiency rapidly increases in the first few cycles to nearly 100% and remains at this value afterwards. CTHSs exhibit a comparable cycling performance with a reversible capacity of 129 mA h g^{-1} after 200 cycles at 5 C (Figure 6.14B).

To evaluate the high-rate performance, both the PTHSs and CTHSs electrodes are cycled at various current rates ranging from 1 to 10 C. The capacities of both samples

Figure 6.14 (A) CVs of CTHSs at a scan rate of 0.5 mV s⁻¹ between 1 and 3 V. (B) Cycling performance of CTHSs at constant current rates of 5 C.

steadily decrease as the current rate increases. PTHSs and CTHSs still deliver a high reversible capacity of ca. 110 and 100 mA h g⁻¹, respectively, at a high current rate of 10 C. And both samples can recover their original capacities when the current rate is reduced back to 1 C, indicating the excellent reversibility of the electrodes. The superior electrochemical performance of these TiO₂ hierarchical spheres could be ascribed to the unique nanostructure, namely the robust and porous hierarchical

structure assembled from nanoscale building blocks. Both the cyclability and high-rate performance of the TiO_2 hierarchical spheres shown in this chapter are much superior to that of quasi-1D rod-like asymmetric nanocrystals and 1D TNWs presented in the previous two chapters. Moreover, the present solvothermal system demonstrates the capability to control the morphology and structure of the LTHSs and as-derived TiO_2 hierarchical spheres, thus offering great potential to optimize the performance for LIBs and many other fields.

Figure 6.15 Rate performances of PTHSs and CTHSs at various current rates from 1 to 10 C.

6.4 Summary

In summary, a facile solvothermal method is presented to synthesize uniform hierarchical spheres constructed from ultrathin LHT NSs. These hierarchical spheres exhibit a porous structure with high specific surface area and good structural robustness,

with tunable size and morphology. Besides, they can be easily transformed into anatase TiO_2 hierarchical spheres with well retained porous structure. Depending on the calcination atmosphere of air or N_2 , pure anatase TiO_2 hierarchical spheres or carbon-supported TiO_2 hierarchical spheres can be obtained, respectively. Remarkably, these two types of TiO_2 hierarchical spheres manifest exceptional lithium storage capabilities with low initial irreversible loss, high capacity at a current rate of as high as 10 C, and excellent capacity retention for more than 200 cycles, which are superior to the previous asymmetric nanocrystals and nanowires, when evaluated as anode materials for high-power LIBs.

The above studies demonstrate the feasibility to improve the lithium storage performance of anatase TiO_2 by properly engineering the nanostructure. Specifically, fast and reversible lithium insertion and extraction could be achieved in a robust architecture with nanoscale building blocks. Additionally, promoting the electron transport in the electrodes is also critically important to realize remarkable high-rate performance. In the next chapter, CNTs with excellent electrical conductivity are hybridized with TiO_2 NSs and serve as “highway” for electron transport in the nanocomposite. Such hybrid nanostructure that combines several design rationales could further increase the power output of the TiO_2 -based electrodes.

Chapter 7. TiO₂ Nanosheets Hierarchically Assembled on Carbon Nanotubes as High-rate Anodes for Lithium-ion Batteries[†]

7.1. Introduction

Developing high-performance LIBs with superior nanostructured electrode materials has attracted enormous efforts worldwide.^[1, 2, 5, 22, 159, 160] In particular, TiO₂ stands out as a low-cost and environmentally friendly anode material, and serves as an excellent alternative to traditional graphite anode with many unique advantages, including improved safety, higher structural stability and great potential to achieve fast lithium insertion/extraction.^[6, 161] Despite the above advantageous features, there are still many difficulties to be tackled in order to promote the further development of TiO₂-based anode materials, especially the relatively low transport of ions and electrons in bulk TiO₂. Nanostructured TiO₂ materials with reduced distance for ion diffusion could partly alleviate the problem associating with the low ionic conductivity.^[52, 61, 62, 73] In previous chapters, various TiO₂ nanostructures, including quasi-1D rod-like asymmetric nanocrystals, 1D TNWs, and hierarchical spheres assembled from NSs or nanoparticles, have demonstrated improved electrochemical properties. TiO₂ NSs with exposed (001) facets have also been previously

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demonstrated with excellent lithium storage properties at high current rates.^[61, 62] It is believed that the unique 2D structure could significantly facilitate the lithium insertion/deinsertion processes due to the small lateral thickness, and provide good structural robustness. Meanwhile, synthesis of nanocomposites incorporating conductive matrix has been widely practiced as well, in order to improve the electronic conductivity of TiO₂-based electrodes.^[31, 50, 88, 162, 163] For instance, mesoporous TiO₂-carbon nanocomposites and coaxial nanocables composed of carbon nanotubes (CNTs) and TiO₂ both demonstrate remarkable capacity retention at high current rates, which could be mainly ascribed to the improved conductivity.^[50, 163] Therefore, it is proposed that a hybrid nanostructure integrating these two design rationales, namely grafting TiO₂ NSs onto conductive supports such as CNTs, would possess improved high-rate performance by taking advantages of facile Li⁺ and electron transport.^[64, 89]

Although several approaches have been employed to prepare CNTs/TiO₂ nanocomposites,^[50, 163-171] it still remains challenging to grow TiO₂ NSs uniformly on carbon supports, partly due to the intrinsic difficulty related to the direct synthesis of 2D sheet-like structures for TiO₂.^[89] Based on the solvothermal system presented in Chapter 6, a novel two-step route is developed to fabricate hierarchically structured nanocables with TiO₂ NSs anchored on CNTs (denoted as CNT@TiO₂-NSs). The synthetic route for the CNT@TiO₂-NSs nanocables is schematically illustrated in Figure 7.1. Such hybrid nanostructure is realized by first growing LHT NSs on CNTs by using the previously presented solvothermal method, followed by an annealing step

in N_2 to convert the LHT NSs into TiO_2 NSs. By such precursor-morphology-controlled conversion route, constructing a uniform and porous sheath with anatase TiO_2 NSs on CNT backbones can be easily achieved.

Figure 7.1 Schematic illustration of the synthesis route of CNT@ TiO_2 -NSs. The first step involves the growth of LHT NSs on the CNT backbone. The second step is a simple calcination in N_2 to convert LHT to anatase TiO_2 .

7.2. Materials Synthesis

In a typical synthesis, 5 mg of acid-treated multi-walled CNTs was dispersed in a mixture of 5 mL of DMF and 15 mL of IPA. After sonication for a few minutes, 0.5 mL of TB was added into the suspension. The mixture was then transferred to a Teflon lined autoclave, and heated in an oven at 180 °C for 20 h. The product was collected by centrifugation, washed thoroughly with ethanol and dried at 60 °C overnight. The as-synthesized CNT@LHT-NSs sample was further calcined in N_2 at 500 °C for 2 h to obtain the CNT@ TiO_2 -NSs sample.

7.3. Results and Discussion

7.3.1. Morphological and compositional characterizations

The pristine CNTs exhibit a diameter of 20 – 60 nm as shown in Figure 7.2. After the solvothermal reaction, the sample becomes a caterpillar-like morphology, with numerous NSs assembled into 1D structure (Figure 7.3). No bare CNT or freestanding hierarchical spheres as those prepared without CNTs is observed, indicating the

Figure 7.2 TEM image of pristine CNTs.

Figure 7.3 (A) FESEM and (B) TEM images of CNT@LHT-NSs.

successful growth of LHT NSs on CNTs. Indeed, the hetero-nucleation and growth of LHT NSs on CNTs is promoted by the rich hydrophilic groups on the surface of acid-treated CNTs. After the thermal transformation process, the morphology and structure of CNT@TiO₂-NSs nanocables are thoroughly characterized by FESEM and TEM as shown in Figure 7.4. Low-magnification FESEM and TEM images (Figure

Figure 7.4 (A, B) FESEM images, (C ~ E) TEM images and (F) elemental mapping of CNT@TiO₂-NSs.

7.4A, C) clearly show the well retained caterpillar-like 1D structures with a diameter of 300~400 nm, which is much larger than that of the pristine CNTs. Thus, the thickness of the TiO₂ sheath is ca. 150 nm. No cracking or detachment of NSs from CNTs is found in the sample, suggesting the good robustness of the hybrid nanostructure. Such good robustness is likely inherited from the direct growth of LHT NSs on CNTs. The TiO₂ sheath is constructed by curved and interconnected NSs as revealed by a closer FESEM and TEM observation (Figure 7.4B, D). These NSs fully cover the CNT backbones, forming a highly porous network with large open channels. The thickness of the TiO₂ NSs is found to be only a few nanometers as depicted in Figure 7.4E, which is consistent with the nearly transparent nature of the flat-lying NSs on the edge of the nanocables. Moreover, the HRTEM image reveals the polycrystalline character of the NSs with lattice fringes assigned to anatase TiO₂ (Figure 7.5). However, due to the

Figure 7.5 HRTEM image of TiO₂ NSs on the CNT@TiO₂-NSs.

relatively large thickness of the TiO_2 sheath and the low contrast of CNTs, the CNT core in the nanocables could be hardly observed from the TEM images. Thus elemental mapping is performed to better illustrate the core/sheath structure. As shown in Figure 7.4F, the CNT core is revealed by the C element mapping in the center region of the nanocable, covered by a uniform sheath consisting of Ti and O elements from TiO_2 . Such hierarchical nanocables are highly porous, as further confirmed by nitrogen adsorption/desorption isotherm (Figure 7.6) with a high BET specific surface area of $112 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $0.46 \text{ cm}^3 \text{ g}^{-1}$.

Figure 7.6 Nitrogen adsorption/desorption isotherm of $\text{CNT@TiO}_2\text{-NSs}$ (inset: pore size distributions calculated using the BJH method from both branches).

The crystal structures of different samples during the synthetic procedure, including CNTs, CNT@LHT-NSs and $\text{CNT@TiO}_2\text{-NSs}$, are examined by XRD analysis as displayed in Figure 7.7A. Pristine CNTs exhibit a strong peak at around $2\theta = \sim 26^\circ$ showing the graphitic character. This peak becomes almost discernible after the

growth of LHT NSs, whereas a new pronounced peak found at $2\theta = \sim 9^\circ$ confirms the formation of LHT with a layered structure, which is consistent with the results in Chapter 6. After the annealing process, the XRD pattern of CNT@TiO₂-NSs can be perfectly assigned to anatase TiO₂ (JCPDS no. 21-1272) without any possible impurity, suggesting the complete transformation of the LHT NSs on CNTs to anatase TiO₂ NSs. The absence of diffraction peak of CNTs in the XRD patterns of CNT@LHT-NSs and CNT@TiO₂-NSs is probably due to the relative low content of CNTs in the composites (see the discussion below) and the thick sheaths that fully cover the CNT cores.

Figure 7.7 (A) XRD patterns of (I) CNTs, (II) CNT@LHT-NSs and (III) CNT@TiO₂-NSs. (B) TGA curves of (I) CNT@LHT-NSs and (II) CNT@TiO₂-NSs.

The average crystallite size estimated using the (101) diffraction peak is ca. 8.7 nm. The phase transformation of CNT@LHT-NSs upon annealing as well as the carbon content in the nanocomposites is studied by TGA as shown in Figure 7.7B. There are generally two stages of weight loss for CNT@LHT-NSs. The first stage of ~12.5% weight loss takes place between 100 °C and 500 °C, and it is mainly attributed to the dehydration process during the phase transformation of LHT to anatase TiO₂. The second stage results in a weight loss of ~11.0% between 500 °C up to 700 °C, which is caused by the combustion and loss of CNTs. Therefore, an annealing temperature of 500 °C would be sufficient for the complete conversion of LHT NSs into TiO₂ NSs, and the annealing is carried in N₂ to avoid burning the CNT cores. For the CNT@TiO₂-NSs nanocables, a total weight loss of ~14.5% is observed up to 700 °C in air, which corresponds to the loss of CNTs. Therefore, the fraction of TiO₂ and CNTs in the nanocomposite is estimated to be 85.5% and 14.5% by weight, respectively.

7.3.2. Electrochemical measurements

In order to evaluate the lithium storage capabilities of the CNT@TiO₂-NSs hierarchical nanocables, systematic electrochemical measurements were carried out. Figure 7.8A depicts the CV curves of CNT@TiO₂-NSs nanocables at a scan rate of 0.5 mV s⁻¹, which is typical for anatase TiO₂ and generally consistent with that of previous anatase TiO₂ hierarchical spheres. In the first cycle, a broad cathodic peak is observed in the range of 1 – 2 V together with a distinct anodic peak at ~2.2 V. The cathodic peak becomes sharper and centers at ~1.7 V with a slightly increased intensity in the

following cycles, which suggests that the shoulder peak below 1.5 V in the initial cathodic peak might correspond to some irreversible processes related to the introduction of CNTs. The intensity of the anodic peak in the subsequent cycles is also increased gradually. The increase of intensity in both cathodic and anodic peaks likely suggests the existence of a possible activation process and/or less trapping of Li^+ ions. The charge/discharge voltage profiles of the CNT@TiO₂-NSs nanocables at 1 C are generally consistent with the CV curves (Figure 7.8B), with two voltage plateaus located at ~1.7 V and ~2.0 V during discharge and charge processes, respectively. A high discharge capacity of 222 mA h g⁻¹ (based on the total mass of CNT@TiO₂-NSs nanocables) is obtained at the end of the first discharge process. An initial irreversible loss of ca. 25% is observed, which is common for anatase TiO₂, and it is likely caused by the irreversible trapping of Li^+ ions in the TiO₂ framework.^[61, 62, 73] The discharge capacity decreases to 176 and 174 mA h g⁻¹ in the 2nd and 5th cycles with rapidly increased Coulombic efficiencies of 94.9 and 97.7%, respectively. Considering the fact that CNTs generally remain electrochemically inactive and deliver little capacity in the voltage range of 1 – 3 V,^[89] the actual discharge capacity of the TiO₂ component excluding CNTs would be as high as 206 mA h g⁻¹ for the second cycle. This reversible capacity is significantly higher than the theoretical value (0.5 Li per TiO₂, corresponding to 167.5 mA h g⁻¹) generally accepted for bulk anatase TiO₂.^[62, 88] It should be pointed out that such phenomenon has also been observed for other anatase TiO₂ nanostructured materials,^[88] which is mainly related to the nanoscale size and promoted charge transport.

Figure 7.8 (A) Cyclic voltammograms of CNT@TiO₂-NSs at a scan rate of 0.5 mV s⁻¹. (B) Charge-discharge voltage profiles of CNT@TiO₂-NSs at a current rate of 1 C (170 mA g⁻¹) for the first, second and fifth cycles.

The cycling stability and rate performance of CNT@TiO₂-NSs nanocables are also evaluated as shown in Figure 7.9 and 7.10. Remarkably, the sample demonstrates excellent capacity retention and high Coulombic efficiency over a prolonged cycling test at a high rate of 5 C (Figure 7.9A). A high reversible discharge capacity of 129 mA h g⁻¹ is retained at the end of 300 charge/discharge cycles, which retains 82% of the value in the second cycle (159 mA h g⁻¹). Hence the electrode only experiences a very slow capacity fading rate of only 0.07% per cycle. The Coulombic efficiency rapidly increases in the first few cycles and then remains nearly 100% thereafter, which agrees

Figure 7.9 Cycling performance of CNT@TiO₂-NSs at constant current rates of (A) 5 C, (B) 1 and 10 C.

well with previous discussion. At other current rates of 1 and 10 C, excellent capacity retention can also be obtained (Figure 7.9B). The fluctuation of the capacity during cycling tests is probably caused by the change of temperature in the lab caused by the air-conditioning system. The rate-dependent capacity of the CNT@TiO₂-NSs nanocables is evaluated by cycling at various current rates as depicted in Figure 7.10. The capacity steadily decreases as the current density increases due to the diffusion-limited process. Nevertheless, the hierarchical architecture constructed by ultrathin TiO₂ NSs building blocks guarantees the easy penetration of electrolyte into

the porous sheath and large contact area with the electroactive TiO_2 . Besides, Li^+ ions can be rapidly inserted into and extracted from the NSs due to the short diffusion path in the 2D structure. Meanwhile, the electrons transport along the conductive CNT cores is also greatly facilitated. These structural merits result in improved high-rate performance. Specifically, the hierarchical nanocables can deliver a reversible capacity of ca. 75 mA h g^{-1} at a very high rate of 20 C. Because of the excellent reversibility of Li^+ ion insertion/extraction processes, the capacity recovers to the original value when the current rate is eventually reduced back to 1 C.

Figure 7.10 Cycling performance of CNT@TiO₂-NSs at different current rates.

7.3.3. Understanding the excellent electrochemical properties

The excellent electrochemical lithium storage performance of the CNT@TiO₂-NSs nanocables could be mainly attributed to two aspects: unique hierarchical cable-like structure enables fast electronic and ionic transport, and excellent structural robustness provides long-term cycling stability. To verify these merits, electrochemical impedance

spectroscopy (EIS) and post-mortem studies were performed. Figure 7.11A shows the comparative Nyquist plots of CNT@TiO₂-NSs nanocables and the pristine PTHSs without CNT backbones (see Chapter 6). Both of the impedance spectra show a depressed semicircle in the high frequency region, followed by a declining line in the low frequency region. The diameter of the semicircle at high frequency typically represents the Faradaic charge transfer resistance. Thus from the zoom-in plot in the high frequency region (Figure 7.11B), it can be seen that the CNT@TiO₂-NSs nanocables exhibit much smaller charge transfer resistance than that of the pure TiO₂ counterpart (i.e., PTHSs). This result corroborates the improved electronic and ionic transfer kinetics in such core-shell hybrid nanostructure, which results in improved

Figure 7.11 Nyquist plots of (A, B) CNT@TiO₂-NSs nanocables and PTHSs fresh cells, and (C, D) CNT@TiO₂-NSs nanocables before and after 200 cycles at 5 C.

high-rate capability especially taking the contribution from TiO_2 only. Moreover, it is found that the charge transfer resistance dramatically reduces after being continuously charged/discharged for 200 cycles, as shown in Figure 7.11C and D. The exact reason for such activation process is not clear at this moment. It is possible that some remaining Ti^{3+} in the TiO_2 framework even at the charged state would greatly improve the electronic conductivity.^[172] Such phenomenon could also be accounted for the promising high-rate capability and long-term cycling stability of anatase TiO_2 despite its poor conductive nature.

Post-mortem FESEM studies on the electrodes after 200 cycles were performed as shown in Figure 7.12. For PTHSs electrode, the discrete spherical particles can be easily identified from the electrode film (Figure 7.12A). However, the pores on the

Figure 7.12 FESEM images of (A, B) PTHSs and (C, D) $\text{CNT@TiO}_2\text{-NSs}$ electrodes after 200 cycles at 5 C.

surface become less discernible (Figure 7.12B). Meanwhile, both the 1D nanocable structure and sheet-like subunits can be seen from Figure 7.12C and D, suggesting the good robustness of the hybrid structure. Almost no cracking or losing of TiO_2 sheaths from CNTs is observed. Besides, the more open framework constructed by nanosheets might better retain the porosity after long-term cycling test, which is crucial to maintain the fast ionic transport. Thus, the excellent structural robustness again corroborates the high electrochemical stability.

7.4. Summary

In summary, a hybrid nanostructure based on TiO_2 NS building blocks and conductive carbon supports is rationally designed and synthesized. Hierarchically structured nanocables with TiO_2 NSs directly anchored on carbon nanotubes (denoted as $\text{CNT@TiO}_2\text{-NSs}$) are synthesized by growing LHT NSs on carbon nanotubes followed by subsequent thermal transformation in N_2 . This unique core-shell structure possesses the advantages of reduced Li^+ ion diffusion length and enhanced electrical conductivity, as well as high structural robustness. As a result, $\text{CNT@TiO}_2\text{-NSs}$ nanocables demonstrate further improved cyclability with very low capacity loss for 300 cycles, and remarkable rate capability at high current rates up to 20 C. These results suggest their promising use as high-rate anode materials for next-generation LIBs.

Chapter 8. Conclusions and Outlook

8.1. Conclusions

This research project focuses on the controllable synthesis of TiO_2 and titanate-based materials as advanced anode materials for LIBs. The crystal growth behavior of titanium dioxide and titanate in mixed organic solvents containing DMF, HAc or IPA has been systematically investigated. Three unique solvothermal systems have been developed for the direct synthesis of TiO_2 or LHT materials with distinct nanostructures. Specifically, the first system using mixture of DMF and HAc as solvent yields asymmetric anatase TiO_2 nanocrystals with exposed high-index (201) and (401) facets, which exhibit a bipyramidal shape and assemble into hierarchical particles. Further modifying the ratio of DMF/HAc together with the addition of lithium salt and high-concentration titanium precursor, one-pot and large-scale synthesis of anatase TiO_2 nanowires has been realized. Finally, hierarchical spheres composed of LHT nanosheets could be synthesized in a solvent containing DMF and IPA with controllable hierarchical architecture. These LHT spheres are readily converted to anatase TiO_2 spheres while maintaining the hierarchical porous structure.

Generally speaking, the organic solvents play dual roles in these syntheses. Firstly, they are the reaction media and provide a nonaqueous environment for the slow and controllable growth of TiO_2 or LHT. At the same time, due to the functional groups of these solvent molecules, they can also serve as structure directing agents by adsorbing

on specific surfaces or guiding the crystal phase of the formed products. These studies demonstrate the feasibility of synthesizing TiO₂ or LHT nanostructured materials via template-free and one-pot solvothermal methods, and greatly expand our knowledge for controllable synthesis of nanostructured metal oxides.

Electrochemical measurements have been performed to study the lithium storage properties of the as-prepared anatase TiO₂ nanostructures and their potential use as high-performance anode materials for LIBs. These nanostructured anatase TiO₂ materials can deliver high specific capacity, remarkable cycling stability and rate capability. The improved electrochemical properties could be attributed to the significantly reduced distance for charge and mass diffusion in nanoscale primary building blocks, as well as the robust hierarchical architecture to ensure long-term cycling stability. In particular, the hierarchical porous spheres composed of NSs or nanoparticles exhibit the best electrochemical performance among the investigated anatase TiO₂ samples, which is due to the well implementation of the above-mentioned structural merits.

To further improve the high-rate performance of anatase TiO₂-based anodes, a unique hierarchical cable-like hybrid nanostructure has been rationally designed and fabricated. LHT NSs are first grown on CNTs, followed by calcination in N₂ to convert LHT NSs into anatase TiO₂ NSs. The TiO₂ NSs serve as building blocks for the porous sheaths on the CNTs backbone, forming the CNT@TiO₂-NSs hierarchical nanocables with high porosity and structural stability. The 2D structure of TiO₂ NSs leads to an extremely short diffusion length for Li⁺ ions, while the CNT backbone will contribute

to the electronic conductivity. Benefitted from these structural features, the CNT@TiO₂-NSs nanocables manifest excellent cyclability with very low capacity loss for 300 cycles, and superior rate capability at high current rates up to 20 C. These results suggest their promising use as high-rate anode materials for lithium-ion batteries. A brief comparison of the cycling stability and rate capability of different TiO₂-based nanostructures reported in this thesis is also given in Figure 8.1.

Figure 8.1 Comparison of (A) cycling performance and (B) rate capability from different TiO₂-based nanostructures in this thesis. Initial capacity in (A) and all the capacity in (B) are obtained from the second cycle at particular current rates.

In principle, the rate capability depends on the kinetics properties, including both the electron and ion transports in the materials and the electrode films. Therefore, the different rate capability of various nanostructured TiO_2 would be highly related to their crystallite size, which reflects the diffusion distance for Li^+ ions, and the electronic conductivity. The LHT-derived TiO_2 nanostructures are all composed of small nanocrystallites of ca. 10 nm, which is compared favorably to those of rod-like NCs and TNWs. Moreover, the higher porosity and surface area of LHT-derived TiO_2 would enlarge the contact between TiO_2 and electrolyte, thus benefiting the improved lithium insertion kinetics. As for the electron transport, besides the improved conductivity offered by incorporating CNTs, the intimate interconnection between nanocrystallites and the uniform size of PTHSs and CTHSs might result in continuous 3D electron transfer path in the fabricated electrodes, which contribute to their superior rate performance.

On the other side, the cycling performance is closely related to the mechanical and electrochemical stability of the electrodes. In this regard, the capacity fading of rod-like NCs might be attributed to certain irreversibility of the repeated lithium insertion/extraction process, which is related to the relatively large crystal size. For TNWs, the small thickness and 1D feature possibly make the electrode film more fragile and subjected to certain degree of mechanical disintegration. On the contrary, the hierarchical structure of LHT-derived TiO_2 offers remarkable mechanical and electrochemical stability. Nevertheless, the introduction of carbon seems to bring minor capacity fading upon cycling, which deserves further study and optimization.

Based on the above discussion, ideally a high-performance TiO_2 -based anode material should possess the following features: nanometer-sized building block with short Li^+ ions diffusion length, micrometer-scaled secondary architecture with high stability, facile electron transfer offered by conducting additives or continuous transfer path, and desirable porosity to ensure electrode/electrolyte contact. Practically, other aspects such as the cost/scalability of materials synthesis and the volumetric/areal capacity of the fabricated electrodes should be taken into consideration as well.

In summary, this research project has systematically investigated the syntheses of various TiO_2 -based nanostructures via solvothermal methods, including hierarchical particles composed of asymmetric rod-like nanocrystals, anatase TiO_2 nanowires, hierarchical spheres composed of LHT nanosheets and their derived anatase TiO_2 spheres, and hierarchical $\text{CNT}@\text{TiO}_2\text{-NSs}$ nanocables. It is demonstrated that remarkable lithium storage properties can be achieved by properly designing and synthesizing the nanostructure and composition of the anatase TiO_2 -based materials. The findings in this project greatly expand our knowledge in the synthesis of TiO_2 -based materials with controllable nanostructures, and also pave the way for the application of high-performance TiO_2 -based nanostructured anodes for next-generation LIBs.

7.2. Outlook

Solvothermal synthesis has been demonstrated as an efficient approach towards

the fabrication of low-dimensional TiO₂-based nanostructured materials with remarkable lithium storage properties and great potential as high-rate and long-life anode materials for next-generation LIBs. Nevertheless, there are still some problems that need to be tackled regarding both the synthesis and practical application of such novel anode material. The future research on nanostructured TiO₂ for electrochemical energy storage is proposed in the following aspects:

(1) In-depth investigation into the formation mechanisms of TiO₂ nanostructures in solvothermal systems. Both experimental and theoretical analysis would be necessary to better illustrate the roles of the organic solvents and additives in various solvothermal systems, for example, how they interact with the TiO₂ or titanate surface, and how the anisotropic growth of these nanocrystals takes place. A better understanding of the fundamental chemistry would possibly provide some guidance for the design and development of novel solvothermal systems that could produce TiO₂ or other inorganic nanostructures in a more controllable way.

(2) Understanding the fundamental correlations between the nanostructures and electrochemical performance. Some brief comparison and discussion have been provided in this thesis to reveal the effects of diverse nanostructures on the lithium storage properties. However, more thorough studies would be necessary to discover how the structural features, including geometric shape, exposed facets, porosity and surface area, influence the electrochemical characteristics, such as the charge transport rate and electrochemical reversibility.

(3) Exploring the solvothermal synthesis of other polymorphs of TiO₂, such as

rutile and $\text{TiO}_2\text{-B}$. Although not as extensively reported as anatase TiO_2 , solution-based synthesis of other TiO_2 polymorphs, including rutile,^[122, 124, 173] brookite,^[174-176] $\text{TiO}_2\text{-B}$ ^[177, 178] has been achieved in particular systems. The synthetic difficulties of these polymorphs with controllable nanostructures greatly hinder the investigation of their electrochemical properties. Further exploring these solution-based synthetic methods, as well as developing novel solvothermal systems would play an important role to evaluate their potential as anode materials for LIBs, and provide feasible nanostructuring strategy to optimize the performance.

(4) Fabrication of electrodes with desirable macroscopic architectures. The present research project and most of the state-of-the-art research in the materials and batteries community focus on the development of electrode materials rather than the architecture of electrodes. Nevertheless, how these electrode materials are assembled and fabricated into macroscopic electrodes will also significantly affect the electrochemical performance. In this context, many novel electrode architectures have been proposed and developed.^[179] For example, integrated electrode based on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ NW or NS arrays have been demonstrated with excellent high-rate performance.^[180, 181] Meanwhile, 3D porous carbon films of carbon nanotubes and/or graphene have been used as lightweight current collectors to make hybrid film electrodes.^[182-186] It would be desirable to fabricate TiO_2 -based integrated electrodes based on low-dimensional TiO_2 building blocks and these 3D porous carbon films in view of the 3D conductive and supporting network, excellent flexibility and improved loading mass of active materials.

(5) Development of full cells with TiO_2 -based electrodes. TiO_2 -based electrodes have demonstrated remarkable lithium storage performance in half-cell with Li as counter and reference electrode. Demonstration of prototype full cells using TiO_2 -based anodes would be a necessary step towards the practical use of this novel anode material. Many scientific and technical issues should be addressed, such as the search of proper cathode materials with comparable cycling stability and rate capability to couple with TiO_2 -based anodes. Additionally, hybrid cells that couple TiO_2 -based electrodes with supercapacitive electrodes would be another choice to achieve high power output while maintaining a satisfactory energy density.

Complete List of Publications

- [1] C. Yuan,[†] **H. B. Wu**,[†] Y. Xie, X. W. Lou, Mixed Transition-Metal Oxides: Design, Synthesis, and Energy-Related Applications, *Angewandte Chemie-International Edition*, 53, (6), 1488-1504 (2014). ([†]*contributed equally*)
- [2] **H. B. Wu**, A. Q. Pan, H. H. Hng, X. W. Lou, Template-Assisted Formation of Rattle-type V₂O₅ Hollow Microspheres with Enhanced Lithium Storage Properties, *Advanced Functional Materials*, 23, (45), 5669-5674 (2013).
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