Anatase titanium dioxide nanosheets with exposed (001) high-energy facets for high-performance lithium-ion batteries

Chen, Junsong

2012

Chen, J. S. (2012). Anatase titanium dioxide nanosheets with exposed (001) high-energy facets for high-performance lithium-ion batteries. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/48027>

<https://doi.org/10.32657/10356/48027>

**ANATASE TITANIUM DIOXIDE NANOSHEETS
WITH EXPOSED (001) HIGH-ENERGY FACETS
FOR HIGH-PERFORMANCE LITHIUM-ION
BATTERIES**

CHEN JUNSONG

**SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING**

2012

Acknowledgement

First of all, I would like to express my greatest appreciation to my supervisor, Assistant Professor Lou Xiong Wen (David), for his warm encouragement and patient instruction. Professor Lou constantly advised, inspired, and supported me throughout the course of my work, especially in times of difficulty. All my research resulted from his brilliant ideas and inspiration. He also imparted his knowledge and experience while providing me with excellent advice during my experiments and manuscript writing. Without his guidance, support, and encouragement, it would not have been possible for me to overcome the setbacks and obstacles that I encountered during the course of this research.

My acknowledgements are extended to all past and present members of Prof. Lou's group, for their friendship over the years, as well as the valuable discussions we had together.

In the end, I would like to thank my parents and my wife, for their love and dedication in raising me, supporting me, and educating me throughout my life.

Table of Contents

Acknowledgement	i
List of Abbreviations	vi
List of Figures	ix
List of Tables	xiv
Summary.....	xv
Chapter 1– Introduction.....	1
1.1. Introduction.....	1
1.2. Motivations	3
1.3. Objectives of Research	4
1.3.1. Synthesis of anatase TiO ₂ nanosheets with exposed (001) high-energy facets for high-power lithium-ion batteries.....	5
1.3.2. Investigation of the lithium storage properties of hierarchical structures assembled from anatase TiO ₂ nanosheets with exposed (001) facets	5
1.3.3. Exploring advanced composite nanomaterials composed of anatase TiO ₂ nanosheets with exposed (001) facets and different carbonaceous support.....	6
1.4. Organization.....	6
Chapter 2 – Literature Review.....	8
2.1. Overview of Lithium-ion Battery	8
2.2. Tin Dioxide	9
2.3. Iron oxide/Cobalt oxide	13
2.4. Titanium oxide	15

2.4.1. Rutile.....	15
2.4.2. Anatase.....	17
2.4.2.1. HF-assisted synthesis of anatase TiO ₂ nanosheets.....	19
2.4.2.2. HF-free synthesis of anatase TiO ₂ nanosheets.....	21
2.4.2.3. Anatase TiO ₂ NSs are ideal hosts for reversible lithium storage.....	24
Chapter 3 – Experimental Section	27
3.1. Material Characterizations	27
3.2. Electrochemical Measurements	27
Chapter 4 – Free-standing Anatase TiO ₂ Nanosheet with Exposed (001) Facets for Fast and Efficient Lithium Storage	29
4.1. Introduction.....	29
4.2. Material preparation.....	30
4.3. Results and discussion	31
4.3.1. Morphology and composition characterizations.....	31
4.3.2. Investigation of the lithium storage properties	32
4.3.3. Comparison of the cycling performance.....	36
4.4. Conclusions.....	37
Chapter 5 – Hierarchical Spheres Assembled from Large Ultrathin Anatase TiO ₂ Nanosheets with Nearly 100% Exposed (001) Facets for Fast Reversible Lithium Storage.....	38
5.1. Introduction.....	38
5.2. Materials Synthesis	40
5.3. Results and Discussions.....	41

5.3.1. Morphology and composition characterizations	41
5.3.2. Investigation of the cycling performance	47
5.3.3. Analysis of the rate capability.....	50
5.3.4. Post-mortem study	52
5.4. Conclusions.....	54
Chapter 6 – TiO ₂ and SnO ₂ @TiO ₂ Hollow Spheres Assembled from Anatase TiO ₂ Nanosheets with Enhanced Lithium Storage Properties	55
6.1. Introduction.....	55
6.2. Materials Synthesis	57
6.2.1. Synthesis of anatase TiO ₂ -NS hollow spheres.....	57
6.2.2. Synthesis of SnO ₂ @TiO ₂ -NS double-shelled hollow spheres	57
6.3. Results and Discussion	58
6.3.1. SiO ₂ @TiO ₂ -NSs and hollow TiO ₂ -NSs.....	60
6.3.2. SiO ₂ @SnO ₂ @TiO ₂ -NSs and double-shell hollow SnO ₂ @TiO ₂ -NSs....	62
6.3.4. Cycling performance measurement	64
6.4. Conclusions.....	66
Chapter 7 – Carbon-supported Ultra-thin Anatase TiO ₂ Nanosheets for Fast Reversible Lithium Storage	67
7.1. Introduction.....	67
7.2. Materials Preparation	69
7.3. Results and discussion	70
7.3.1. Characterization of the morphology and composition.....	70
7.3.2. Characterization of the surface texture	75

7.3.3. Analysis of the cyclic voltammograms	75
7.3.4. Investigation of the lithium storage properties	77
7.4. Conclusions	81
Chapter 8 – Graphene-supported Anatase TiO ₂ Nanosheets for Fast Lithium Storage.....	82
8.1. Introduction.....	82
8.2. Materials Synthesis	84
8.3. Results and Discussion	84
8.3.1. Characterization of the morphology and composition.....	84
8.3.2. Investigation of the lithium storage properties	89
8.4. Conclusions.....	93
Chapter 9 – Conclusions and Outlook	94
9.1. Conclusions.....	94
9.2. Outlook	97
Reference.....	98
Complete List of Publications.....	124

List of Abbreviations

LIB: lithium-ion Batteries

Li^+ : lithium ion

CV: cyclic voltammogram

SEI: solid-electrolyte-interface

NS: nanosheet

NSHS: nanosheet hierarchical sphere

NC: nanocrystal

MO: metal oxide

TiO_2 : titanium dioxide

SnO_2 : tin dioxide

SiO_2 : silica

PS: polystyrene

Pt: platinum

$\alpha\text{-Fe}_2\text{O}_3$: iron (III) oxide (hematite)

Fe_3O_4 : iron (II, III) oxide (magnetite)

CoO: cobalt monoxide

Co_3O_4 : tricobalt tetraoxide

LiCoO_2 : lithium cobalt oxide

$\text{Li}_4\text{Ti}_5\text{O}_{12}$: lithium titanium oxide

LiPF_6 : lithium phosphate fluoride

LiFePO_4 : Lithium hexafluorophosphate

FESEM: field-emission scanning electron microscopy

TEM: transmission electron microscopy

HR: high-resolution

SAED: selected-area electron diffraction

FFT: fast Fourier transform

XRD: X-ray diffraction

BET: Brunauer–Emmett–Teller

BJH: Barrett–Joyner–Halenda

TGA: thermogravimetric analysis

EDX: energy-dispersive X-ray spectroscopy

TIP: titanium isopropoxide

TiF_4 : titanium tetrafluoride

TiN: titanium nitride

TiB₂: titanium diboride

Ti(SO₄)₂: titanium sulfate

IPA: isopropyl alcohol

DETA: diethylenetriamine

EDTA: ethylene diamine tetraacetate

HF: hydrofluoric acid

NH₄F: ammonium fluoride

F: fluorine

PVDF: poly(vinylidene difluoride)

K₂SnO₂: potassium stannate

SnCl₄: tin tetrachloride

KOH: potassium hydroxide

H₂O₂: hydrogen peroxide

List of Figures

Fig. 1.1 Basic components and the working principle of a lithium-ion battery.	2
Fig. 2.1 The SnO ₂ hollow nanospheres prepared by Lou et al. (A), and the corresponding cyclic performance (B). Reprinted with permission from ref. 40. Copyright 2006 Wiley.....	11
Fig. 2.2 The SnO ₂ hollow nanospheres prepared by Han et al. (A), and the corresponding cyclic performance (B). Reprinted with permission from ref. 41. Copyright 2005 Wiley.....	11
Fig. 2.3 The as-prepared SnO ₂ -C nanocolloids by Lou et al. (A) and the corresponding cyclic performance with pure SnO ₂ used as comparison (B). Reprinted with permission from ref. 32. Copyright 2009 ACS.....	12
Fig. 2.4 (A) SEM image of Fe ₃ O ₄ electrodeposited onto nano-architected current collectors for 150 s at 50 °C with an applied current density of -5 mA cm^{-2} . (B) The cyclic retention of the sample in A cycled first at 1 Li ⁺ /4 h for 15 cycles followed by a higher rate value of 1 Li ⁺ /2 h. Reprinted with permission from ref. 51. Copyright 2006 Nature Publishing Group.	13
Fig. 2.7 Crystal structure of rutile TiO ₂ . The black arrow indicates the diffusion path of Li ⁺	16
Fig. 2.10 (A – C, E) Electron micrograph and (D) selected-area electron diffraction pattern of the anatase TiO ₂ single crystal nanosheets. Reprinted with permission from ref. 102. Copyright 2011 ACS.....	19
Fig. 2.11 (A) XRD pattern and (B – D) TEM images of the TiO ₂ nanosheets. Reprinted with permission from ref. 72. Copyright 2011 ACS.....	20
Fig. 2.12 SEM images of the TiO ₂ nanotube array (a) obtained via electrochemical oxidation, and anatase TiO ₂ nanocrystals (b) obtained by treating the sample in a via thermal annealing at high temperature. Reprinted with permission from ref. 104. Copyright 2009 ACS.....	22
Fig. 2.13 TEM images of TiO ₂ nanosheets (a – c) and nanocrystals (d – c). Reprinted with permission from ref. 106. Copyright 2008 ACS.....	23
Fig. 2.14 Schematic illustration showing the diffusion path (dotted line) of Li ⁺ in anatase TiO ₂ unit cell.	25

Fig. 2.15 Comparative cycling performance of anatase TiO ₂ single crystals with dominant (101) (I) and (001) (II) facets at current rates of 1 C (A) and 10 C (B). Reprinted with permission from ref. 89. Copyright 2011 RSC.	26
Fig. 4.1 Characterization results of the as-prepared TiO ₂ nanosheets: transmission electron microscopy (TEM) images (A and B); field-emission scanning electron microscopy (FESEM) image (C); (D) X-ray diffraction (XRD) pattern.	32
Fig. 4.2 Electrochemical measurements of the as-prepared TiO ₂ nanosheets: (A) Representative cyclic voltammograms at scan rate of 0.1 mV/s; (B) Charge-discharge profile of the first (I) and second (II) cycles at a current rate of 4 C; (C) Cycling performance at current rates of 10 C (I) and 20 C (II). All measurements were conducted with a voltage window of 1 V – 3 V.	34
Fig. 4.3 (A) FESEM image of the as-prepared anatase TiO ₂ nanobeads. The inset shows a high-magnification FESEM image. (B) Rate behavior of TiO ₂ nanosheets (I), Degussa P25 TiO ₂ nanoparticles (II) and anatase TiO ₂ nanobeads (III) shown in A at 1-C rate with a voltage window of 1 V – 3 V.	36
Fig. 5.1 (A) Field-emission scanning electron microscopy (FESEM) image of the as-synthesized TiO ₂ -NS spheres. (B) X-ray diffraction (XRD) patterns of the TiO ₂ -NS spheres: (I) as synthesized, and (II) after calcination at 400 °C.	41
Fig. 5.2 Thermogravimetric analysis (TGA) curve of the as-synthesized TiO ₂ -NS spheres in an air flow at a temperature ramp of 5 °C min ⁻¹	42
Fig. 5.3 FESEM images (A and B) and transmission electron microscopy (TEM) images (C and D) of as-prepared TiO ₂ nanospheres. (E) Energy-dispersive X-ray spectroscopy (EDX) analysis of the anatase TiO ₂ -NS spheres. The Pt signal arises from the Pt coating during sample preparation. (F) N ₂ adsorption/desorption isotherm of the as-prepared anatase TiO ₂ -NS spheres. The inset shows the pore size distribution calculated by the Barrett-Joyner-Halenda (BJH) method.	44
Fig. 5.4 (A) HRTEM image of an ultrathin TiO ₂ -NS showing two sets of perpendicular lattice fringes with a spacing of 0.19 nm. The inset shows the FFT pattern indexed to the [001] zone. (B) TEM image recorded around the edge of a TiO ₂ -NS sphere. (C) and (D) HRTEM images of regions 1 and 2 marked with white dotted circles in (B), respectively. Both images show lattice fringes with a spacing of 0.19 nm.	45
Fig. 5.5 FESEM (A) and TEM (B) images of the chain-like structure assembled from ultra-thin TiO ₂ -NSs, using 0.6 ml DETA and 0.6 ml TIP instead. The inset in A shows an FESEM image with higher magnification.	46

Fig. 5.6 (A) Representative CVs at a scan rate of 0.1 mV s^{-1} for the 1 st , 2 nd , and 5 th cycles. (B) charge-discharge profiles at current rate of 5 C (850 mA g^{-1}) for the 1 st , 2 nd , and 5 th cycles. (C) Cycling performance at different C-rates. All measurements were conducted with a voltage window of 1 V – 3 V.....	49
Fig. 5.7 (A) Cycling performance of the $\text{TiO}_2\text{-NSHS}$ at various charge-discharge rates. (B) The current rate dependence of the discharge capacities of the $\text{TiO}_2\text{-NSHS}$. The data are extracted from the second cycle. All measurements were conducted with a voltage window of 1 V – 3 V.	51
Fig. 5.8 FESEM images of the $\text{TiO}_2\text{-NSHS}$ before galvanostatic test (A), and after 100 charge-discharge cycles at 5 C (850 mA g^{-1}) (B). The insets in A and B are the FESEM images with higher magnification of the corresponding sample. XRD patterns (C) of the samples shown in A (I) and B (II).	53
Fig. 6.1 XRD patterns of the sample hollow $\text{TiO}_2\text{-NSs}$ (A), and hollow $\text{SnO}_2\text{@TiO}_2\text{-NS}$ (B) after (I) and before (II) calcination at 400°C . The absence of diffraction peaks due to SnO_2 in B is probably because that the SnO_2 shell deposited on the SiO_2 nanospheres is generally amorphous even after calcination.	58
Fig. 6.2 TGA data of the sample hollow $\text{TiO}_2\text{-NSs}$ (A), and hollow $\text{SnO}_2\text{@TiO}_2\text{-NS}$ (B) before calcination.	59
Fig. 6.3 Typical N_2 adsorption-desorption isotherm of the $\text{TiO}_2\text{-NS}$ hollow nanospheres. The hysteresis loop indicates a mesoporous structure. The inset shows the pore size distribution by Barrett-Joyner-Halenda (BJH) method from both branches of the isotherm.	59
Fig. 6.4 FESEM image (A) and TEM image (B) of $\text{SiO}_2\text{@TiO}_2\text{-NS}$ core-shell structure. HRTEM image (C) of part of a TiO_2 nanosheet and the corresponding FFT pattern (D) of the same area. FESEM image (E) and TEM image (F) of hollow $\text{TiO}_2\text{-NS}$ spheres.	61
Fig. 6.5 (A) FESEM image of $\text{SiO}_2\text{@TiO}_2\text{-NS}$ core-shell nanostructure; (B) EDX analysis of the sample shown in A; (C) FESEM image and (D) EDX analysis of $\text{TiO}_2\text{-NS}$ hollow spheres after removing the SiO_2 cores.....	61
Fig. 6.6 FESEM image (A) and TEM images (B, C) of $\text{TiO}_2\text{-NS}$ shells grown on $400 \text{ nm SiO}_2\text{@SnO}_2$ core-shell particles. FESEM image (D) and TEM images (E, F) of $\text{SnO}_2\text{@TiO}_2\text{-NS}$ double-shelled hollow spheres.	62

Fig. 6.7 (A) FESEM image of $\text{SiO}_2@\text{SnO}_2@\text{TiO}_2$ -NS nanostructures, and (B) its corresponding EDX analysis. (C) FESEM image of $\text{SnO}_2@\text{TiO}_2$ -NS double-shelled hollow spheres, and (D) its EDX analysis.	63
Fig. 6.8 TEM images of TiO_2 -NS nanostructure assembled on ~ 200 nm $\text{SiO}_2@\text{SnO}_2$	63
Fig. 6.9 Electrochemical analysis: (A) Charge-discharge voltage profiles of the first cycles, and (B) cycling performance showing the discharge capacities of TiO_2 -NS hollow spheres at current rates of 1 C and 10 C. (C) Cycling performance of $\text{SnO}_2@\text{TiO}_2$ -NS hollow spheres at 10 C. All measurements were conducted with a voltage window of 1 V – 3 V.....	65
Fig. 7.1 Scanning electron microscopy (SEM) images (A and B) and transmission electron microscopy (TEM) images (C and D) of sample I.....	71
Fig. 7.2 SEM images (A and B), TEM image (C), and energy dispersive X-ray analysis (EDX; D) of sample II.	72
Fig. 7.3 SEM images (A and B) and TEM images (C and D) of sample III.	73
Fig. 7.4 X-ray diffraction (XRD) patterns (A) and Thermogravimetric analysis (TGA; B) of sample I, II and III.	74
Fig. 7.5 N_2 adsorption-desorption isotherms of samples I (A), II (B) and III (C). The insets are the pore size distribution of the corresponding sample.	76
Fig. 7.6 Representative cyclic voltammograms (CV) of sample I (A), II (B), and III (C) at a scan rate of 0.5 mV s^{-1} between 1 V and 3 V. The inset in C shows the CV of the carbon-free counterpart of sample III.	78
Fig. 7.7 (A) Charge-discharge voltage profiles of the first cycles at 1 C. Cycling performance at current rates of 1 C (B) and 5 C (C). (D) Post-mortem XRD analysis of the samples at 5 C after 100 cycles. All measurements were conducted with a voltage window of 1 V – 3 V.....	80
Fig. 8.1 Schematic illustration of the formation of graphene-supported TiO_2 nanosheets (G- TiO_2 NSs).....	85
Fig. 8.2 Electron microscopy images of as-prepared graphene oxide sheets.	86
Fig. 8.3 Scanning electron microscope (SEM) images (A, B) and Transmission electron microscope (TEM) images (C, D) of the as-prepared G- TiO_2 NSs.	87

- Fig. 8.4** (A) X-ray diffraction (XRD) patterns of the samples: graphene oxide (I), graphene (II) and G-TiO₂ NSs (III). (B) Thermogravimetric analysis (TGA) of the G-TiO₂ NSs. The weight loss of ~5% below 100 °C is probably due to the evaporation of the absorbed moisture contents, which is common for materials with large surface area. 88
- Fig. 8.5** N₂ adsorption-desorption isotherm of the G-TiO₂ NSs. The inset shows the pore size distribution calculated from the adsorption branch of the isotherm. 89
- Fig. 8.6** Electrochemical measurements of G-TiO₂ NSs. (A) Representative cyclic voltammograms (CVs) at a scan rate of 0.5 mV s⁻¹. (B) Charge-discharge voltage profiles of the first 3 cycles at a current rate of 1 C. (C) Cycling performance at constant current rates of 1 C, 5 C, and 10 C. (D) Cycling performance at different current rates from 1 C to 20 C. All measurements were conducted with a voltage window of 1 – 3 V. 91
- Fig. 8.7** Comparative cycling performance between G-TiO₂ NSs and pure TiO₂ NSs prepared using similar method without graphene support at the current rate of 1 C (A) and 5 C (B). All measurements were conducted between 1 V and 3 V. ... 92

List of Tables

Table 7.1 Key parameters and electrochemical results of the three samples.....	74
--	----

Summary

Lithium-ion batteries have become the dominate power sources for portable electronic devices, because of their unmatched energy density. However, the low power density hinders their practical application in electric vehicles. The major challenge lies in the significant deterioration of battery performance at increased current rates.

The research work presented in this thesis is focused on the synthesis of novel anatase titanium dioxide (TiO_2) nanosheets with exposed (001) high-energy facets and their application as the anode material for high-power lithium-ion batteries.

A facile hydrothermal method is first developed to synthesize free-standing TiO_2 nanosheets with approximately 60% exposed (001) facets, using titanium isopropoxide as the TiO_2 precursor and hydrofluoric acid as the F donor to stabilize the high-energy facets. These as-prepared unique nanosheets demonstrate excellent lithium storage properties with superior high-rate performance, because of the exposed (001) facets granting highly efficient diffusion of Li^+ in the anatase framework.

Secondly, a simple F-free solvothermal method is proposed to synthesize hierarchical structure assembled from large ultrathin TiO_2 nanosheets bound by (001) facets on the top and bottom, where diethylenetriamine (DETA) serves as the capping agent to stabilize the high-energy facets. Due to the ultrathin feature of these nanosheet constituents, the percentage of the exposed (001) facets is close to 100%. Such hierarchical structure also renders the material with high thermal stability, as no morphological change is observed when the sample is calcined at

600 °C for the removal of the organic compound. Moreover, by adding different nanotemplates into this solvothermal system, various types of hollow structures with shells constructed by these TiO₂ nanosheets are produced. When applied in LIBs, the samples demonstrate greatly enhanced lithium storage properties, owing to the ultrathin TiO₂ nanosheets with highly efficient lithium diffusion and short diffusion path.

Lastly, different carbonaceous supports, e.g., amorphous carbon or graphene, are incorporated with these unique TiO₂ nanosheets, forming nanocomposites with advanced chemical properties. The amorphous carbon is formed by the *in-situ* carbonization of the organic stabilizing agent (DETA), while graphene is used as a support for the direct growth of these TiO₂ nanosheets. When applied as the anode material for LIBs, both these two types of carbon-based additives provide excellent buffering matrixes which absorb the volume change during the lithium insertion/deinsertion processes, leading to an improved cyclic retention. They can also increase the electrical conductivity of the composite, giving rise to a better LIB performance.

In brief, this research has uncovered the great potential of anatase TiO₂ nanosheets as the anode material for high-performance lithium-ion batteries. Because of the exposed (001) high-energy facets, lithium diffusion is significantly facilitated in the anatase framework, leading to superior high-rate performance. The enhanced physicochemical properties of the materials achieved by proper nanostructuring make them possible candidate for electric vehicles, provided that a

low-cost, large-scale and environment-friendly synthesis scheme can be successfully developed.

Chapter 1 – Introduction[†]

1.1. Introduction

Lithium ion batteries (LIBs) have for decades attracted enormous interest, from industry and from the scientific community, due to their high energy density and longer shelf life, relative to other secondary battery technologies. Today LIBs are the dominant power source for myriad types of portable electronic devices. The ever increasing need for lighter-weight, smaller, faster, more powerful portable electronics platforms guarantees that this interest in LIBs will continue for decades to come as more reliable, lighter, smaller, safer secondary batteries are sought to meet ever growing performance demands.^[1-7] Nanostructured materials are widely recognized to offer multiple attractive degrees of freedom: particle chemistry, size, mass-distribution (e.g. hollow, core-shell, rattles), shape, surface functionality (e.g. carbon coated, polymer stabilized); which can be used to build LIBs with longer cycling life, higher energy storage capacity, greater power density, and lower direct and life-cycle costs.^[2]

Fig. 1.1 shows the major components of a LIB, including a *cathode* (e.g., LiCoO_2), an *anode* (e.g., graphite), and a non-aqueous electrolyte, which usually consists of LiPF_6 in a mixed organic solvent of ethylene carbonate and diethyl carbonate. The two electrodes are separated by a polymer membrane, termed a *separator*, which is designed to prevent internal short-circuit of the battery. During

[†] Reproduced in part from [J. S. Chen, L. A. Archer, and X. W. Lou, *J. Mater. Chem.*, 11, 9912 – 9924 (2011)] by permission from *The Royal Society of Chemistry*. Copyright 2011.

discharge, Li^+ ions will diffuse from the anode to the cathode driven by the difference in the electrochemical potential between the two electrodes; electrons

Fig. 1.1 Basic components and the working principle of a lithium-ion battery.

must simultaneously flow through the external circuit to maintain the charge balance. The rechargeability of LIBs comes from the directed diffusion of Li^+ ions in the opposite direction during the charge process. To ensure consistent performance over hundreds of discharge/charge cycles required in applications, the LIB components (anode/electrolyte/cathode) are designed, respectively, to facilitate repeated de-insertion/intercalation, selective shuttling, and efficient insertion/intercalation of Li^+ ions during charge/discharge cycles.

Among the many materials candidates that could potentially replace commercial graphite as the LIB anode, titanium dioxide (TiO_2) has received considerable attention. Compare to other high-capacity anode materials such as tin dioxide, TiO_2 offers a lower theoretical capacity (170 mA h g^{-1}) than graphite; its signature advantage is the potential to accommodate faster discharging/charging (higher power) processes without compromising the structure and energy storage

capacity of the anode material.^[8] To take advantage of the high-rate capabilities of a TiO₂ anode, processes are required for rapidly transporting Li⁺ ions into/out of the poorly conducting metal oxide. Nanostructure engineering has been a widely practiced strategy to overcome this drawback of TiO₂-based anodes. An added benefit of nanostructuring comes from the fact that it creates additional capacity to store charge (i.e., surface storage), thus partially mitigating the inherently low lithium storage capacity of TiO₂. A particularly striking manifestation of both effects was recently reported for anatase TiO₂ nanosheets (NSs) with exposed (001) high-energy facets.^[9] Recently, following the first demonstration by Yang et al.,^[10] the synthesis and applications of unique anatase TiO₂ nanocrystals (NCs) with exposed (001) high-energy facets have been reported in a series of works. However, their potential use in LIBs has hardly been investigated.

1.2. Motivations

LIBs have become the dominant power sources for portable electronic devices because of their unmatched energy density. Even though they are regarded as the most promising candidate to power up electric vehicles, the relatively low power density hinders their practical application. Graphite is the currently commercialized anode material for LIB. This layered carbon-based material suffers from significant capacity deterioration when a higher current rate is applied, leading to poor high-rate performance of the cell. It is thus essential to discover a new anode material with enhanced lithium storage properties even cycled at high current rates.

As the most electroactive polymorph in the titania family, anatase TiO_2 has been widely studied in different applications. When TiO_2 serves as the anode material for LIB, it only undergoes negligible structural changes during lithium insertion/deinsertion processes, which usually leads to improved cyclic retention. However, it has some major drawbacks including low specific capacity and electrical conductivity which would lead to a poor LIB performance. Therefore, a new method needs be discovered to synthesize anatase TiO_2 with novel nanostructures and/or advanced chemical compositions which the abovementioned disadvantages could be overcome. Anatase TiO_2 nanosheets with exposed (001) high-energy facets have become one of the new rising stars in materials science. Theoretical studies have shown that such unique nanostructure will facilitate the lithium diffusion in the anatase framework, leading to promising LIB performance. It is thus intriguing to develop novel synthetic routes to fabricate TiO_2 -based nanomaterials and investigate the lithium storage properties of these interesting nanomaterials.

1.3. Objectives of Research

The main aim of this research is to find suitable metal oxide with unique nanostructure for high-performance lithium-ion batteries. This PhD project focuses on developing unique anatase TiO_2 nanosheets with exposed (001) high-energy facets, creating hierarchical or even hollow nanostructures assembled from such interesting subunits, and discovering novel composite nanomaterials containing these electroactive TiO_2 component and other carbonaceous support, such as

amorphous carbon, graphene, or carbon nanotubes. Specifically, the objective of this study can be divided into the following three categories.

1.3.1. Synthesis of anatase TiO₂ nanosheets with exposed (001) high-energy facets for high-power lithium-ion batteries

To overcome the disadvantages of TiO₂, including low electronic conductivity and low specific capacity, one good way is to create nanostructured TiO₂ with exposed (001) facets, where the diffusion of lithium in the anatase framework would be greatly enhanced, leading to significantly enhanced LIB performance. To achieve this goal, a facile hydrothermal method was developed, and the lithium storage properties of the as-prepared free-standing TiO₂ nanosheets with exposed (001) facets were investigated.

1.3.2. Investigation of the lithium storage properties of hierarchical structures assembled from anatase TiO₂ nanosheets with exposed (001) facets

Even though anatase TiO₂ nanocrystals with different morphologies has been synthesized, the percentage of the exposed (001) facets is usually low due to the thickness along the *c*-axis. We thus developed a facile solvothermal method to synthesize uniform hierarchical spheres assembled from anatase TiO₂ nanosheets with exposed (001) high-energy facets. Because of the ultrathin nature of these nanosheet constituents, we estimate that the percentage of the exposed (001) facets is nearly 100%. Furthermore, by introducing different nanotemplates, e.g., silica

nanospheres, or $\text{SnO}_2@\text{SiO}_2$ core-shell nanospheres, into the solvothermal system, different hollow structures with shells assembled from these ultrathin TiO_2 nanosheets can be created after selective removal of the SiO_2 core. These as-prepared unique TiO_2 hierarchical structures demonstrate greatly enhanced lithium storage properties with superior high-rate performance.

1.3.3. Exploring advanced composite nanomaterials composed of anatase TiO_2 nanosheets with exposed (001) facets and different carbonaceous support

It has been suggested that by incorporating carbonaceous material into the metal oxides will generally lead to improved electrochemical properties, because of dual role that the carbon plays: it acts like a buffering agent which absorbs any volume change during the lithium insertion/deinsertion process, giving the composite material a better structural stability; it also helps to increase the electronic conductivity. Thus, we have developed different approaches to create composite nanomaterials consisting of the highly electroactive anatase TiO_2 nanosheets and carbonaceous support. Two different types of carbon support were studied, which include amorphous carbon, and graphene. The as-derived nanocomposites demonstrate superior LIB performance with improved cyclic retention.

1.4. Organization

In chapter 1, a brief introduction of the study is given and an overview of the motivation behind and objective of this PhD research is presented. Next, some

recent development of the synthesis of the anatase TiO_2 nanosheets with exposed (001) facets and their application in LIBs is reviewed in chapter 2. Some common methods for material characterizations and electrochemical measurements are summarized in chapter 3. In chapter 4, a facile hydrothermal method to synthesize free-standing TiO_2 nanosheets is presented, and lithium storage properties of the as-prepared product are investigated. For chapter 5 and 6, a simple solvothermal system is introduced to synthesize hierarchical structures assembled with ultrathin TiO_2 nanosheets with nearly 100% exposed (001) facets. Furthermore, different hollow structures with shells constructed by these nanosheets are produced via employing different nanotemplates into the synthetic system, and their LIB performance is subsequently studied. In chapter 7 and 8, novel composite nanomaterials consisting of anatase TiO_2 nanosheets and different carbonaceous support, e.g., amorphous carbon or graphene, are synthesized via a simple solvothermal method, and their lithium storage properties are examined. In the last chapter, a conclusion is given, and some possible avenues for future research are raised.

Chapter 2 – Literature Review[†]

2.1. Overview of Lithium-ion Battery

Rechargeable lithium batteries, which are also called lithium-ion batteries (LIB), have become the power sources for many electronic devices in this modern world, largely due to their superior energy density which is unmatched by conventional rechargeable batteries.^[2, 4] In the 1990s, the first successfully commercialized LIB comprises lithiated metal oxide as the cathode and graphite as the anode.^[11] It is important to mention that lithium metal was once used as the anode material with high energy density because it is the lightest metal with most negative electropotential (-3.04 V vs. standard hydrogen electrode).^[2] A rechargeable system was thus constructed by combining this lithium anode with a positive electrode material, such as transition-metal oxide, and it was brought to market in the mid 1970s.^[12-19] However, even if high capacity, variable discharge rate as well as high reversibility of the positive electrode can be provided by such system, incorporation of metallic lithium creates a serious safety issue called dendrite problem.^[20-22] Namely, Li^+ will redeposit onto the anode during charge before being extracted during discharge. Usually the extracted Li ions are not the ones that have redeposited during last charge, and this will lead to the formation of a dendrite structure due to the accumulation of Li on the anode surface. This gives rise to a low Coulombic efficiency, and the protrusion made of fine Li metal may

[†] Reproduced in part from [J. S. Chen, L. A. Archer, and X. W. Lou, *J. Mater. Chem.*, 11, 9912 – 9924 (2011)] by permission from *The Royal Society of Chemistry*. Copyright 2011.

easily penetrate the separator and eventually cause internal short circuit which will create serious consequences. Lithium metal is thus not used in the commercialized rechargeable lithium batteries due to the above-mentioned safety concerns. Instead, different metal oxides have gained considerable research attentions to replace lithium or the currently used graphite as better anode materials. In the following sections, three types of metal oxides serving as the anode materials with different reaction mechanisms for LIB will be reviewed, and anatase titanium oxide (TiO₂) nanosheets with exposed (001) high-energy facets will be discussed in detail.

2.2. Tin Dioxide

As an n-type wide-bandgap semiconductor, tin oxide (SnO₂) has attracted much attention because of its application potential in many fields, including gas sensor and lithium-ion batteries (LIB).^[23-31] SnO₂ has been intensively studied as the anode material for LIB because of its high theoretical capacity of 790 mA h g⁻¹, which is twice that of currently used graphite (370 mA h g⁻¹). In a SnO₂-based LIB anode, the electrochemical processes are governed by two principal reactions: SnO₂ + 4Li⁺ + 4e⁻ → Sn + Li₂O (1); Sn + xLi⁺ + xe⁻ ↔ Li_xSn (0 ≤ x ≤ 4.4) (2).^[32-35] The first reduction reaction of SnO₂ to Sn is widely accepted as irreversible, even though recent findings suggested its partial reversibility.^[2, 32, 36] The second reaction which describes the formation of the Li_xSn alloy is believed to be reversible and contributes to the major lithium storage capacity. Thus, in such a battery system, the charge/discharge process can generally be considered as the alloy/dealloy process between Li and Sn. The charging process is the alloying

reaction, where Li^+ is intercalated into Sn and lithiated Li_xSn is formed; during discharge, Li_xSn dealloys and Li is extracted back to the cathode while Sn returns to its elemental state. Even though SnO_2 can offer very high lithium storage capacity, it also has two major drawbacks which hinder its widespread applications: the first is related to the huge initial capacity loss during the first few charge/discharge cycles, which is ascribed to the reduction of SnO_2 to Sn, and also the formation of solid-electrolyte-interface (SEI);^[32] the second issue is quick capacity fading upon extended cycling. This is due to the large volume change (up to 200%)^[5] during the alloy/dealloy process, which will cause the disintegration of electrode material and subsequently the loss of electrical contact.

So far, different approaches have been proposed in order to alleviate the so-called “pulverization” problem^[37-39] mentioned above, and these methods can be generally divided into two types: constructing unique nanostructures of pure SnO_2 , or forming nanocomposites. In the first category, one typical example could be the formation of SnO_2 hollow spheres. Recently, Lou et al.^[40] have demonstrated a facile one-pot hydrothermal synthesis of SnO_2 hollow nanospheres (Fig. 2.1), and the formation mechanism was based on a novel inside-out Ostwald ripening process. When such material was applied for LIB, it showed significant improvement in performance: it gave a much higher initial discharge capacity than previously reported data,^[41-45] which could be attributed to the hollow interior as well as the mesopores present in the SnO_2 shell created during the ripening process. Furthermore, it demonstrated much better cyclic retention when compared to other SnO_2 nanomaterials, which evidently proved the positive impact of hollow

Fig. 2.1 The SnO₂ hollow nanospheres prepared by Lou et al. (A), and the corresponding cyclic performance (B). Reprinted with permission from ref. 40. Copyright 2006 Wiley.

nanostructure upon lithium storage properties. Another example of forming SnO₂ hollow microspheres by a resorcinol-formaldehyde (RF) gel-mediated technique was illustrated by Han et al. (Fig. 2.2).^[41] Even though several incidents of broken shell or collapse of hollow structure were identified after the removal of the template through combustion, the as-prepared sample exhibited improved discharge capacity as well as Columbic efficiency.

Fig. 2.2 The SnO₂ hollow nanospheres prepared by Han et al. (A), and the corresponding cyclic performance (B). Reprinted with permission from ref. 41. Copyright 2005 Wiley.

As mentioned earlier, forming hybrid nanocomposite is another approach to mitigate the pulverization problem. There are some examples regarding the growth of crystalline SnO₂ nanotube against multiwalled carbon nanotube (MWCNT).^{[43,}

^{46-47]} They generally demonstrated good LIB performance which could be ascribed to the following structural properties: ^{1.} the large internal void space of the tube can effectively accommodate the volume change during charge/discharge; ^{2.} the CNT backbone ensures good conductivity which facilitates the electron transfer; ^{3.} large surface area is available on both sides of the tube which grants more active sites for lithium insertion. In addition to CNT, carbon is also used in the form of graphite in the SnO₂-C nanocomposites.^[32-34, 48-49] It is said that the incorporated carbon can both increase the conductivity of the hybrid material as well as serve as a buffer layer which cushions the stress induced during volume expansion. SnO₂-C composite nanocolloids synthesized by a simple one-pot hydrothermal route was demonstrated by Lou et al. (Fig. 2.3),^[32] which manifests significantly improved cycling performance up to 100 cycles. Besides direct formation of SnO₂-C composite, other methods like coating hollow SnO₂ nanospheres with a thin layer of carbon have also been elucidated.^[33-34] By combining these two characteristics, the as-formed composites exhibit greatly enhanced lithium storage properties.

Fig. 2.3 The as-prepared SnO₂-C nanocolloids by Lou et al. (A) and the corresponding cyclic performance with pure SnO₂ used as comparison (B). Reprinted with permission from ref. 32. Copyright 2009 ACS.

2.3. Iron oxide/Cobalt oxide

Another intensively studied category of anode materials is the transition metal oxides, and two typical examples are iron oxides (Fe_2O_3 and Fe_3O_4) and cobalt oxides (CoO and Co_3O_4). Generally the electrochemical reaction occurs in the electrode is $\text{MO} + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Li}_2\text{O} + \text{M}$.^[35] This proposed displacement redox reaction^[36] between MO and Li^+ is actually thermodynamically favorable and the conversion from Fe^{3+} to elemental Fe can produce a theoretical capacity of 1000 mA h g^{-1} .^[50] It is argued that the formed metal nanoparticles (M) during the first discharge will facilitate the reversible formation and decomposition of Li_2O matrix,^[35] and the use of nanostructured electrode possessing large surface area with high surface energy and enhanced electrochemical reactivity can also facilitate the backward reaction, even though the extraction of Li from Li_2O seems to be thermodynamically unachievable.^[50] One example of constructing Fe_3O_4 deposited Cu nanorod has been reported by Simon et al. (Fig. 2.4),^[51] and the as-prepared composite shows high capacity as well as excellent rate capability for LIB. At the same time, huge hysteresis between the charge and discharge profiles was

Fig. 2.4 (A) SEM image of Fe_3O_4 electrodeposited onto nano-architected current collectors for 150 s at 50°C with an applied current density of -5 mA cm^{-2} . (B) The cyclic retention of the sample in A cycled first at $1 \text{ Li}^+/4 \text{ h}$ for 15 cycles followed by a higher rate value of $1 \text{ Li}^+/2 \text{ h}$. Reprinted with permission from ref. 51. Copyright 2006 Nature Publishing Group.

identified, which may originate from the high activation barrier triggering the redox reactions. This difference would lead to poor energy efficiency, and should be overcome in future Fe_3O_4 nanostructured materials. Zhang et al.^[52] (Fig. 2.5) have demonstrated carbon coated Fe_3O_4 nanospindles for LIB anodes. The as-prepared samples show enhanced LIB performance which could be attributed to the following reasons: the carbon layers can maintain the integrity of the structure, increase the electronic conductivity and stabilizes the formed SEI films.

Fig. 2.5 (A) SEM image of the carbon coated Fe_3O_4 spindles. The inset shows a HRTEM image. (B) Comparative cycling performance among different samples. Reprinted with permission from ref. 52. Copyright 2008 Wiley.

As for Co_3O_4 , virus-templated Au- Co_3O_4 hybrid nanowires were prepared by Belcher and co-workers.^[53] with superior lithium storage properties, which could be ascribed to its large surface area, structural integrity, dense packing, and also favorable crystallinity.^[50] Lou et al. have presented the formation of needle-like Co_3O_4 nanotube with excellent rate capability and ultrahigh capacity with nearly 100% capacity retention for over 30 cycles (Fig. 2.6).^[54] After that, the same group reported the synthesis of Co_3O_4 nanoneedle calcined at different temperatures in air.^[55] Their results showed that the Co_3O_4 sample with both high surface area and total pore volume possess the best LIB performance among the three samples.

Fig. 2.6 (A) FESEM images of needlelike Co_3O_4 nanotubes. (B) Cycling performance of Co_3O_4 nanotubes at current density of 50 mA g^{-1} . Reprinted with permission from ref. 54. Copyright 2008 Wiley.

2.4. Titanium oxide

2.4.1. Rutile

Being the most common and thermodynamically stable form of titania, there are a few reports studied the property of rutile TiO_2 as the anode material for LIB. This is because that rutile has a tetragonal crystal structure with TiO_6 octahedra sharing edges in the c -direction and sharing corners in the ab plane.^[56] During discharge, Li^+ ions have to travel through the ab -plane in order to reach the favored insertion site, which is the oxygen octahedral vacancy (Fig. 2.7).^[57] It has been shown that the diffusion coefficient for Li^+ in the c -direction is about $10^{-6} \text{ cm}^2 \text{ s}^{-1}$, while that in the ab -direction is 9-orders smaller, which gives rise to nearly one-dimensional diffusion of Li^+ .^[58-60] However, these Li^+ diffusion channels in the c -direction are only available along the (001) plane which possesses the highest surface energy calculated through different methods.^[61-62] Thus, under equilibrium conditions, these high-energy (001) facets are always minimized, and large portion of (110) planes with the lowest surface energy are exposed. In such case Li insertion generally can only take place on the surface, as the diffusion into the bulk

Fig. 2.7 Crystal structure of rutile TiO₂. The black arrow indicates the diffusion path of Li⁺.

sample is greatly limited.^[56] Recent findings^[63-64] (Fig. 2.8) indicate that constructing of nanosized rutile TiO₂ can lead to a better capacity as well as rate capability. However, the capacity loss after the first cycle is very large, indicating that the full extraction of inserted Li during the previous discharge will be impossible.

Fig. 2.8 The cyclic performances of nanostructured rutile TiO₂. The inset shows the morphologies of the corresponding samples. Reprinted with permission from ref. 64. Copyright 2008 Wiley.

2.4.2. Anatase

The importance of anatase TiO_2 as a material has been highlighted by its myriad potential applications in multiple fields, such as photocatalysis,^[65-78] dye-sensitized solar cell,^[35, 79-80] biology,^[81-83] and LIBs.^[9, 46, 84-96] Anatase TiO_2 has a tetragonal crystal structure, and is the most electrochemically active polymorph of the titania family.^[8] Even though TiO_2 has been engineered into a broad range of nanostructures through numerous approaches,^[97-101] the concept of creating anatase TiO_2 NCs with exposed high-energy facets has only recently been realized.^[10] We show later that this material forms an ideal host for highly reversible lithium storage in secondary batteries.

Anatase TiO_2 crystals are usually bound by dominantly (101) facets as well as some small fraction of (001) facets because of their contrasting surface energies of 0.44 and 0.90 J m⁻², respectively.^[9] As a result, these H- and O-terminated (001) facets^[10] with high reactivity are quickly diminished during synthesis. Recently, Yang et al. reported that F species, which binds strongly to Ti, can effectively stabilize the highly reactive surfaces, allowing them to survive the process of crystal growth (Fig. 2.9).^[10] Consequently, micron-sized sheet-like anatase TiO_2 single crystals with 47% exposed (001) high-energy facets have been successfully prepared.

Inspired by this work, intensive efforts have been devoted to this exciting new area. As a result, different approaches have been developed to synthesize various types of anatase TiO_2 with exposed (001) facets. These synthesis methods can be broadly categorized into two classes: one involving hydrofluoric acid (HF) as a

Fig. 2.9 Slab models and calculated surface energies of anatase TiO_2 (001) and (101) surfaces. The optimized ratios of B/A and percentage of (001) facets (S_{001}/S), where S and S_{001} are respectively the total surface area and that contributed by the {001} facets, are also shown. a, b, Unrelaxed, clean (001) and (101) surfaces. Ti and O atoms are represented by grey and red spheres, with sixfold Ti, fivefold Ti, threefold and twofold O labelled as 6c-Ti, 5c-Ti, 3c-O and 2c-O, respectively. c, d, Unrelaxed (001) and (101) surfaces surrounded by adsorbate X atoms. e, Calculated energies of the (001) and (101) surfaces surrounded by X atoms. f, Plots of the optimized value of B/A and percentage of (001) facets for anatase single crystals with various adsorbate atoms X. Reprinted with permission from ref. 10. Copyright 2008 Nature Publishing Group.

stabilizing agent; and second that includes all other stabilization methods, i.e., without the addition of HF, which means that either different F-containing species, or distinct F-free capping agents are employed.

2.4.2.1. HF-assisted synthesis of anatase TiO_2 nanosheets

Shortly after their first demonstration, Yang et al. reported a modified solvothermal method to synthesize anatase TiO_2 nanosheets using a 2-propanol/ H_2O mixture as the solvent, and titanium tetrafluoride (TiF_4) and HF as the precursor and capping agent, respectively.^[102] The as-prepared anatase TiO_2 NSs are smaller in size and thickness (Fig. 2.10 A and B) than those reported in the original study. The selected-area electron diffraction (SAED) pattern (Fig. 2.2D) and high-resolution TEM (HRTEM; Fig. 2.10E)

Fig. 2.10 (A – C, E) Electron micrograph and (D) selected-area electron diffraction pattern of the anatase TiO_2 single crystal nanosheets. Reprinted with permission from ref. 102. Copyright 2011 ACS.

confirm that the top and bottom surfaces of these TiO_2 NSs are (001) facets. This significantly increases the percentage of high-energy facets to 64%. By changing the precursor to titanium nitride (TiN),^[69] titanium diboride (TiB_2)^[68] powders, or

titanium sulfate ($\text{Ti}(\text{SO}_4)_2$),^[65] TiO_2 NSs with different morphologies and enhanced photocatalytic activities were obtained. Using Ti powder as the precursor, Wang's group has reported flower-like TiO_2 nanostructures with probably a low percentage of exposed (001) facets.^[70] Interestingly, if hydrogen peroxide (H_2O_2) is added into the above system, the morphology of the product switches dramatically to large TiO_2 single crystals with exposed (001) as well as a small portion of (110) facets.^[70] Despite its dramatic effect, the role of H_2O_2 in the synthetic environment is not understood. More remarkably, Han et al. reported a simple solvothermal method to synthesize TiO_2 NSs by direct addition of concentrated HF solution into tetrabutyl titanate, producing NSs with only ~40 nm in edge size and ~6 nm in thickness with as high as 89% exposed (001) facets (Fig. 2.11).^[72] This method is highly

Fig. 2.11 (A) XRD pattern and (B – D) TEM images of the TiO_2 nanosheets. Reprinted with permission from ref. 72. Copyright 2011 ACS.

reproducible and the product yield is very high; it is consequently of great potential practical importance because it is compatible with large-scale applications. By decorating these TiO₂ NSs with Pt nanoparticles, via photochemical reduction deposition, Yu et al. found that the resultant Pt/TiO₂ hybrid NSs exhibit significantly enhanced photocatalytic activity for H₂-production, when compared to Degussa P25 and pure TiO₂ nanoparticles.^[67]

2.4.2.2. HF-free synthesis of anatase TiO₂ nanosheets

Despite the fact that HF is a very effective capping agent for stabilizing the (001) high-energy facet of anatase TiO₂, it is a quite harmful chemical and its toxicity and corrosiveness are of concern when used on a large scale. Thus, it is highly desirable to develop synthetic strategies that use other F-containing species or ideally F-free surface stabilizing agents. Zhu et al. have reported that directly treating TiF₄ in *tert*-butanol solvothermally will produce anatase TiO₂ NCs with approximately 43% of exposed (001) facets.^[75] Using the same precursor and disodium ethylene diamine tetraacetate (EDTA) as the capping agent, anatase TiO₂ microparticles can be fabricated with 22.8% of exposed (001) facets.^[103]

In addition to the traditional synthetic techniques such as hydro/solvothermal methods discussed above, other unconventional systems have also been developed. Through a microwave-assisted method, micron-sized anatase TiO₂ single-crystals with 80% exposed (001) facets can be synthesized using TiF₄ as precursor in a tetrafluoroborate-based ionic liquid environment, where 1-butyl-3-methylimidazolium serves as the capping agent.^[73] Alivov and Fan reported a two-

Fig. 2.12 SEM images of the TiO₂ nanotube array (a) obtained via electrochemical oxidation, and anatase TiO₂ nanocrystals (b) obtained by treating the sample in a via thermal annealing at high temperature. Reprinted with permission from ref. 104. Copyright 2009 ACS.

step synthesis of anatase TiO₂ nanocrystals with exposed (001) facets through the transformation of TiO₂ nanotubes (Fig. 2.12).^[104] In this method, a well-defined TiO₂ nanotube array is first grown on Ti sheets via electrochemical oxidation, with NH₄F and ethylene glycol as the electrolyte. The as-obtained TiO₂ nanotube array is subsequently annealed in air at a high temperature, causing its transformation into nanocrystals with exposed (001) facets. The concentration of NH₄F in the electrolyte plays an important role in controlling the size of the obtained TiO₂ nanocrystals. Ohtani's group employed a gas-phase reaction process with rapid heating and quenching to fabricate well-faceted TiO₂ crystals with ~40% exposure of (001) surfaces and few defects.^[71] Dai et al. successfully obtained truncated octahedra-shaped TiO₂ NCs with ~9.6% exposed (001) facets, through hydrothermal treatment of electrospun TiO₂ nanofibers.^[105]

When TiF₄ is used as the precursor, the concentration is generally very low. This greatly limits the product yield and hence renders large scale application unfeasible. Jaroniec and co-workers reported a modified fluoride-mediated self-

transformation strategy, utilizing titanium sulfate as the precursor and ammonium fluoride (NH_4F) as the F donor in an ethanol/ H_2O mixed solvent,^[74] to synthesize hollow anatase TiO_2 microspheres consisting of polyhedral subunits with ~20% (001) facets. To achieve completely F-free synthesis, Wu et al. reported a solvothermal method using titanium isopropoxide as the precursor and oleylamine as the stabilizing agent in benzyl alcohol to produce ultrathin anatase TiO_2 NSs and NCs with exposed high-energy facets (Fig. 2.13).^[106]

Fig. 2.13 TEM images of TiO_2 nanosheets (a – c) and nanocrystals (d – c). Reprinted with permission from ref. 106. Copyright 2008 ACS.

As discussed above, producing ultrathin TiO_2 NSs appears to provide a possible solution to overcome the drawback of low active surface area possessed by most of the anatase TiO_2 NCs due to the relatively large thickness along the

[001] direction.^[106] However, these ultrathin NSs are stabilized by a large amount of amine compound, and the removal of the surfactant through thermal treatment will most likely lead to the condensation of the NS structure or formation of irregular TiO₂ large crystals.^[9] It is thus an open challenge to produce TiO₂ nanosheets with high percentage of exposed (001) facets with good thermal stability.

2.4.2.3. Anatase TiO₂ NSs are ideal hosts for reversible lithium storage

In a TiO₂/Li half cell, the following equation governs the electrochemical reactions between Li⁺ and anatase TiO₂:^[9]

where x is the lithium insertion coefficient with a maximal value of ~ 0.5 , leading to a theoretical lithium storage capacity of 167.5 mA h g⁻¹.^[9] Several theoretical studies have pointed out that due to the special crystal structure of anatase, the diffusion pathway of Li⁺ ions can be viewed as a zigzag route along the c -direction (i.e., [001] direction) connecting the octahedral vacancy sites, where the Li⁺ is surrounded by 6 O atoms (Fig. 2.14).^[107-109] It is further suggested that Li⁺ insertion/extraction will be probably facilitated through the (001) facets.^[9, 89, 110]

To elucidate the possible role played by the exposed (001) facets, we have performed in-depth experimental and theoretical studies. For example, we successfully synthesized two types of well-faceted anatase TiO₂ NCs with contrasting percentages of exposed (001) and (101) surfaces.^[89] The theoretical

calculation using Spin-polarized density functional theory with the generalized-gradient approximation and the exchange-correlation function of

Fig. 2.14 Schematic illustration showing the diffusion path (dotted line) of Li^+ in anatase TiO_2 unit cell.

Perdew–Burke–Ernzerhof shows that the energy barriers for Li^+ insertion into the (001) and (101) are 1.33 eV and 2.73 eV, respectively, suggesting much easier insertion/extraction of Li^+ ions through the high-energy (001) facets compared to the most-stable (101) surfaces.^[89] When these two types of TiO_2 NCs are evaluated for lithium storage properties, the one with dominant (001) facets demonstrates much better lithium storage capability at a high current rate of 10 C, even though the advantage is less significant at a lower current rate of 1 C (Fig. 2.15). Both the theoretical calculation and the experimental data are in good agreement with the prediction that the lithium storage in anatase TiO_2 is greatly facilitated through the exposed (001) facets. A recent study with more detailed electrochemical investigations attributed the enhanced activity of these (001) facets for lithium

insertion to a possible synergistic contribution of a faster interfacial charge transfer and a more open pathway along the *c*-axis.^[85]

Fig. 2.15 Comparative cycling performance of anatase TiO₂ single crystals with dominant (101) (I) and (001) (II) facets at current rates of 1 C (A) and 10 C (B). Reprinted with permission from ref. 89. Copyright 2011 RSC.

Inspired by these promising results, it is thus essential to conduct a thorough investigation on the synthesis as well as the lithium storage properties of these unique anatase TiO₂ NSs with exposed (001) facets.

Chapter 3 – Experimental Section

3.1. Material Characterizations

The chemical composition of products was confirmed by X-ray powder diffraction (XRD; Bruker, D8 - Advance X-Ray Diffractometer, Cu K α , $\lambda = 1.5406$ Å). Morphology and structure of the samples were examined by transmission electron microscope (TEM; JEOL, JEM-2100F, 200 kV), field-emission scanning electron microscope (FESEM; JEOL, JSM-6700F, 5 kV), and energy dispersive X-ray spectroscopy attached to the FESEM. The surface area of the sample was measured using Quantachrome Instruments, Autosorb AS-6B. The thermogravimetric analysis (TGA) was carried out in a flow of air with a temperature ramp of 5 °C min⁻¹.

3.2. Electrochemical Measurements

The electrochemical measurements were carried out using two-electrode Swagelok cells with pure lithium metal as the counter and also the reference electrodes at room temperature. The working electrode consists of active material, a conductive agent (carbon black, Super-P-Li), and a polymer binder (polyvinylidene difluoride, PVDF, Aldrich) in a weight ratio of 70:20:10. The electrolyte used was 1.0 M LiPF₆ in a 50:50 (w/w) mixture of ethylene carbonate and diethyl carbonate. Cell assembly was carried out in an Ar-filled glovebox with concentrations of moisture and oxygen below 1.0 ppm. Cyclic voltammetry (CV, 1 V - 3 V, 0.2 - 0.5 mV/s) was performed using an electrochemical workstation

(CHI 660C). The charge/discharge tests were performed using a NEWARE battery tester at different current rates ($1\text{ C} = 170\text{ mA g}^{-1}$) with a voltage window of $1\text{ V} - 3\text{ V}$.

Chapter 4– Free-standing Anatase TiO₂ Nanosheet with Exposed (001) Facets for Fast and Efficient Lithium Storage[†]

4.1. Introduction

Titanium Oxide (TiO₂) is probably the most widely studied semiconducting metal oxides due to its great application potential in many fields, such as photocatalysis, sensors, solar cells, and lithium-ion batteries.^[35, 79, 111-113] For example, anatase TiO₂ has been long studied as a lithium insertion host material because of its crystal structure which can be viewed as a stacking of zigzag chains consisting of highly distorted edge-sharing TiO₆ octahedra.^[114] This special 3D arrangement creates open channels which facilitate the insertion/extraction of Li⁺ during discharge/charge.^[56] In a TiO₂/Li half-cell, the principal reaction that governs the electrochemical processes is as follows: $\text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2$

(1). As studied previously, the maximum number of Li⁺ that can be inserted is determined to be 0.5,^[114] leading to a theoretical capacity of 167.5 mA h g⁻¹.^[84]

Very recently, anatase TiO₂ nanocrystals/nanosheets with large fraction of exposed high-energy (001) facets have been successfully synthesized in different reaction systems following the first report by Yang et al. (Nature 2008, 453, 638).^[10, 69, 102, 115-118] Among them, hydrofluoric acid (HF) appears to be a very

[†] Reproduced from [J. S. Chen, X. W. Lou, *Electrochem. Comm.*, 11, 2332 – 2335 (2009)] by permission from Elsevier. Copyright 2009.

effective capping agent, as element F has a low F-F bonding energy^[119] but bonds strongly to Ti atom,^[10] thus stabilizing the highly reactive (001) facets. Based on these methods, the percentage of exposed reactive (001) facets in the as-prepared TiO₂ crystals has been reported to be 47%,^[10] 60%,^[120] 80%,^[121] and even 89%.^[116] Because of these highly active crystal facets, their photocatalytic activities have been shown indeed superior by different groups.^[117, 120-121] However, to the best of our knowledge, there has been no report on the lithium storage properties of these TiO₂ nanosheets. It is thus intriguing to investigate the potential use of these TiO₂ nanosheets in lithium-ion batteries (LIB). Inspired by this idea, herein we investigate the lithium storage capabilities of the anatase TiO₂ nanosheets with exposed high-energy (001) surfaces. The TiO₂ nanosheets are synthesized following a recently reported method with modification, and the electrochemical results indicate that these nanosheets exhibit much lower initial irreversible capacity losses compared to other conventional anatase TiO₂ nanocrystals, and excellent capacity retention upon prolonged cycling.

4.2. Material preparation

Pure anatase TiO₂ nanosheets with largely exposed (001) facets are synthesized through a modified hydrothermal method.^[116] In a typical synthesis, 5 mL of titanate isopropoxide (97%, Sigma-Aldrich) was added into a 40 ml Teflon-lined autoclave. Then 0.6 mL of 48 % HF solution was added drop-wise. **Caution! HF is highly corrosive, should be handled with great care!** After that, the mixed solution was sealed and put into an electric oven heated at 180 °C for 24 h. It was

cooled down naturally to room temperature. The white precipitate was collected and washed with ultra-pure water several times before drying at 60 °C overnight. Amorphous TiO₂ nanobeads were synthesized through a reported protocol with little modification^[122] followed by calcination at 600 °C in air to transform into pure anatase phase.

4.3. Results and discussion

4.3.1. Morphology and composition characterizations

Fig. 4.1 shows the material characterization results of the as-prepared TiO₂ nanosheets. It can be clearly seen from the transmission electron microscopy (TEM) images (Fig. 4.1A and 4.1B) and the field-emission scanning electron microscopy (FESEM) image (Fig. 4.1C) that the nanosheets are generally rectangular or square-shaped with the edge length in the range of 20 – 100 nm. The thickness is about 10 nm, which is about twice the thickness of the nanosheets prepared in the original report.^[116] This should be considered advantageous for reversible lithium insertion/extraction as the as-prepared TiO₂ nanosheets are more robust against the volume change during charge/discharge cycles. It was confirmed previously that the top and bottom facets of the nanosheets are the (001) planes.^[116] According to the energy dispersive X-ray spectroscopy (EDX) analysis data, the amount of fluorine present in the as-prepared TiO₂ nanosheets is about 6.5 % (atomic). This amount of F is essential for the stabilization of these high energy facets, as F has a low bonding energy ($D_0^{\text{F-F}} = 158.8 \text{ kJ mol}^{-1}$), while it also bonds strongly to Ti atom ($D_0^{\text{F-Ti}} = 569.0 \text{ kJ mol}^{-1}$)^[10]. Thus it can effectively stabilize the H- and O-

terminated (001) surfaces. Based on the above observations, the percentage of exposed (001) facets is estimated to be 62%. The crystal structure of the sample is confirmed by the X-ray diffraction (XRD) pattern (Fig. 4.1D). All the identified peaks can be unambiguously assigned to tetragonal anatase TiO_2 (JCPDS No. 21-1272, S.G.: $I4_1/amd$, $a_o = 3.7852 \text{ \AA}$, $c_o = 9.5139 \text{ \AA}$).

Fig. 4.1 Characterization results of the as-prepared TiO_2 nanosheets: transmission electron microscopy (TEM) images (A and B); field-emission scanning electron microscopy (FESEM) image (C); (D) X-ray diffraction (XRD) pattern.

4.3.2. Investigation of the lithium storage properties

A series of electrochemical measurements are carried out in order to study the lithium storage capabilities of these as-prepared TiO_2 nanosheets. Fig. 4.2A shows the representative cyclic voltammograms (CV). Consistent with previous

reports,^[123-124] two well-defined current peaks are observed at about 1.75 V and 2.1 V during cathodic and anodic sweeps, respectively. The cathodic peak at 1.75 V marks the two-phase transition of the structure from tetragonal anatase ($I4_1/amd$) to orthorhombic $\text{Li}_{0.5}\text{TiO}_2$ ($Imma$) when the insertion coefficient x in reaction (1) has reached about 0.05.^[84] The corresponding anodic peak with almost the same current intensity shows that the Li^+ extraction takes place to the equal extent, indicating a nearly perfect Coulombic efficiency. It can also be observed that the current of both peaks increases in the subsequent cycles, indicating a possible activation process in the electrode material. Furthermore, there is no substantial change in the peak positions after the first scan, showing the high reversibility of the insertion/extraction reactions.

Fig. 4.2B shows the charge/discharge voltage profiles of the first two cycles at a high current drain of 4 C-rate. Remarkably, after reaching a high first discharge capacity of $164.8 \text{ mA h g}^{-1}$ (almost equals the theoretical capacity of $167.5 \text{ mA h g}^{-1}$), a reversible capacity of $147.1 \text{ mA h g}^{-1}$ can be delivered in the subsequent charge process. This corresponds to an irreversible capacity loss of only 10.7%. The sample has been discharged/charged at other C-rates, and the initial irreversible loss is generally in the range of 5 – 15 %. This is in good agreement with the CV analysis, and should be regarded as very small for anatase TiO_2 materials. It has been reported in previous studies that the initial irreversible capacity loss is usually in the range of 30 – 40% for anatase phase TiO_2 nanotubes^[124-125] and hollow micro/nanostructures.^[84, 123] One possible reason for such a significantly reduced irreversible loss of the as-prepared TiO_2 nanosheets

might be attributed to its unique structure. Specifically, the largely exposed (001) facets provide more accessible sites for Li^+ insertion, and the ultrathin feature (ca.

Fig. 4.2 Electrochemical measurements of the as-prepared TiO_2 nanosheets: (A) Representative cyclic voltammograms at scan rate of 0.1 mV/s; (B) Charge-discharge profile of the first (I) and second (II) cycles at a current rate of 4 C; (C) Cycling performance at current rates of 10 C (I) and 20 C (II). All measurements were conducted with a voltage window of 1 V – 3 V.

10 nm) facilitates the efficient extraction. Furthermore, it is important to mention that the F^- introduced in the present synthetic system has a high probability to be absorbed on the surface of the TiO_2 nanosheets. It is evident that the doping of F^- will decrease the bandgap of the active material,^[126] and thus increase the electronic conductivity. One of our previous studies reported the synthesis of anatase TiO_2 nanostructure where TiF_4 solution was used as the TiO_2 precursor, and it is very similar to this case with abundant F^- in the reaction environment. The lithium storage properties of the as-prepared TiO_2 nanostructure in that work showed good cyclic retention but lower capacity compared to current TiO_2 nanosheets. This further confirms that the advantageous electrochemical properties of TiO_2 nanosheets in the present study come from its unique structure. The second cycle gives a slightly lower discharge capacity of $151.6 \text{ mA h g}^{-1}$, and the charge capacity is $146.5 \text{ mA h g}^{-1}$, leading to an irreversible loss of only 3.4%.

Fig. 4.2C shows the cyclic performance of the as-prepared TiO_2 nanosheets at different current rates of 10 C and 20 C. It can be clearly seen that the cycling performance at a 20 C-rate is very close to the 10 C-rate one, indicating the high efficiency of solid state diffusion of Li^+ in these TiO_2 nanosheets. At the end of 200 charge/discharge cycles, a reversible capacity of 99.2 mA h g^{-1} and 87.5 mA h g^{-1} can still be retained for 10 C and 20 C, respectively. These values suggest that the as-synthesized TiO_2 nanosheets manifest good high rate performance.

4.3.3. Comparison of the cycling performance

In order to further understand the source of the outstanding lithium storage properties of the TiO_2 nanosheets, some comparative studies were carried out subsequently with the results shown in Fig. 4.3. Fig. 4.3A displays the morphology of TiO_2 nanobeads of ~ 200 nm in size, and the XRD pattern (result not shown) indicates that these nanobeads are composed of pure anatase TiO_2 . The comparative cycling performances of TiO_2 nanosheets, nanobeads, as well as

Fig. 4.3 (A) FESEM image of the as-prepared anatase TiO_2 nanobeads. The inset shows a high-magnification FESEM image. (B) Rate behavior of TiO_2 nanosheets (I), Degussa P25 TiO_2 nanoparticles (II) and anatase TiO_2 nanobeads (III) shown in A at 1-C rate with a voltage window of 1 V – 3 V.

commercially available Degussa P25 nanoparticles are shown in Fig. 4.3B. Obviously, the as-prepared TiO_2 nanosheets deliver a much higher capacity than the other two samples throughout the cycling. Thus it can be concluded that

the advantageous lithium storage properties of the as-prepared TiO₂ nanosheets originate from its unique structure.

4.4. Conclusions

In conclusion, anatase TiO₂ nanosheets with a thickness of about 10 nm are synthesized in large scale through a modified hydrothermal method. They possess large percentage of exposed (001) facets. When evaluated for lithium storage capabilities, these as-prepared TiO₂ nanosheets exhibit excellent performance. It shows a significantly lower initial irreversible capacity loss compared to other anatase TiO₂ materials. This has been attributed to its unique nanostructure which could facilitate efficient lithium insertion and extraction. The TiO₂ nanosheets also demonstrate excellent capacity retention after prolonged cycling at a 10 C-rate. The present study suggests that these anatase TiO₂ nanosheets are very promising as anode materials for high-power lithium-ion batteries.

Chapter 5 – Hierarchical Spheres Assembled from Large Ultrathin Anatase TiO₂ Nanosheets with Nearly 100% Exposed (001) Facets for Fast Reversible Lithium Storage[†]

5.1. Introduction

Shape-controlled synthesis of nanocrystals with exposed high-energy/reactive facets is of great importance for both fundamental studies and technological applications (e.g., energy storage in electrochemical capacitors and catalysis) in multiple fields.^[101, 127-132] Anatase titanium oxide (TiO₂) with a tetragonal crystal structure is probably the most studied metal oxide.^[79, 97, 133-134] The surface energies of its (001) and (101) facets have been calculated to be 0.90 and 0.44 J m⁻², respectively.^[118] As a result, anatase nanocrystals are usually observed in a truncated bipyramidal shape dominated by energetically stable (101) facets. Although as likely to form during the earliest stages of crystal growth, the more reactive (001) facets are quickly eliminated.^[101, 118, 135]

Following the first report of anatase TiO₂ microcrystals with around 47% exposed (001) facets,^[10] a series of studies by research groups world-wide have demonstrated synthesis of sheet-like anatase TiO₂ single-crystals with as high as

[†] Reproduced from [J. S. Chen, et al., *J. Am. Chem. Soc.*, 132, 6124 – 6130 (2010)] by permission from *The American Chemical Society*. Copyright 2009.

89% exposed (001) facets.^[7, 115-118, 136] However, the construction of hierarchical structures from these interesting anatase TiO₂ nanosheets has not been realized. Another observation is that despite the high percentages of (001) facets that survive crystal growth, the specific surface area of the TiO₂ bearing these facets is unacceptably low, due to the relatively large crystal thickness in the [001] direction. For example, the specific surface area of anatase TiO₂ nanosheets (1.09 μm in width; 260 nm in thickness) with 64% exposed (001) facets is only $1.6 \text{ m}^2 \text{ g}^{-1}$.^[7]

By reducing the thickness in the [001] direction and increasing the two-dimensional lateral size of (001) planes, it should be possible to simultaneously increase the percentage of exposed (001) facets and the specific surface area of sheet-like anatase TiO₂ crystals. Stucky and coworkers have used this approach to synthesize anatase TiO₂ nanosheets (NS) with thickness less than 1 nm employing a facile nonaqueous route.^[117] Although bounded by the dominant (001) facets, these ultrathin TiO₂-NSs are stabilized by large amounts of oleylamine (ca. 43% in weight), and form stacked lamellar structures. Surfactant removal by calcination to obtain pure anatase TiO₂ from the ultrathin TiO₂-NS lamellar structure is unattractive for at least two reasons: (i) it will likely lead to complete condensation and destruction of the NS; and (ii) it might promote formation of irregular, large anatase TiO₂ crystals, which defeat the very purpose of the oleylamine stabilizing layer. One way to obtain thermally stable ultrathin NSs is to grow them into a three-dimensionally self-organized architecture as nicely demonstrated for ultrathin zeolite NSs most recently.^[137]

Herein, we report a simple synthesis of hierarchical spheres self-organized from ultrathin anatase TiO_2 nanosheets (NS) with nearly 100% exposed (001) facets. Several earlier studies have demonstrated that the highly-reactive (001) facets of anatase TiO_2 -NS exhibit superior photocatalytic activities when normalized by the surface area.^[116, 118, 136] Here we show that these facets also provide unusual opportunities for electrochemical energy storage. In this particular application we take advantage of both the high surface activity of the synthesized anatase TiO_2 -NS hierarchical spheres (TiO_2 -NSHS) and the excellent “bulk” properties imparted by their geometry. Specifically, the extremely short transport length-scales in the [001] direction and a well-defined nanoporous structure facilitate fast, reversible lithium insertion/extraction, a requirement for high-power lithium-ion batteries.^[138-139]

5.2. Materials Synthesis

In a typical synthesis, 0.03 ml of diethylenetriamine (DETA; 99%, Sigma-Aldrich) was added into 42 ml of isopropanol (IPA). After the solution was gently stirred for a few minutes, 1.5 ml of titanium (IV) isopropoxide (TIP; 97%, Sigma-Aldrich) was added. The reaction solution was then transferred into a 60 ml Teflon-lined stainless steel autoclave and kept in an electric oven at 200 °C for 24 h. It should be noted that any disturbance during the reaction, e.g., opening of oven door, need to be avoided to assure the successful formation of the desired structure. The autoclave was then taken out from the oven and left to cool down naturally to room temperature. The white precipitate was harvested via centrifugation and washed

thoroughly with ethanol before drying at 60 °C overnight. All products are calcined at 400 °C for 2 h with a heating rate of 1 °C min⁻¹ to obtain highly crystalline anatase phase.

5.3. Results and Discussions

5.3.1. Morphology and composition characterizations

Our anatase TiO₂-NSHSs are obtained by calcining the solvothermally synthesized amine-stabilized TiO₂-NSHS (Fig. 5.1A) at 400 °C in static air (see the experimental section). The high crystallinity and phase purity of the resultant

Fig. 5.1 (A) Field-emission scanning electron microscopy (FESEM) image of the as-synthesized TiO₂-NS spheres. (B) X-ray diffraction (XRD) patterns of the TiO₂-NS spheres: (I) as synthesized, and (II) after calcination at 400 °C.

material are confirmed by X-ray diffraction (XRD, Fig. 5.1B). All the identified peaks (pattern II in Fig. 5.1B) can be perfectly indexed to anatase TiO_2 (JCPDS card no. 21-1272, S.G.: $I4_1/amd$, $a_o = 3.7852 \text{ \AA}$, $c_o = 9.5139 \text{ \AA}$). The pristine uncalcined TiO_2 -NSHS is poorly crystalline in anatase phase (pattern I in Fig. 5.1B), where the two weak peaks located at 2θ of 25° and 48° can be attributed to anatase (101) and (200) diffractions, respectively. Thermogravimetric analysis (TGA, Fig. 5.2) and CHN elemental analysis reveal that it contains approximately 21 wt% of organic species, while the weight loss of about 12 wt% below 100°C in Fig. 5.2 could be attributed to the evaporation of adsorbed moisture or gaseous contents in this highly porous material (discussed shortly).

Fig. 5.2 Thermogravimetric analysis (TGA) curve of the as-synthesized TiO_2 -NS spheres in an air flow at a temperature ramp of 5°C min^{-1} .

The morphology of the as-obtained anatase TiO_2 -NSHSs is characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) as shown in Fig. 5.3. It is immediately apparent that the spheres are quite uniform, with an average size of $\sim 1 \mu\text{m}$ (Fig. 5.3 A and C). From the high-magnification micrographs (Fig. 5.3 B and D), the constituent NSs are easily visible, and seen to

adopt random orientations. The gradual contrast of the TEM image (Fig. 5.3D) from the edge to the center of the sphere indicates that the entire sphere is indeed composed of self-organized TiO₂-NSs. Phase purity and chemical composition of the product are confirmed by energy-dispersive X-ray spectroscopy (EDX, Fig. 5.3E) analysis, which shows strong Ti and O signals. The self-assembly of TiO₂-NSs renders a nanoporous structure as confirmed by the N₂ adsorption/desorption isotherm shown in Fig. 5.3F. It gives a type IV isotherm with a type H3 hysteresis loop indicating a mesoporous structure.^[140] The relatively narrow pore size distributions (Fig. 5.3F, inset) calculated by the Barrett-Joyner-Halenda (BJH) method from both branches of the isotherm signify that most of the pores are in the range of 5 – 15 nm in size. Such a porous structure gives rise to a very high specific surface area of 170 m² g⁻¹, calculated by the Brunauer-Emmett-Teller (BET) method.

High resolution (HR) TEM analysis is employed to determine the crystal facets. Fig. 5.4A shows part of a single nanosheet with visible lattice fringes. It can be observed that two sets of lattices are present and that they are oriented perpendicular to each other with an equal inter-fringe spacing of 0.19 nm, corresponding to anatase (020) and (200) planes. The fast-Fourier-transform (FFT) pattern (Fig. 5.4A, inset) of the same region can be indexed to diffraction spots of the [001] zone.^[10] Therefore it can be concluded that the TiO₂-NS is bounded by (001) facets on both the top and bottom. Fig. 5.4C displays the HRTEM image taken from region 1 (marked by a dotted circle) in Fig. 5.4B. The distance of the visible lattice fringes over a large area is measured to be 0.19 nm, indicating that

the TiO_2 -NSs are single crystals when lying flat. The dark line in the TEM image (Fig. 5.4B, region 2) demarcates the edge of a curved NS that is approximately perpendicular to the support film. The corresponding HRTEM image (Fig. 5.4D) also reveals lattice fringes with a distance of 0.19 nm, which is again precisely the

Fig. 5.3 FESEM images (A and B) and transmission electron microscopy (TEM) images (C and D) of as-prepared TiO_2 nanospheres. (E) Energy-dispersive X-ray spectroscopy (EDX) analysis of the anatase TiO_2 -NS spheres. The Pt signal arises from the Pt coating during sample preparation. (F) N_2 adsorption/desorption isotherm of the as-prepared anatase TiO_2 -NS spheres. The inset shows the pore size distribution calculated by the Barrett-Joyner-Halenda (BJH) method.

inter-plane spacing of (020) or (200) of anatase. These dark lines can be used to estimate the thickness of the NS to be only 3 nm, which explains its curved feature and high specific surface area of $170 \text{ m}^2 \text{ g}^{-1}$. Assuming that each TiO_2 -NS is as long as it is wide, a sheet thickness of $\sim 3 \text{ nm}$ and size of $100 - 300 \text{ nm}$ implies that 95 – 99 % of the exposed surfaces are (001) facets.

Fig. 5.4 (A) HRTEM image of an ultrathin TiO_2 -NS showing two sets of perpendicular lattice fringes with a spacing of 0.19 nm. The inset shows the FFT pattern indexed to the [001] zone. (B) TEM image recorded around the edge of a TiO_2 -NS sphere. (C) and (D) HRTEM images of regions 1 and 2 marked with white dotted circles in (B), respectively. Both images show lattice fringes with a spacing of 0.19 nm.

To understand the mechanism of forming such a nanosheet-based hierarchical structure, different experimental conditions were investigated. Generally, no nanosheet structures were formed using amines with other chain lengths, e.g., methylamine, ethylenediamine, oleylamine, or 1-hexadecylamine, indicating that DETA is particularly suitable and effective to produce nanosheet-like structures in

the current solvothermal synthetic system. On the other hand, TiO_2 -NSs can be formed with the presence of 0.03 – 0.6 ml of DETA in the synthetic system. For example, when equal amounts of DETA and TIP are used (0.6 ml each), chain-like structures assembled from ultrathin TiO_2 -NSs are formed (Fig. 5.5), where the organization of the NSs is much lesser compact. It is hypothesized that, the emerging (001) high energy surfaces will be most effectively stabilized by the tridentate DETA in the solvothermal system, which prohibits their growth along the [001] direction. After prolonged reaction, due to the 2-dimensional lateral growth of such facets, they will develop into large ultrathin NSs. Because of their ultrathin feature, these NSs are highly flexible and can thus readily self-organize

Fig. 5.5 FESEM (A) and TEM (B) images of the chain-like structure assembled from ultra-thin TiO_2 -NSs, using 0.6 ml DETA and 0.6 ml TIP instead. The inset in A shows an FESEM image with higher magnification.

into different hierarchical architectures while still maintaining the maximized exposure of (001) facets.

5.3.2. Investigation of the cycling performance

Anatase TiO_2 has been intensively studied both experimentally and theoretically as the host structure for reversible lithium insertion/extraction.^[56, 84, 88, 92, 108, 141-145] The principal reaction that governs the electrochemical processes in a TiO_2/Li half-cell is thought to be: $\text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2$ (1), with the maximum insertion coefficient x determined to be about 0.5.^[146-149] This leads to a theoretical charge storage capacity of $167.5 \text{ mA h g}^{-1}$.^[84] It is known that the diffusion of Li^+ ions in the anatase framework occurs along a reaction path connecting the vacant octahedral interstitial sites,^[56, 108, 142] which makes diffusion along the c -axis (i.e., the [001] direction) more efficient compared to in the ab -plane. The preponderance of accessible (001) facets in our TiO_2 -NSHSs presages unusual (fast) lithium insertion/extraction kinetics.

Fig. 5.6A displays representative cyclic voltammograms (CV) of the anatase TiO_2 -NSHS. In agreement with previous studies, two well-defined current peaks are observed at 1.55 V (cathodic sweep) and 2.2 V (anodic sweep). The peak at 1.55 V corresponds to the biphasic transition from tetragonal anatase ($I4_1/amd$) to orthorhombic $\text{Li}_{0.5}\text{TiO}_2$ ($Imma$) when the insertion coefficient x in reaction (1) reaches about 0.05.^[84, 108, 142] Interestingly, it can be observed that the intensity of both peaks increases during the subsequent scans, suggesting a possible activating process in the electrode material.^[150] More strikingly, there is no apparent

irreversible process observed in the first cathodic scan indicating a high Coulombic efficiency for lithium extraction. This observation is quite unusual for anatase TiO_2 . Fig. 5.6B depicts the charge-discharge voltage profiles of the TiO_2 -NSHS electrode for the first few cycles at a current rate of 5 C (850 mA g^{-1}). The result is generally consistent with the above CV analysis as well as previously reported data,^[46, 88] where two voltage plateaus appear at about 1.7 V and 2.1 V during the discharge and charge processes, respectively. The discharge curves clearly show that the lithium insertion process can be divided into three different stages.^[46] The first stage is represented by the sharp drop of the potential from the open circuit voltage to a value around 1.7 V, which is just before onset of the plateau region. The next stage is the process of lithium insertion into the vacancy sites of the TiO_2 crystal structure, corresponding to the short horizontal plateau region. The final stage is the gradual decay of the voltage after the plateau region, reflecting that the lithium ions are further inserted into the surface layer of the electrode material.^[46] The insertion process gives a first discharge capacity of 204 mA h g^{-1} , and a subsequent charge capacity of 169 mA h g^{-1} , leading to an irreversible capacity loss of only 17%. This should be considered very low when compared to other anatase TiO_2 electrodes, as the initial irreversible capacity loss reported is generally in the range of 30 – 40%.^[84, 87, 124-125] In the second cycle, the discharge capacity decreases to 175 mA h g^{-1} with a corresponding charge capacity of 165 mA h g^{-1} , leading to a much higher Coulombic efficiency of 94%. This value further increases to 97% in the fifth charge-discharge cycle, indicating that the irreversible capacity loss due to trapping of Li^+ inside TiO_2 framework decreases rapidly upon cycling.^[88]

Fig. 5.6 (A) Representative CVs at a scan rate of 0.1 mV s^{-1} for the 1st, 2nd, and 5th cycles. (B) charge-discharge profiles at current rate of 5 C (850 mA g^{-1}) for the 1st, 2nd, and 5th cycles. (C) Cycling performance at different C-rates. All measurements were conducted with a voltage window of 1 V – 3 V.

Fig. 5.6C displays the high reversibility of the underlying electrochemical reactions over many charge/discharge cycles, at different current densities (C-rates). When charged at a rate of 1C, a lithium ion battery requires about 1 hour to approach its full charge capacity. Remarkably, at a rate of 1C (170 mA g^{-1}) a reversible capacity of 174 mA h g^{-1} can be retained after more than 100 charge-discharge cycles. This corresponds to a lithium insertion coefficient of 0.52, which is slightly higher than the previously determined maximum value of 0.5. This difference is not unusual for high-surface area nanostructures and is here attributed to the presence of an abundance of active surface sites for lithium storage.^[86] As usual, the reversible capacity decreases to 136 mA h g^{-1} after 100 cycles when the C-rate is increased to 5 C (850 mA g^{-1}). Further increasing the C-rate to 10 C (1700 mA g^{-1}) leads to small decrease in capacity, nicely confirming that the short diffusion path length in our ultrathin TiO_2 nanosheets leads to highly efficient solid state diffusion of Li^+ ions. These high-rate capacities are probably among the best reported values for any TiO_2 -based electrodes tested under similar conditions.

5.3.3. Analysis of the rate capability

To investigate the rate capability, our TiO_2 -NSHS is discharged and charged at various current rates, with the results shown in Fig. 5.7A. It can be clearly observed that our TiO_2 -NSHS shows excellent capacity retention at different rates. Even at a high current rate of 20 C (3400 mA g^{-1}), a reversible capacity of 95 mA h g^{-1} can still be delivered, demonstrating a magnificent high rate performance. Moreover, a capacity of 169 mA h g^{-1} can be resumed when the rate is reduced

back to 1 C. Fig. 5.7B illustrates the current rate dependence of the discharge capacities of the $\text{TiO}_2\text{-NSHS}$. Apparently, the capacities drop with increasing current densities (equivalent to power density when multiply by the average

Fig. 5.7 (A) Cycling performance of the $\text{TiO}_2\text{-NSHS}$ at various charge-discharge rates. (B) The current rate dependence of the discharge capacities of the $\text{TiO}_2\text{-NSHS}$. The data are extracted from the second cycle. All measurements were conducted with a voltage window of 1 V – 3 V.

discharge voltage). At current rates of 0.5 C (85 mA g^{-1}), 1 C, and 5 C, specific capacities of 224 mA h g^{-1} , 192 mA h g^{-1} , and 170 mA h g^{-1} can be obtained, respectively. It is important to mention that, the first discharge capacity of 300 mA h g^{-1} can be reached at the current rate of 0.5 C, corresponding to a lithium

insertion coefficient of 0.88, which is significantly higher than the theoretical value of 0.5. This first-cycle high discharge capacity is generally attributed to surface phenomena such as the irreversible decomposition of electrolyte accompanying the formation of solid electrolyte interface (SEI),^[46, 86, 151] as well as the ultrathin nanosheets granting efficient transport of lithium ions.^[88] When a current as high as 10 C (1700 mA g⁻¹) is used, our TiO₂-NSHS is still able to deliver a reversible capacity of 150 mA h g⁻¹.

5.3.4. Post-mortem study

In order to further understand the enhanced lithium storage properties of these anatase TiO₂-NSHS, we have carried out post-mortem studies after 100 charge-discharge cycles at 5 C (850 mA g⁻¹). As shown in Fig. 5.8 A and B, the overall spherical structures can be fairly retained although the detailed nanosheet structures become somehow diminished. This is understandable as these nanosheets might be too thin but large to withstand the high-rate insertion/extraction of lithium ions over extended cycling. Nevertheless, the nanosheet structure might still exist in the resulting fine particles. Our recent study shows that the nanosheet structure can be completely retained for smaller but thicker (about 10 nm) free-standing anatase TiO₂ nanosheets.^[150] Surprisingly, the XRD analysis suggests that the anatase crystal structure can also be sustained (Fig. 5.8C), as there is no noticeable change in the intensities of the dominant (101) peaks before and after the electrochemical test. This observation is a good demonstration of the bulk structural stability of our TiO₂-NSHS, considering that

the long-range crystal ordering of the electrode material is usually lost after extended galvanostatic cycling.^[8]

Fig. 5.8 FESEM images of the TiO_2 -NSHS before galvanostatic test (A), and after 100 charge-discharge cycles at 5 C (850 mA g^{-1}) (B). The insets in A and B are the FESEM images with higher magnification of the corresponding sample. XRD patterns (C) of the samples shown in A (I) and B (II).

5.4. Conclusions

In summary, a simple approach is presented for synthesizing uniform hierarchical spheres self-assembled from ultrathin anatase TiO₂ nanosheets (~ 3 nm in thickness and a few hundred nm in lateral size) with nearly 100% exposed (001) facets. These hierarchical spheres manifest a 3D nanoporous structure with a high specific surface area of about 170 m² g⁻¹. Inspired by the unique structure and inherently short transport path length of the assembled TiO₂ nanosheets, we evaluate their ability to reversibly insert/release lithium for high power density electrochemical energy storage in batteries. Our results show that anatase TiO₂-NS spheres manifest unusually high Coulombic efficiency for lithium extraction, excellent capacity retention, and superior rate behavior. In addition to their promise for high-power lithium-ion battery electrodes, we anticipate that anatase TiO₂ nanosheet assemblies will provide long sought after materials solutions in multiple fields, including photocatalysis and dye-sensitized solar cells.

Chapter 6 – TiO₂ and SnO₂@TiO₂ Hollow Spheres Assembled from Anatase TiO₂ Nanosheets with Enhanced Lithium Storage Properties[†]

6.1. Introduction

Hollow nanostructures have attracted considerable attention due to their wide applications in numerous fields like catalysis, drug delivery, gas sensing, and lithium-ion batteries.^[152-160] As summarized previously, the strategies for synthesizing hollow structures can be broadly divided into two categories: templating and template-free methods. The template-free formation of hollow structures is generally based on some self-assembly or novel mechanisms such as inside-out Ostwald ripening.^[155, 161-162] Although templating methods generally involve multiple steps, they are more widely employed because of their general versatility in fabricating narrow-size-distribution hollow colloids of a wide range of materials with well-defined shapes.^[162-163] For example, a lost-wax approach was developed to produce highly uniform spherical and non-spherical hollow structures with tunable shell thickness.^[163] By templating against sulfonated polystyrene particles, Yang et al.^[160] introduced a new method to generate titania (TiO₂) hollow spheres with controllable cavity size. More recently, we have demonstrated the formation of single- and double-shelled tin oxide (SnO₂) hollow nanospheres with

[†] Reproduced from [J. S. Chen, et al., *Chem. Commun.*, 46, 8252 – 8254 (2010)] by permission from *The Royal Society of Chemistry*. Copyright 2010.

uniform size distribution using silica (SiO_2) spheres as templates.^[164] Shortly after that, by utilizing $\alpha\text{-Fe}_2\text{O}_3$ nanospindles as the starting material, we reported the construction of more challenging non-spherical rattle-type/hollow structures of SnO_2 and TiO_2 .^[84, 165] Until now, the research focus is mainly on control of the shape and hollow interior by engineering the templates, while tailoring of the outer shell structure remains a great challenge as the shell is usually formed via irregular aggregation/deposition of precursor particles on the templates. In order to further expand the application potential of hollow nanostructured materials, it is also important to engineer the shell with unique structures, advanced chemical compositions and built-in functionalities. To the best of our knowledge, such complex hollow nanostructures have rarely been reported.

Herein, we report a templating route to create two types of complex hollow nanostructures assembled from ultrathin anatase TiO_2 nanosheets ($\text{TiO}_2\text{-NSs}$) with exposed high-energy (001) facets. Several very recent studies have demonstrated that anatase $\text{TiO}_2\text{-NSs}$ with exposed highly-reactive (001) facets exhibit superior photocatalytic activities as well as lithium storage capabilities.^[116, 136, 150, 166] In the present study, ultrathin $\text{TiO}_2\text{-NSs}$ with exposed (001) facets are synthesized and assembled into hollow shells, which might allow one to harvest advantages of both parties thus making them attractive candidates for many applications.

6.2. Materials Synthesis

6.2.1. *Synthesis of anatase TiO₂-NS hollow spheres*

0.04 g of ~400 nm SiO₂ spheres synthesized by the Stöber method was dispersed in 41.7 ml of isopropanol (IPA) before 0.03 ml of diethylenetriamine (DETA) was added. After stirring gently by hand, 1.8 ml of titanium (IV) isopropoxide (TIP) was added into the solution. The reaction mixture was transferred into a 60 ml Teflon-lined stainless steel autoclave and kept at 200 °C for 24 h. After the reaction was completed, the white product was collected through centrifugation and washed thoroughly with ethanol before drying at 60 °C overnight. After that, the powder was calcined at 400 °C in air for 2 h with a ramping rate of 1 °C min⁻¹ to obtain highly crystalline anatase phase. For removal of silica, several milligrams of calcined SiO₂@TiO₂-NS core-shell spheres were dispersed into 0.6 wt% hydrofluoric acid (HF) solution and shaken under room temperature for 1 h before washing with water.

6.2.2. *Synthesis of SnO₂@TiO₂-NS double-shelled hollow spheres*

The synthesis is similar to the steps for synthesizing TiO₂-NS hollow spheres, except that 0.05 g of SiO₂@SnO₂ core-shell nano-template was dispersed in 41.5 ml of IPA with the addition of 0.03 ml of DETA and 2 ml of TIP. The subsequent calcination and removal of SiO₂ are the same as described above. The SiO₂@SnO₂ core-shell spheres are synthesized following our previously reported method (Small 2007, 3, 261).

6.3. Results and Discussion

The ultrathin anatase TiO_2 -NSs which serve as building blocks of the hollow structures are obtained by calcining the solvothermally synthesized amine-stabilized products at 400 °C in static air (see supporting information, experimental section). The high crystallinity and phase purity of the resulting materials are confirmed by X-ray diffraction (XRD; Fig. 6.1). The pristine uncalcined products

Fig. 6.1 XRD patterns of the sample hollow TiO_2 -NSs (A), and hollow SnO_2 @ TiO_2 -NS (B) after (I) and before (II) calcination at 400 °C. The absence of diffraction peaks due to SnO_2 in B is probably because that the SnO_2 shell deposited on the SiO_2 nanospheres is generally amorphous even after calcination.

are poorly crystalline in anatase phase by XRD analysis. Thermogravimetric analysis (TGA; Fig. 6.2) reveals that the as-synthesized products contain approximately 15 ~ 18 wt% of adsorbed organic amines, while the weight loss below 100 °C could be from the evaporation of adsorbed gaseous or moisture

contents. Moreover, the assembly of TiO₂-NSs renders a highly mesoporous outer shell with a large surface area of 159.7 m² g⁻¹, and a total pore volume of 0.57 cm³ g⁻¹.

Fig. 6.2 TGA data of the sample hollow TiO₂-NSs (A), and hollow SnO₂@TiO₂-NS (B) before calcination.

Fig. 6.3 Typical N₂ adsorption-desorption isotherm of the TiO₂-NS hollow nanospheres. The hysteresis loop indicates a mesoporous structure. The inset shows the pore size distribution by Barrett-Joyner-Halenda (BJH) method from both branches of the isotherm.

6.3.1. SiO₂@TiO₂-NSs and hollow TiO₂-NSs

To create TiO₂-NS hollow spheres, uniform silica (SiO₂) nanospheres (~400 nm in diameter) synthesized by the Stöber method^[167-168] are employed as templates upon which a robust TiO₂-NS outer shell is grown. The as-formed SiO₂@TiO₂-NS core-shell particles are displayed in Fig. 6.4A. As shown in Fig. 6.4B, the core-shell structure is comprised of a well-defined shell of self-organized anatase TiO₂-NSs and a SiO₂ core (identified as a dark sphere inside the thick TiO₂-NS shell). High resolution (HR) TEM analysis is employed to determine the crystal facets. Fig. 6.4C shows some visible lattice fringes on part of a single nanosheet. It can be clearly observed that there are two sets of lattice present which are oriented perpendicular to each other with an equal inter-fringe spacing of 0.19 nm, corresponding to anatase (020) and (200) planes. The fast-Fourier-transform (FFT) pattern (Fig. 6.4D) of the same region can be indexed to diffraction spots of the [001] zone.^[10] Therefore it can be concluded that the TiO₂-NSs are bound by (001) facets on both the top and bottom.^[150]

By selectively dissolving away the SiO₂ core in a dilute HF solution (~ 0.6 wt%), anatase TiO₂-NS hollow spheres are obtained. EDX analysis confirms the nearly complete removal of the SiO₂ core (Fig. 6.5), resulting in a large void space inside the TiO₂-NS shell (Fig. 6.4F). Also shown in Fig. 6.4E, removal of the SiO₂ core produces no noticeable collapse of the TiO₂-NS shell, but results in a slightly altered texture of the TiO₂-NS shell, compared to the counterparts before HF treatment (Fig. 6.4A). Nevertheless, the individual TiO₂ ultrathin NS is somewhat unaffected and can be clearly observed under TEM (Fig. 6.4F).

Fig. 6.4 FESEM image (A) and TEM image (B) of $\text{SiO}_2@\text{TiO}_2\text{-NS}$ core-shell structure. HRTEM image (C) of part of a TiO_2 nanosheet and the corresponding FFT pattern (D) of the same area. FESEM image (E) and TEM image (F) of hollow $\text{TiO}_2\text{-NS}$ spheres.

Fig. 6.5 (A) FESEM image of $\text{SiO}_2@\text{TiO}_2\text{-NS}$ core-shell nanostructure; (B) EDX analysis of the sample shown in A; (C) FESEM image and (D) EDX analysis of $\text{TiO}_2\text{-NS}$ hollow spheres after removing the SiO_2 cores.

6.3.2. $\text{SiO}_2@\text{SnO}_2@\text{TiO}_2$ -NSs and double-shell hollow $\text{SnO}_2@\text{TiO}_2$ -NSs

As a second demonstration of the versatility of our reaction system, we construct composite $\text{SnO}_2@\text{TiO}_2$ -NS double-shelled hollow spheres by employing ~ 500 nm $\text{SiO}_2@\text{SnO}_2$ core-shell spheres as templates.^[164] Fig. 6.6A displays the self-organized TiO_2 -NS shell on the $\text{SiO}_2@\text{SnO}_2$ core-shell templates. The inner SnO_2 shell can be clearly identified as a dark ring encapsulating the central SiO_2 core inside the thick TiO_2 -NS shell (Fig. 6.6 B and C). Afterwards, complete removal of the SiO_2 core is achieved by the same HF treatment described earlier, and confirmed by EDX analysis (Fig. 6.7). As shown in Fig. 6.6D, the double-shelled $\text{SnO}_2@\text{TiO}_2$ -NS structure can better sustain the template-removal process in comparison to TiO_2 -NS hollow spheres, which is attributed to the presence of the SnO_2 inner-shell granting extra mechanical support to the architecture. Despite the fact that the TiO_2 -NS shell is eroded to a small extent, the large void space

Fig. 6.6 FESEM image (A) and TEM images (B, C) of TiO_2 -NS shells grown on 400 nm $\text{SiO}_2@\text{SnO}_2$ core-shell particles. FESEM image (D) and TEM images (E, F) of $\text{SnO}_2@\text{TiO}_2$ -NS double-shelled hollow spheres.

bound by the SnO_2 inner-shell can be clearly observed (Fig. 6.6 E and F). It is also worth mentioning that TiO_2 -NS shells have also been successfully grown on much smaller ~ 200 nm $\text{SiO}_2@ \text{SnO}_2$ core-shell templates (Fig. 6.8), where as expected the organization of TiO_2 -NSs appears less compact.

Fig. 6.7 (A) FESEM image of $\text{SiO}_2@ \text{SnO}_2@ \text{TiO}_2$ -NS nanostructures, and (B) its corresponding EDX analysis. (C) FESEM image of $\text{SnO}_2@ \text{TiO}_2$ -NS double-shelled hollow spheres, and (D) its EDX analysis.

Fig. 6.8 TEM images of TiO_2 -NS nanostructure assembled on ~ 200 nm $\text{SiO}_2@ \text{SnO}_2$.

6.3.4. Cycling performance measurement

Since TiO_2 has been widely studied as anode materials for lithium-ion batteries,^[6-7, 150] we further investigate the lithium storage properties of the TiO_2 -NS hollow spheres as an example. Fig. 6.9A shows the charge-discharge voltage profiles of the sample at different currents rates. At a current rate of 1 C, a high first-cycle discharge capacity of $264.8 \text{ mA h g}^{-1}$ can be delivered, corresponding to a lithium insertion coefficient (x) of 0.79 in Li_xTiO_2 .^[150] A subsequent charge capacity of 175 mA h g^{-1} can be obtained, leading to a coulombic efficiency of 66.1%. When the rate is increased to 10 C, a discharge capacity of 180 mA h g^{-1} and a charge capacity of $148.8 \text{ mA h g}^{-1}$ can be delivered, resulting in a much lower irreversible loss of only 17%. Fig. 6.9B shows the cycling performance of the sample.

Apparently, it shows a superior cyclic retention up to 100 charge- discharge cycles even cycled at a very high rate of 10 C. Despite the considerable capacity loss in the second cycle, high capacities of 158 mA h g^{-1} at 1C and 138 mA h g^{-1} at 10 C can be retained after 100 cycles. These results show that the TiO_2 -NS hollow spheres demonstrate enhanced lithium storage properties than previously reported hollow TiO_2 nanostructures without the feature of ultrathin nanosheets,^[84] the commercialized Degussa P25 TiO_2 nanoparticles, and other anatase TiO_2 -based anodes tested under similar conditions.^[86, 88, 169] This excellent cycling performance could be attributed to the ultrathin anatase TiO_2 nanosheets with exposed (001) facets, which allows fast and efficient transport of lithium ions and electrons,^[170] and also the high specific surface area granting more lithium insertion sites.

Fig. 6.9 Electrochemical analysis: (A) Charge-discharge voltage profiles of the first cycles, and (B) cycling performance showing the discharge capacities of $\text{TiO}_2\text{-NS}$ hollow spheres at current rates of 1 C and 10 C. (C) Cycling performance of $\text{SnO}_2@\text{TiO}_2\text{-NS}$ hollow spheres at 10 C. All measurements were conducted with a voltage window of 1 V – 3 V.

Furthermore, the large internal voids of these hollow structures may provide more space to buffer the volume change during extended charge-discharge processes. A similar effect has been reported for different types of hollow nanostructures.^[171-172] The $\text{SnO}_2@\text{TiO}_2$ -NS hollow spheres also show comparably good high-rate performance at a current rate of 10 C (Fig. 6.9C). However, the composite sample demonstrates a slightly lower capacity compared to the pure TiO_2 -NS hollow spheres, probably due to the presence of the inner SnO_2 ring, which contributed no capacity within the current voltage window, and only the TiO_2 component as lithium storage capability.

6.4. Conclusions

In summary, a simple approach is presented for synthesizing two types of complex hollow structures assembled from anatase TiO_2 nanosheets (NSs) with exposed (001) facets. By introducing different nano-templates, it is shown that stable TiO_2 -NS hollow spheres, $\text{SnO}_2@\text{TiO}_2$ -NS double-shelled hollow spheres can be facilely constructed. When evaluated as an anode material for lithium-ion batteries, the as-prepared TiO_2 -NS hollow spheres exhibit excellent cyclic retention even cycled at a very high rate of 10 C, and such almost unmatched electrochemical performance can probably be attributed to the integration of hollow structure with the TiO_2 shell composed of highly functional nanosheets. We anticipate that these unique hollow nanostructures from ultrathin anatase TiO_2 nanosheets will provide the long sought after materials solutions in multiple fields, including photocatalysis and dye-sensitized solar cells.

Chapter 7 – Carbon-supported Ultra-thin Anatase TiO₂

Nanosheets for Fast Reversible Lithium Storage[†]

7.1. Introduction

Searching for new anode materials for lithium-ion batteries has been one of focus areas in material science for decades.^[1-2, 4-5, 173-174] Titanium oxide (TiO₂) has emerged as one of the attractive candidates^[6-7] because of its low cost and environmental benignity.^[8] Anatase TiO₂ is generally known to be more electrochemically active compared with thermodynamically stable rutile TiO₂, for which some recent findings reported by us and others suggested high electrochemical lithium reactivity.^[8, 64, 97, 169, 175] Based on the following electrochemical reaction: $\text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2$ ($0 \leq x \leq 0.5$) (1), a negligible volume change of less than 4% is usually induced in the anatase crystal structure during the Li⁺ insertion/deinsertion process, which accounts for the enhanced structural stability and prolonged cycle life of anatase TiO₂.^[56] On the other hand, the drawbacks of TiO₂-based anodes, e.g., low specific capacity (~167.5 mA h g⁻¹ calculated from equation (1)) and poor electronic conductivity, could be alleviated through proper nanostructuring.^[56] For example, it is suggested that constructing anatase TiO₂ nanosheets with exposed (001) facets will facilitate Li⁺ ion diffusion in the crystal structure, as Li⁺ ion travels along a zigzag pathway

[†] Reproduced from [J. S. Chen, et al., *J. Mater. Chem.*, 21, 5687 – 5692 (2011)] by permission from *The Royal Society of Chemistry*. Copyright 2011.

which is approximately along the *c*-axis, i.e., the [001] direction.^[107-109] Theoretical calculation indicates that the (001) facets possess a lower surface energy barrier for Li⁺ ion insertion compared with other common facets like (101) in anatase TiO₂. This leads to much higher lithium storage capacities especially at high current rates as verified by experimental measurement.^[176]

Inspired by these ideas, we have first investigated the electrochemical lithium storage capabilities of free-standing anatase TiO₂ nanosheets (NSs) with exposed (001) high-energy facets.^[150] Such anatase TiO₂ NSs exhibit unusually low initial irreversible loss, excellent cyclic capacity retention and superior high-rate performance. This observation is in good agreement with the theoretical studies. We have also recently constructed hierarchical spheres assembled from large ultrathin anatase TiO₂ NSs with nearly 100% exposed (001) facets, expectedly exhibiting outstanding lithium storage properties.^[177] As the positive effect of carbon on electrochemical performance of many anode materials has been well demonstrated,^[41-43, 52, 85, 88, 178-182] it is thus anticipated that enhanced lithium storage capabilities could be harvested if these structure-tailored anatase TiO₂ NSs are stabilized by ultrathin nanocarbon support. In this work, we report a straightforward method to synthesize three types of distinct structures which are assembled from carbon-supported ultrathin anatase TiO₂ NSs (C-TiO₂ NSs), namely, uniform hierarchical spheres assembled from these C-TiO₂ NSs (designated as sample I) and their hollow counterparts (designated as sample II), and randomly-oriented C-TiO₂ NSs (designated as sample III). In the first step of solvothermal synthesis, the organic additive, diethylenetriamine (DETA), acts as

the capping agent that stabilizes the (001) high-energy facets, allowing the formation of the ultrathin TiO₂ NSs.^[177] The adsorbed organic residues then serve as the *in situ* carbon source during the subsequent carbonization step, providing nanocarbon support to these electroactive TiO₂ NSs. Electrochemical measurements show that all three samples demonstrate greatly enhanced lithium storage properties with excellent capacity retention at a current rate as high as 5 C after 100 charge-discharge cycles. This superior performance could be attributed to the nice integration of the ultrathin TiO₂ NSs with largely exposed (001) facets, which facilitate the diffusion of Li⁺,^[176-177] and the nanocarbon which provides additional structural support leading to improved cyclic retention upon extended cycling.

7.2. Materials Preparation

Carbon-supported hierarchical structures from ultrathin anatase TiO₂ NSs are prepared by a modified solvothermal method. For the two spherical samples (sample I and II), the synthetic procedures are similar to those reported in our previous works,^[177, 183] except that the calcination in air is not performed. Instead, the samples were carbonized first at 400 °C for 2 h, and then at 600 °C for 2 h at a ramping rate of 2 °C min⁻¹ under a dynamic flow of N₂. To synthesize sample III, 0.6 ml of DETA was added into 42 ml of isopropanol. After gentle stirring, 0.6 ml of titanium isopropoxide was added into the solution. The solution was then transferred into a 60 ml Teflon-lined stainless steel autoclave. The autoclave was kept in a pre-heated electric oven at 200 °C for 24 h. It was then cooled naturally to

room temperature. The yellowish product was collected via centrifugation and washed thoroughly with absolute ethanol. After being dried at 60 °C in an oven, the powder is carbonized in N₂ at 400 °C for 4 h with a heating rate of 2 °C min⁻¹. After annealing, the powder becomes completely black.

7.3. Results and discussion

7.3.1. Characterization of the morphology and composition

Fig 7.1 depicts the morphology of sample I. As can be seen, this sample contains very uniform spheres with diameter about 1.5 μm (Fig. 7.1A), indicating that the introduction of the nanocarbon support does not lead to noticeable alteration to its morphology, as compared to the carbon-free counterpart. The C-TiO₂ NS constituents of these microspheres can be easily identified under a higher magnification (Fig. 7.1B). The uniformity of sample I is confirmed by transmission electron microscopy (TEM) observation (Fig. 7.1C), and it is verified that these spheres are indeed assembled from the NS building blocks (Fig. 7.1D).

The morphology of sample II is displayed in Fig. 7.2. Apparently, even after the removal of the inner silica core by hydrofluoric acid,^[183] the overall spherical structure as well as the ultrathin NSs are still intact (Fig. 7.2, A and B). The hollow interior of sample II is revealed by TEM (Fig. 7.2C), as a large void space can be clearly observed in each sphere, suggesting the complete removal of the silica core, which is also confirmed by the energy-dispersive X-ray (EDX) analysis (Fig. 7.2D). Our recent findings have shown that analogous carbon@TiO₂-NSs hollow spheres can also be constructed by templating against polystyrene hollow spheres followed

by carbonization,^[184] highlighting the versatility of the current approach. Fig. 7.3 shows the morphology of sample III. It can be clearly seen that the sample is composed of interconnected chain-like structures with a relatively uniform size of ~200 nm in diameter (Fig. 7.3, A and C). Under higher magnifications, the thickness of these NS subunits can be estimated to be 3 – 6 nm (Fig. 7.3, B and D). In all three samples, the capping agent DETA can effectively stabilize the (001) high-energy facets, allowing the formation of large ultrathin anatase TiO₂ NSs that

Fig. 7.1 Scanning electron microscopy (SEM) images (A and B) and transmission electron microscopy (TEM) images (C and D) of sample I.

subsequently self-organize into more complex 3D nanostructures.^[177] As a result, it is very challenging to visualize the ultrathin nanocarbon support derived from *in situ* carbonization of adsorbed organic species even under high-magnification TEM observation. This is in contrast to carbon-coated materials where the carbon

nanolayer usually with a thickness of > 5 nm is deposited via a separate treatment.^[52] Nonetheless, the observation of a black color readily indicates the formation of amorphous carbon.

Fig. 7.2 SEM images (A and B), TEM image (C), and energy dispersive X-ray analysis (EDX; D) of sample II.

The phase purity of the as-prepared samples is confirmed by X-ray diffraction (XRD; Fig. 7.4A), where all the identified peaks can be perfectly assigned to anatase TiO_2 (JCPDS card no. 21-1272, S.G.: $I4_1/amd$, $a_o = 3.7852$ Å, $c_o = 9.5139$ Å), noting the amorphous nature of such derived carbon. It can be seen that samples I and II show stronger peak intensities compared to sample III, implying that better crystalline structures are achieved in the former two samples due to the higher carbonization temperature. The carbon contents of the samples are determined by thermogravimetric analysis (TGA; Fig. 7.4B). Sample I

demonstrates the lowest carbon content of only 4 wt % among the three samples. Surprisingly, sample II appears to have a much higher carbon content of 15 wt %.

Fig. 7.3 SEM images (A and B) and TEM images (C and D) of sample III.

This might be related to the lower TiO_2 yield of sample II, while the absolute amount of carbon present in the sample should be similar to that of sample I, as same amount of DETA is used during the synthesis for both samples (see Table 7.1). Because much more DETA was used (see Table 7.1) in the synthesis of sample III, it is expected that sample III will contains relatively more carbon. From the TGA curve, it shows a weight loss of 11% from 100 °C to 600 °C. All three samples demonstrate different amount of weight loss below 100 °C. This weight loss can be attributed to the removal of adsorbed gaseous or moisture contents,^[177] as the samples have relatively high surface areas (see discussion below).

Fig. 7.4 X-ray diffraction (XRD) patterns (A) and Thermogravimetric analysis (TGA; B) of sample I, II and III.

Table 7.1 Key parameters and electrochemical results of the three samples.

Sample Number		I	II	III
Morphology		Solid spheres with C-TiO ₂ NSs	Hollow spheres with C-TiO ₂ NSs	Randomly-oriented C-TiO ₂ NSs
DETA amount (ml)		0.03	0.03	0.6
Carbon content (wt %)		4	15	11
Surface area (m² g⁻¹)		91.1	205	267.4
Total pore volume (cm³ g⁻¹)		0.33	0.44	0.89
Average pore size (nm)		14.5	8.6	13.3
Capacity (mA h g⁻¹) after 100 cycles	1 C	162	149.5	172.6
	5 C	127.2	128.6	147.8

7.3.2. Characterization of the surface texture

The surface structures of these samples are characterized by the N₂ adsorption-desorption measurement at 77 K with the isotherms shown in Fig. 7.5. The insets display the pore size distributions calculated by the Barrett-Joyner-Halenda (BJH) method. Generally, all three samples exhibit a similar pattern of isotherm, which could be approximately categorized to type IV with a type-H3 hysteresis loop,^[185] indicating the presence of a mesoporous structure. This type of porous structure renders the samples with relatively high surface areas and large total pore volumes. The detailed information about the surface structures of these samples are summarized in Table 7.1 for easy comparison.

7.3.3. Analysis of the cyclic voltammograms

We have then investigated the electrochemical lithium storage capabilities of these three samples. Fig. 7.6 shows representative cyclic voltammograms (CV). It is obvious that both samples I and II demonstrate similar CV patterns which are consistent with that in the previous reports (Fig. 7.6, A and B),^[85] with a pair of redox peaks signifying the insertion (cathodic sweep) and deinsertion (anodic sweep) processes of the Li⁺ into and out of the anatase framework. These peaks show no significant change in amplitude and voltage positions during the subsequent cycles, indicating the high reversibility of these electrochemical reactions. On the other hand, sample III exhibits a distinct CV behavior (Fig. 7.6C).

Fig. 7.5 N_2 adsorption-desorption isotherms of samples I (A), II (B) and III (C). The insets are the pore size distribution of the corresponding sample.

It is apparent that in addition to the characteristic pair of current peaks from anatase TiO_2 , a pair of broad peaks is also observed in the lower voltage range, which is not observed in the CV of pure TiO_2 NSs obtained by calcining the amine-stabilized sample in air instead of N_2 (Fig. 7.6C, inset). This is analogous to the CV curve of our latest sandwich-like ultrathin TiO_2 nanosheets with intercalated carbon.^[186] One might attribute this pair of current peaks to the nanocarbon support which suggests that additional electrochemical processes might take place in carbon-supported samples. Nevertheless, further fundamental studies are required to understand how the presence of amorphous carbon layer will alter the lithium insertion mechanism in some TiO_2 materials. It can also be observed from the CV curve that the current of the cathodic peak drops slightly during the subsequent scans, indicating the occurrence of some irreversible reaction inside the electrode material. While no noticeable change in current is observed for the anodic peak, implying that the deinsertion process has taken place to a similar extent during prolonged sweeps.

7.3.4. Investigation of the lithium storage properties

Fig. 7.7A shows the charge-discharge voltage profiles of the three samples at a current rate of 1 C. Consistent with the above CV measurement, two distinct voltage plateaus are clearly visible at ~ 1.75 V (discharge) and ~ 2.0 V (charge) for samples I and II, reflecting the dominant Li^+ insertion/deinsertion processes, while for sample III, both plateaus appear less pronounced. Sample III delivers the highest discharge capacity of 314 mA h g^{-1} amongst the three samples,

Fig. 7.6 Representative cyclic voltammograms (CV) of sample I (A), II (B), and III (C) at a scan rate of 0.5 mV s^{-1} between 1 V and 3 V. The inset in C shows the CV of the carbon-free counterpart of sample III.

corresponding to an insertion coefficient (x in equation (1)) of 0.92. This could be probably due to its long sloping region after the short voltage plateau at ~ 1.7 V, and it contributes ~ 200 mA h g⁻¹ to the total capacity. This final stage of the lithium insertion is believed to be related to the interaction between Li⁺ and the surface layer of the electrode material,^[46, 86] considering that sample III has the highest surface area. Sample II also shows a slightly higher discharge capacity of 269 mA h g⁻¹ than that of sample I (219 mA h g⁻¹), and this might be related to the large hollow interior as well as the higher surface area of the former, which, to a certain extent, help to store more lithium. The subsequent charge capacities delivered by the three samples are 176 mA h g⁻¹, 167 mA h g⁻¹, and 203 mA h g⁻¹, giving rise to an irreversible capacity loss of 20%, 38%, and 35%, for sample I, II, and III, respectively.

Fig. 7.7 B and C compare the cycling performance of the three samples at the different current rates. It clearly shows that at a current rate of 1 C, all three samples demonstrate similarly good cyclic capacity retention (Fig. 7.7B). At the end of 100 charge-discharge cycles, a reversible capacity of 150 – 170 mA h g⁻¹ (see Table 7.1) can still be retained, corresponding to 90% ~ 100% of the theoretical capacity of anatase TiO₂ (167.5 mA h g⁻¹). The capacity only drops slightly to 130 – 150 mA h g⁻¹ (see Table 7.1) when the current rate is increased to 5 C (Fig. 7.7C), indicating that 76% ~ 88% of the theoretical capacity can still be recovered. It can also be seen that sample III exhibits improved lithium storage capabilities compared to the other two samples. This may be attributed to the significantly higher surface area and total pore volume of sample III (see Table 7.1),

which allow much better contact between the electrolyte and the electrode material, thus providing a good interface that guarantees efficient lithium diffusion even at a high current rate of 5 C. The excellent cyclic capacity retention and good high-rate performance are advantageous compared to the reported data of the same material tested under similar conditions.^[124] This enhancement could be associated with the integration of the ultrathin (001) high-energy facets, which allows the fast and efficient lithium diffusion, and the nanocarbon layer which provides extra support

Fig. 7.7 (A) Charge-discharge voltage profiles of the first cycles at 1 C. Cycling performance at current rates of 1 C (B) and 5 C (C). (D) Post-mortem XRD analysis of the samples at 5 C after 100 cycles. All measurements were conducted with a voltage window of 1 V – 3 V.

to the structure, leading to improved cyclic capacity retention upon prolonged cycling. Lastly we have also carried out the post-mortem XRD analysis (Fig. 7.7D) of the electrode materials. Surprisingly, it shows that anatase crystal framework in all three samples can be retained even after 100 cycles at a high rate of 5C, suggesting excellent local stability of the C-TiO₂ NSs. At the same time, slight broadening of the diffraction peaks can also be observed, indicating the possible deterioration in crystallinity during the repeated lithium insertion/deinsertion cycling.

7.4. Conclusions

In summary, we have demonstrated a simple route to generate three samples assembled from carbon-supported ultrathin anatase TiO₂ NSs with different nanostructures. The organic additive DETA serves as both the capping agent during the initial solvothermal synthesis that stabilizes the (001) facets and the carbon source during the subsequent carbonization process. When evaluated for electrochemical lithium storage, the as-prepared samples exhibit high reversible capacities with excellent cyclic capacity retention at high current rates. This enhanced lithium storage performance could be attributed to the ultrathin NS structure allowing efficient Li⁺ ion diffusion, and the effective nanocarbon support granting better structural stability. These findings suggest that carbon-supported TiO₂ NSs may be used as a promising anode material for high-power lithium-ion batteries.

Chapter 8 – Graphene-supported Anatase TiO₂

Nanosheets for Fast Lithium Storage[†]

8.1. Introduction

Graphene, a monolayer of carbon atoms which has a tight packing of honeycomb lattice and serves as the basic building block of graphitic materials, has recently become one of the most appealing stars in material science.^[10, 187-188] Due to its unique optical, mechanical, electronic, and biological properties,^[189-190] graphene has been intensively studied in many fields including photocatalysis,^[191] biotechnology,^[169, 192-194] and energy storage devices^[195] like solar cells,^[192] supercapacitors,^[196] and lithium-ion batteries (LIBs).^[65, 70, 75, 169, 197-208] In most of these applications, the function of graphene is perhaps realized through its integration with many other functional materials, such as noble metal nanoparticles, oxides, chalcogenides, and polymers.^[209-211]

Among all the intriguing properties of graphene, its superior electrical conductivity and mechanical flexibility have rendered graphene particularly attractive for LIBs, where its major role is to increase the electrical conductivity of the electrode material, and to buffer the volume strain generated during the charge/discharge process.^[204] Very recently, many types of hybrid materials consisting of graphene and electroactive materials, such as silicon,^[197-198, 202]

[†] Reproduced from [S, Ding, J. S. Chen, et al.(co-first author), *Chem. Commun.*, 47, 5780 – 5782 (2011)] by permission from *The Royal Society of Chemistry*. Copyright 2011.

Fe₂O₃/Fe₃O₄,^[207-208] CoO/Co₃O₄,^[203-204, 208] SnO₂,^[70, 75, 199, 205-206] Li₄Ti₅O₁₂/TiO₂,^[169, 200, 212] etc., have been successfully synthesized. To generate metal oxide (MO)/graphene composites, the synthesis strategies can be broadly divided into two categories: one-pot growth of MO nanoparticles onto graphene sheets, and assembly of nanostructured materials with graphene via multi-step methods. Since MOs with unique nanostructures, such as porous or hollow structure, possess significantly enhanced lithium storage capabilities than their simple particle-like counterparts,^[40, 213] it is thus highly desirable, but yet very challenging, to develop a simple approach to integrate nanostructured materials with graphene support.

Herein, we report a facile solvothermal method to synthesize graphene-supported ultrathin anatase TiO₂ nanosheets (G-TiO₂ NSs). Both theoretical and experimental studies have previously suggested that lithium diffusion is greatly facilitated in two-dimensional anatase TiO₂ NSs with exposed (001) high-energy facets.^[85, 108, 142, 214] Thus, by directly growing such unique TiO₂ nanosheets on the graphene support, one is able to take advantage of both components. As expected, the as-prepared G-TiO₂ NSs nanocomposite demonstrates greatly improved lithium storage properties. Specifically, this unique hybrid structure is able to deliver high reversible capacities with magnificent cyclic capacity retention at different current rates for prolonged cycling, and exhibit excellent high-rate performance at a current rate as high as 20 C.

8.2. Materials Synthesis

The graphene oxide (GO) sheets were first synthesized by a modified Hummers' method.^[191, 215] Anatase TiO₂ NSs were then grown onto the GO support following our previous method.^[177] In a typical synthesis of G-TiO₂ NSs, 40 mg of GO sheets was dispersed into 40 mL of isopropyl alcohol (IPA) by sonication for 20 minutes, followed by the addition of 0.03 mL of diethylenetriamine (DETA; 99 %, Sigma-Aldrich). After the solution was gently stirring for 2 minutes, 0.6 mL of titanium (IV) isopropoxide (TIP; 97 %, Sigma-Aldrich) was added. The reaction solution was then transferred into a 60 mL Teflon-lined stainless steel autoclave and kept in an electric oven at 200 °C for 24 h. The autoclave was then taken out of the oven and left to cool down to room temperature. The black precipitate was collected by centrifugation, washed thoroughly with ethanol, and dried at 60 °C overnight. The as-prepared GO-TiO₂ NSs were treated at 400 °C in H₂/Ar for 2 h with a heating rate of 1 °C min⁻¹ to obtain G-TiO₂ NSs. In the absence of GO, TiO₂ NS spheres were obtained, and also treated at 400 °C in N₂ for 4 h as a comparison.

8.3. Results and Discussion

8.3.1. Characterization of the morphology and composition

Fig. 8.1 illustrates the synthesis procedure of the G-TiO₂ NSs. Graphene oxide (GO) nanosheets are first synthesized via a modified Hummers' method (Fig. 8.2),^[191, 215] and used as the support for the solvothermal growth of TiO₂ NSs. GO is then reduced to graphene via a thermal treatment under a mixed gas of N₂/H₂,

giving rise to G-TiO₂ NSs. Fig. 8.3 depicts the morphology of the as-prepared G-TiO₂ NSs. Due to the relatively large size of the GO sheets, large plate-like film structures with tens of micrometer in size are obtained (Fig. 8.3A), and clearly the film is completely covered with TiO₂ NSs on its surface. Only micron-sized spheres composed of TiO₂ NSs will be formed under similar synthesis conditions without the addition of substrates,^[177] thus the formation of such two-dimensional structures suggests that the NSs have been successfully grown on the GO support. Better revealed by the high-magnification SEM image (Fig. 8.3B), the NS constituents exhibit a curved structure and are densely oriented on the graphene support. Fig. 8.3C shows the transmission electron microscopy (TEM) image of a smaller piece of G-TiO₂ NSs, where the NS subunits are quite loosely packed. A closer observation (Fig. 8.3D) reveals that these NSs are very thin with a thickness

Fig. 8.1 Schematic illustration of the formation of graphene-supported TiO₂ nanosheets (G-TiO₂ NSs).

of a few nanometers only. It was previously shown that such anatase TiO₂ nanosheets are bound by the (001) high-energy facets on both the upper and lower surfaces.^[72, 102] Due to the very small dimension along the [001] direction, we

suppose that the percentage of the exposed (001) facets is nearly 100%. Because of the low contrast of graphene and the presence of the large amount of TiO_2 NSs, the graphene support cannot be directly observed under TEM.

X-ray diffraction (XRD) is employed to determine the crystallographic phases of the samples (Fig. 8.4A). A strong diffraction peak is observed at $\sim 10^\circ$ in pattern I, indicating that GO has been successfully obtained via the chemical oxidation of

Fig. 8.2 Electron microscopy images of as-prepared graphene oxide sheets.

graphite powder. This peak completely disappears after the thermal treatment (pattern II), accompanied by the emergence of a new peak at $\sim 25^\circ$, which is due to the (002) diffraction of graphene. Therefore it can be concluded that GO is completely reduced to graphene, marking the effectiveness of the present thermal

reduction process. The phase purity of the as-prepared G-TiO₂ NSs is also confirmed (pattern III), where all the diffraction peaks can be perfectly assigned to anatase TiO₂ (JCPDS card no. 21-1272, S.G.: I41/amd, $a_0 = 3.7852 \text{ \AA}$, $c_0 = 9.5139 \text{ \AA}$).^[177] The characteristic stacking peak of graphene cannot be discerned in this pattern, suggesting the homogeneous dispersion of GO sheets during the solvothermal synthesis that are successfully covered with TiO₂ NSs.^[204] The graphene content is determined by thermogravimetric analysis (TGA) (Fig. 8.4B).

Fig. 8.3 Scanning electron microscope (SEM) images (A, B) and Transmission electron microscope (TEM) images (C, D) of the as-prepared G-TiO₂ NSs.

Apparently, a large weight loss can be observed at $\sim 500^\circ\text{C}$, and the total amount of graphene present in the composite is measured to be $\sim 11.5 \text{ wt\%}$ till 600°C . While

the weight loss below 100 °C is probably due to the evaporation of adsorbed moisture contents, considering the relatively high surface area of the sample (see discussion below). The textural properties of the sample are characterized by N₂ adsorption/desorption measurement (Fig. 8.5). The isotherm can be categorized into a type-IV isotherm with a type-H3 hysteresis loop at the relative pressure of

Fig. 8.4 (A) X-ray diffraction (XRD) patterns of the samples: graphene oxide (I), graphene (II) and G-TiO₂ NSs (III). (B) Thermogravimetric analysis (TGA) of the G-TiO₂ NSs. The weight loss of ~5% below 100 °C is probably due to the evaporation of the absorbed moisture contents, which is common for materials with large surface area.

Fig. 8.5 N_2 adsorption-desorption isotherm of the G-TiO₂ NSs. The inset shows the pore size distribution calculated from the adsorption branch of the isotherm.

0.5 – 0.9, indicating the presence of a highly mesoporous structure.^[140] This gives rise to a very high Brunauer-Emmett-Teller (BET) surface area of $\sim 190 \text{ m}^2 \text{ g}^{-1}$. However, the mesopores show a relatively broad size distribution (Fig. 8.5, inset) in the range of 3 – 10 nm.

8.3.2. Investigation of the lithium storage properties

We have investigated the electrochemical properties of the G-TiO₂ NSs as a potential anode material for high-power LIBs. Fig. 8.6A shows the representative cyclic voltammograms (CVs) of the sample. Consistent with previous studies,^[177] two current peaks appear at $\sim 1.7 \text{ V}$ and $\sim 2.1 \text{ V}$ during the cathodic and anodic scans, respectively. These two peaks can be regarded as the signature of the lithium insertion/deinsertion processes in the anatase framework. There is a slight decrease in the peak current during the subsequent cycles, indicating the existence of irreversible reactions. Fig. 8.6B shows the charge-discharge voltage profiles at a current rate of 1 C. In agreement with the above CV analysis, two distinct voltage

plateaus can be observed during the charge/discharge processes. Apparently, each discharge (lithium insertion) can be divided into three stages. The first stage is marked by the fast decrease in voltage starting from the open-circuit potential to ~ 1.7 V. The second stage is the plateau region at ~ 1.7 V, reflecting the process of lithium insertion. The third stage displays as the long gradual decay of the voltage after the plateau region, which indicates the insertion of lithium into the surface structure of the material. As a result, a high capacity of 285 mA h g^{-1} can be delivered in the first discharge, with a corresponding charge capacity of 200 mA h g^{-1} . This leads to an irreversible capacity loss of $\sim 30\%$, which is relatively low for anatase TiO_2 -based materials.^[177] In the second cycle, a lower discharge capacity of 213 mA h g^{-1} and a charge capacity of 193 mA h g^{-1} can be reached, leading to a much higher Coulombic efficiency of 90.6% . This value increases further to 94% in the third cycle, showing that the irreversible loss is diminishing rapidly upon cycling.

Fig. 8.6C shows the cycling performance of the G- TiO_2 NSs at different current rates. Remarkably, the sample demonstrates excellent cyclic capacity retention at each current rate. At the end of 120 charge-discharge cycles, a reversible capacity of 161 mA h g^{-1} can be retained at a current rate of 1C , close to the theoretical capacity of 170 mA h g^{-1} . When the current rate is increased to 5C , a capacity of 125 mA h g^{-1} can still be delivered. It is quite interesting to discover that a further increase of the current rate to 10C leads only to an insignificant drop in capacity to 119 mA h g^{-1} , implying that the lithium diffusion is highly efficient in the present G- TiO_2 NSs composite.^[177] The as-prepared hybrid material

Fig. 8.6 Electrochemical measurements of G-TiO₂ NSs. (A) Representative cyclic voltammograms (CVs) at a scan rate of 0.5 mV s⁻¹. (B) Charge-discharge voltage profiles of the first 3 cycles at a current rate of 1 C. (C) Cycling performance at constant current rates of 1 C, 5 C, and 10 C. (D) Cycling performance at different current rates from 1 C to 20 C. All measurements were conducted with a voltage window of 1 – 3 V.

demonstrates much better performance compared to the TiO₂ NSs without graphene support (Fig. 8.7), indicating the positive effect of the graphene sheets. It also shows better lithium storage capabilities than other graphene-TiO₂ composites tested under similar condition.^[169, 212] The rate capability of the sample is then evaluated by charging/discharging at various current rates from 1 C to 20 C (Fig. 8.6D). It is very obvious that the sample shows magnificent cyclic capacity retention at each rate. Remarkably, a reversible capacity of 107 mA h g⁻¹ can be sustained at the highest current rate of 20 C, further proving the efficient solid-state diffusion of lithium. More importantly, a stable capacity of 180 mA h g⁻¹ can be

resumed when the current rate is reduced back to 1 C, suggesting the good structural stability of the sample. This is partly verified by the post-mortem analysis (data not shown), which shows the existence of the nanosheet structure as well as the complete retention of the anatase crystal structure at the end of the test.

Fig. 8.7 Comparative cycling performance between G-TiO₂ NSs and pure TiO₂ NSs prepared using similar method without graphene support at the current rate of 1 C (A) and 5 C (B). All measurements were conducted between 1 V and 3 V.

8.4. Conclusions

In summary, we have designed a unique hybrid structure by directly growing ultrathin anatase TiO_2 nanosheets onto graphene support for fast lithium storage. Exposed by (001) high-energy facets, these TiO_2 nanosheets serve as the ideal host for fast and efficient lithium storage. While the graphene support serves as a highly conductive substrate that is beneficial to the high-rate performance. At the same time, it buffers the volume strain generated during the charge/discharge process, which enhances the cyclic capacity retention over extended cycling. It is believed that such graphene-containing hybrid nanomaterials with designed structure and advanced chemical composition will be useful in energy storage and other important applications such as solar cells and photocatalysis.

Chapter 9– Conclusions and Outlook

9.1. Conclusions

This research work focuses on the development of new methods to synthesize novel nanostructured anatase TiO_2 nanosheets with exposed (001) facets. Theoretical studies have shown that by exposing (001) facets, lithium diffusion would be greatly facilitated due to increased availability of open channels along the *c*-axis. Thus, a facile hydrothermal method was first developed to synthesize free-standing anatase TiO_2 nanosheets. HF was used as the F donor to stabilize the (001) high-energy facets, prevent their diminishment during the crystal growth process. The as-prepared product has a relatively narrow size distribution with square- or rectangle-shaped sheet-like structure. After thorough characterization using TEM and SEM, the percentage of exposed (001) facets was estimated to be ~60%. When applied as the anode material for lithium-ion batteries, the above theoretical prediction was verified that these unique TiO_2 nanosheets exhibit greatly enhanced cycling performance at current rate as high as 20 C, and demonstrate highly efficient solid-state diffusion with insignificant capacity drop at high current rates.

In order to achieve higher percentage of the exposed (001) facets, a facile solvothermal method was discovered, where DETA was selected as the surfactant such that the (001) facets were stabilized and only lateral growth was allowed. This gives rise to the formation of large ultrathin anatase TiO_2 nanosheets bound by (001) facets on the top and bottom with hundreds of nanometers in size while only a few nanometers in thickness. Due to the ultrathin feature of these large

nanosheets, they self-organize into a spherical hierarchical structure with nearly 100% exposed (001) facets. This hierarchical structure shows a high surface area of $170 \text{ m}^2 \text{ g}^{-1}$ and a good thermal stability. Furthermore, by introducing different nanotemplates, e.g., SiO_2 or $\text{SnO}_2@ \text{SiO}_2$ nanospheres, hollow or $\text{SnO}_2@ \text{TiO}_2$ double-shell hollow structures with shells assembled from there TiO_2 nanosheets were readily produced after the selected removal of the inner SiO_2 core. When these samples were applied in lithium-ion batteries, they demonstrated superior lithium storage capacities with promising high-rate performance and cyclic retention.

Carbon is usually suggested as a good additive when compositing with electroactive metal oxides for lithium-ion batteries. Thus, composite nanomaterials consisting of the unique anatase TiO_2 nanosheets with exposed (001) facets and two types of carbonaceous additives, i.e., amorphous carbon and graphene, were created. The amorphous carbon was introduced by an *in-situ* carbonization of the surfactant DETA, while graphene oxide was initially served as the support for the growth of the TiO_2 nanosheets follow by thermal reduction. Both these two types of composite nanomaterials manifested good lithium storage properties with enhanced cyclic retention over prolonged cycling. This could probably be attributed to the carbonaceous support which served as a buffering matrix that helped to absorb the volume change during charge/discharge cycles, and also increases the electrical conductivity of the composite.

In summary, this project has thoroughly investigated the enhanced lithium storage properties of the anatase TiO_2 nanosheets with exposed (001) high-energy

facets from different aspects, such as novel structures, including free-standing nanosheets, and hierarchical or even hollow structures, and also advanced chemical composite consisting of different carbonaceous support and these unique nanosheets. These findings not only serve as evidence confirming the theoretical studies, but also shed light on the great commercial potential of these unique nanomaterials.

9.2. Outlook

Anatase TiO_2 nanosheets with exposed (001) facets have demonstrated superior lithium storage properties, which could serve as promising candidate for high-power lithium-ion batteries. The future researches are proposed in the following aspects:

- 1) A green synthetic scheme is to be developed for a scale synthesis of such TiO_2 nanomaterials with inexpensive precursors without using any hazardous chemicals such as HF. The product can even be commercialized if the proposed method can be discovered.
- 2) Application of the as-prepared TiO_2 nanosheets with exposed high-energy facets could be extended to photocatalysis, and solar cell. Due to the unique nanostructure, the material is believed to have attractive performance in these fields as well.
- 3) Introduction of other materials, such as noble metals, or Lanthanide elements, to the anatase TiO_2 nanosheets would likely lead to further improved physicochemical properties.
- 4) As another important member of the titania family, rutile TiO_2 also possesses different crystal facets with contrasting surface energies. It is thus very important to develop a method to synthesize nanostructured rutile TiO_2 with exposed high-energy facets and to investigate their application potentials.

Reference

- [1] M. Armand, J. M. Tarascon, Building better batteries, *Nature* **2008**, *451*, 652-657.
- [2] J. M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, *Nature* **2001**, *414*, 359-367.
- [3] J. B. Goodenough, Y. Kim, Challenges for Rechargeable Li Batteries, *Chem. Mater.* **2010**, *22*, 587-603.
- [4] P. G. Bruce, B. Scrosati, J. M. Tarascon, Nanomaterials for rechargeable lithium batteries, *Angew. Chem. Int. Ed.* **2008**, *47*, 2930-2946.
- [5] D. Larcher, S. Beattie, M. Morcrette, K. Edstroem, J. C. Jumas, J. M. Tarascon, Recent findings and prospects in the field of pure metals as negative electrodes for Li-ion batteries, *J. Mater. Chem.* **2007**, *17*, 3759-3772.
- [6] J. Liu, G. Z. Cao, Z. G. Yang, D. H. Wang, D. Dubois, X. D. Zhou, G. L. Graff, L. R. Pederson, J. G. Zhang, Oriented Nanostructures for Energy Conversion and Storage, *Chemsuschem* **2008**, *1*, 676-697.
- [7] Z. G. Yang, D. Choi, S. Kerisit, K. M. Rosso, D. H. Wang, J. Zhang, G. Graff, J. Liu, Nanostructures and lithium electrochemical reactivity of lithium titanates and titanium oxides: A review, *J. Power Sources* **2009**, *192*, 588-598.
- [8] J. S. Chen, X. W. Lou, The superior lithium storage capabilities of ultra-fine rutile TiO₂ nanoparticles, *J. Power Sources* **2010**, *195*, 2905-2908.
- [9] J. S. Chen, D. Luan, C. M. Li, F. Y. C. Boey, S. Qiao, X. W. Lou, TiO₂ and SnO₂@TiO₂ hollow spheres assembled from anatase TiO₂ nanosheets with enhanced lithium storage properties, *Chem. Comm.* **2010**, *46*, 8252-8254.

- [10] H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng, G. Q. Lu, Anatase TiO₂ single crystals with a large percentage of reactive facets, *Nature* **2008**, 453, 638-U634.
- [11] D. R. Linden, T. B., *Handbook of Batteries*, 3rd ed. ed., McGraw-Hill: New York, **2002**.
- [12] K. Brandt, A 65-Ah rechargeable lithium molybdenum-disulfide battery, *J. Power Sources* **1986**, 18, 117-125.
- [13] K. Brandt, Testing methods for lithium molybdenum-disulfide intercalation batteries, *J. Power Sources* **1986**, 17, 153-159.
- [14] I. Faul, J. Knight, Lithium rechargeable batteries - a review of recent trends, *Chem. Ind.* **1989**, 820-825.
- [15] D. Fouchard, J. B. Taylor, The molicele rechargeable lithium system - multicell aspects, *J. Power Sources* **1987**, 21, 195-205.
- [16] F. C. Laman, K. Brandt, Effect of discharge current on cycle life of a rechargeable lithium battery, *J. Power Sources* **1988**, 24, 195-206.
- [17] J. J. Murray, J. E. A. Alderson, Precision cycling and coulombic efficiency measurements on Li/MoS₂ and Li,Al/FeS cells, *J. Power Sources* **1989**, 26, 293-299.
- [18] M. S. Whittingham, Electrical energy-storage and intercalation chemistry, *Science* **1976**, 192, 1126-1127.
- [19] D. P. Wilkinson, H. Blom, K. Brandt, D. Wainwright, Effects of physical constraints on Li cyclability, *J. Power Sources* **1991**, 36, 517-527.
- [20] G. A. Nazri, G. Pistoia, *Lithium batteries : science and technology*, Springer, **2004**.

- [21] F. Orsini, A. du Pasquier, B. Beaudouin, J. M. Tarascon, M. Trentin, N. Langenhuisen, E. de Beer, P. Notten, In situ SEM study of the interfaces in plastic lithium cells, *J. Power Sources* **1999**, 81-82, 918-921.
- [22] B. M. L. Rao, R. W. Francis, H. A. Christopher, Lithium-Aluminum Electrode, *J. Electrochem. Soc.* **1977**, 124, 1490-1492.
- [23] Y. Wang, X. Jiang, Y. Xia, A Solution-Phase, Precursor Route to Polycrystalline SnO₂ Nanowires That Can Be Used for Gas Sensing under Ambient Conditions, *J. Am. Chem. Soc.* **2003**, 125, 16176-16177.
- [24] M. Law, H. Kind, B. Messer, F. Kim, P. D. Yang, Photochemical sensing of NO₂ with SnO₂ nanoribbon nanosensors at room temperature, *Angew. Chem. Int. Ed.* **2002**, 41, 2405-2408.
- [25] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, Tin-based amorphous oxide: A high-capacity lithium-ion-storage material, *Science* **1997**, 276, 1395-1397.
- [26] V. Juttukonda, R. L. Paddock, J. E. Raymond, D. Denomme, A. E. Richardson, L. E. Slusher, B. D. Fahlman, Facile Synthesis of Tin Oxide Nanoparticles Stabilized by Dendritic Polymers, *J. Am. Chem. Soc.* **2005**, 128, 420-421.
- [27] H.-J. Ahn, H.-C. Choi, K.-W. Park, S.-B. Kim, Y.-E. Sung, Investigation of the Structural and Electrochemical Properties of Size-Controlled SnO₂ Nanoparticles, *J. Phys. Chem. B* **2004**, 108, 9815-9820.
- [28] D. Chen, L. Gao, Facile synthesis of single-crystal tin oxide nanorods with tunable dimensions via hydrothermal process, *Chem. Phys. Lett.* **2004**, 398, 201-206.
- [29] B. Cheng, J. M. Russell, Shi, L. Zhang, E. T. Samulski, Large-Scale, Solution-Phase Growth of Single-Crystalline SnO₂ Nanorods, *J. Am. Chem. Soc.* **2004**, 126, 5972-5973.

- [30] Z. W. Pan, Z. R. Dai, Z. L. Wang, Nanobelts of Semiconducting Oxides, *Science* **2001**, *291*, 1947-1949.
- [31] Z. Lili, Y. Maekelle, S. Martin, G. Petra, H. Herbert, G. Ulrich, S. Sabine, Porous Silicon and Alumina as Chemically Reactive Templates for the Synthesis of Tubes and Wires of SnSe, Sn, and SnO₂, *Angew. Chem. Int. Ed.* **2006**, *45*, 311-315.
- [32] X. W. Lou, J. S. Chen, P. Chen, L. A. Archer, One-Pot Synthesis of Carbon-Coated SnO₂ Nanocolloids with Improved Reversible Lithium Storage Properties, *Chem. Mater.* **2009**, *21*, 2868-2874.
- [33] X. W. Lou, D. Deng, J. Y. Lee, L. A. Archer, Preparation of SnO₂/Carbon Composite Hollow Spheres and Their Lithium Storage Properties, *Chem. Mater.* **2008**, *20*, 6562-6566.
- [34] X. W. Lou, C. M. Li, L. A. Archer, Designed Synthesis of Coaxial SnO₂@carbon Hollow Nanospheres for Highly Reversible Lithium Storage, *Adv. Mater.* **2009**, *21*, 2536-2539.
- [35] D. H. Chen, F. Z. Huang, Y. B. Cheng, R. A. Caruso, Mesoporous Anatase TiO₂ Beads with High Surface Areas and Controllable Pore Sizes: A Superior Candidate for High-Performance Dye-Sensitized Solar Cells, *Adv. Mater.* **2009**, *21*, 2206-2210.
- [36] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J. M. Tarascon, Nano-sized transition-metaloxides as negative-electrode materials for lithium-ion batteries, *Nature* **2000**, *407*, 496-499.
- [37] L. Y. Beaulieu, K. W. Eberman, R. L. Turner, L. J. Krause, J. R. Dahn, Colossal reversible volume changes in lithium alloys, *Electrochem. Solid State Lett.* **2001**, *4*, A137-A140.

- [38] L. Fransson, E. Nordstrom, K. Edstrom, L. Haggstrom, J. T. Vaughey, M. M. Thackeray, Structural transformations in lithiated η' - Cu_6Sn_5 electrodes probed by in situ Mossbauer spectroscopy and X-ray diffraction, *J. Electrochem. Soc.* **2002**, *149*, A736-A742.
- [39] B. Veeraraghavan, A. Durairajan, B. Haran, B. Popov, R. Guidotti, Study of Sn-coated graphite as anode material for secondary lithium-ion batteries, *J. Electrochem. Soc.* **2002**, *149*, A675-A681.
- [40] X. W. Lou, Y. Wang, C. L. Yuan, J. Y. Lee, L. A. Archer, Template-free synthesis of SnO_2 hollow nanostructures with high lithium storage capacity, *Adv. Mater.* **2006**, *18*, 2325-2329.
- [41] S. J. Han, B. C. Jang, T. Kim, S. M. Oh, T. Hyeon, Simple synthesis of hollow tin dioxide microspheres and their application to lithium-ion battery anodes, *Adv. Funct. Mater.* **2005**, *15*, 1845-1850.
- [42] K. T. Lee, Y. S. Jung, S. M. Oh, Synthesis of Tin-Encapsulated Spherical Hollow Carbon for Anode Material in Lithium Secondary Batteries, *J. Am. Chem. Soc.* **2003**, *125*, 5652-5653.
- [43] Y. Wang, H. C. Zeng, J. Y. Lee, Highly reversible lithium storage in porous SnO_2 nanotubes with coaxially grown carbon nanotube overlayers, *Adv. Mater.* **2006**, *18*, 645-649.
- [44] Y. Wang, J. Y. Lee, H. C. Zeng, Polycrystalline SnO_2 Nanotubes Prepared via Infiltration Casting of Nanocrystallites and Their Electrochemical Application, *Chem. Mater.* **2005**, *17*, 3899-3903.
- [45] Y. Wang, F. Su, J. Y. Lee, X. S. Zhao, Crystalline Carbon Hollow Spheres, Crystalline Carbon- SnO_2 Hollow Spheres, and Crystalline SnO_2 Hollow Spheres: Synthesis and Performance in Reversible Li-Ion Storage, *Chem. Mater.* **2006**, *18*, 1347-1353.

- [46] C. H. Jiang, M. D. Wei, Z. M. Qi, T. Kudo, I. Honma, H. S. Zhou, Particle size dependence of the lithium storage capability and high rate performance of nanocrystalline anatase TiO₂ electrode, *J. Power Sources* **2007**, *166*, 239-243.
- [47] Z. Wen, Q. Wang, Q. Zhang, J. Li, In Situ Growth of Mesoporous SnO₂ on Multiwalled Carbon Nanotubes: A Novel Composite with Porous-Tube Structure as Anode for Lithium Batteries, *Adv. Funct. Mater.* **2007**, *17*, 2772-2778.
- [48] H. Qiao, Z. Zheng, L. Z. Zhang, L. F. Xiao, SnO₂@C core-shell spheres: synthesis, characterization, and performance in reversible Li-ion storage, *J. Mater. Sci.* **2008**, *43*, 2778-2784.
- [49] J. Fan, T. Wang, C. Yu, B. Tu, Z. Jiang, D. Zhao, Ordered, Nanostructured Tin-Based Oxides/Carbon Composite as the Negative-Electrode Material for Lithium-Ion Batteries, *Adv. Mater.* **2004**, *16*, 1432-1436.
- [50] Z. Tao, J. Liang, J. Chen, Template-Directed Materials for Rechargeable Lithium-Ion Batteries, *Chem. Mater.* **2007**, *20*, 667-681.
- [51] L. Taberna, S. Mitra, P. Poizot, P. Simon, J. M. Tarascon, High rate capabilities Fe₃O₄-based Cu nano-architected electrodes for lithium-ion battery applications, *Nat. Mater.* **2006**, *5*, 567-573.
- [52] W. M. Zhang, X. L. Wu, J. S. Hu, Y. G. Guo, L. J. Wan, Carbon Coated Fe₃O₄ Nanospindles as a Superior Anode Material for Lithium-Ion Batteries, *Adv. Funct. Mater.* **2008**, *18*, 3941-3946.
- [53] K. T. Nam, D.-W. Kim, P. J. Yoo, C.-Y. Chiang, N. Meethong, P. T. Hammond, Y.-M. Chiang, A. M. Belcher, Virus-Enabled Synthesis and Assembly of Nanowires for Lithium Ion Battery Electrodes, *Science* **2006**, *312*, 885-888.

- [54] X. W. Lou, D. Deng, J. Y. Lee, J. Feng, L. A. Archer, Self-supported formation of needlelike Co_3O_4 nanotubes and their application as lithium-ion battery electrodes, *Adv. Mater.* **2008**, *20*, 258-262.
- [55] X. W. Lou, D. Deng, J. Y. Lee, L. A. Archer, Thermal formation of mesoporous single-crystal Co_3O_4 nano-needles and their lithium storage properties, *J. Mater. Chem.* **2008**, *18*, 4397-4401.
- [56] D. Deng, M. G. Kim, J. Y. Lee, J. Cho, Green energy storage materials: Nanostructured TiO_2 and Sn-based anodes for lithium-ion batteries, *Energy Environ. Sci.* **2009**, *2*, 818-837.
- [57] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, J. D. Joannopoulos, Iterative minimization techniques for abinitio total-energy calculations - molecular-dynamics and conjugate gradients, *Rev. Mod. Phys.* **1992**, *64*, 1045-1097.
- [58] M. V. Koudriachova, N. M. Harrison, S. W. de Leeuw, Diffusion of Li-ions in rutile. An ab initio study, *Solid State Ionics* **2003**, *157*, 35-38.
- [59] M. V. Koudriachova, N. M. Harrison, S. W. de Leeuw, Density-functional simulations of lithium intercalation in rutile, *Phys. Rev. B* **2002**, *65*.
- [60] A. Stashans, S. Lunell, R. Bergstrom, A. Hagfeldt, S. E. Lindquist, Theoretical study of lithium intercalation in rutile and anatase, *Phys. Rev. B* **1996**, *53*, 159-170.
- [61] M. Ramamoorthy, D. Vanderbilt, R. D. Kingsmith, 1st-principles calculations of the energetics of stoichiometric TiO_2 surfaces, *Phys. Rev. B* **1994**, *49*, 16721-16727.
- [62] B. J. Morgan, G. W. Watson, A Density Functional Theory plus U Study of Oxygen Vacancy Formation at the (110), (100), (101), and (001) Surfaces of Rutile TiO_2 , *J. Phys. Chem. C* **2009**, *113*, 7322-7328.

- [63] Y. S. Hu, L. Kienle, Y. G. Guo, J. Maier, High lithium electroactivity of nanometer-sized rutile TiO₂, *Adv. Mater.* **2006**, *18*, 1421-1426.
- [64] D. Wang, D. Choi, Z. Yang, V. V. Viswanathan, Z. Nie, C. Wang, Y. Song, J.-G. Zhang, J. Liu, Synthesis and Li-Ion Insertion Properties of Highly Crystalline Mesoporous Rutile TiO₂, *Chem. Mater.* **2008**, *20*, 3435-3442.
- [65] G. Liu, C. H. Sun, H. G. Yang, S. C. Smith, L. Z. Wang, G. Q. Lu, H. M. Cheng, Nanosized anatase TiO₂ single crystals for enhanced photocatalytic activity, *Chem. Comm.* **2010**, *46*, 755-757.
- [66] F. Amano, T. Yasumoto, O. O. Prieto-Mahaney, S. Uchida, T. Shibayama, B. Ohtani, Photocatalytic activity of octahedral single-crystalline mesoparticles of anatase titanium(IV) oxide, *Chem. Comm.* **2009**, 2311-2313.
- [67] J. G. Yu, L. F. Qi, M. Jaroniec, Hydrogen Production by Photocatalytic Water Splitting over Pt/TiO₂ Nanosheets with Exposed {001} Facets, *J. Phys. Chem. C* **2010**, *114*, 13118-13125.
- [68] G. Liu, H. G. Yang, X. W. Wang, L. N. Cheng, H. F. Lu, L. Z. Wang, G. Q. Lu, H. M. Cheng, Enhanced Photoactivity of Oxygen-Deficient Anatase TiO₂ Sheets with Dominant {001} Facets, *J. Phys. Chem. C* **2009**, *113*, 21784-21788.
- [69] G. Liu, H. G. Yang, X. W. Wang, L. N. Cheng, J. Pan, G. Q. Lu, H. M. Cheng, Visible Light Responsive Nitrogen Doped Anatase TiO₂ Sheets with Dominant {001} Facets Derived from TiN, *J. Am. Chem. Soc.* **2009**, *131*, 12868-12869.
- [70] M. Liu, L. Y. Piao, W. M. Lu, S. T. Ju, L. Zhao, C. L. Zhou, H. L. Li, W. J. Wang, Flower-like TiO₂ nanostructures with exposed {001} facets: Facile synthesis and enhanced photocatalysis, *Nanoscale* **2010**, *2*, 1115-1117.

- [71] F. Amano, O.-O. Prieto-Mahaney, Y. Terada, T. Yasumoto, T. Shibayama, B. Ohtani, Decahedral Single-Crystalline Particles of Anatase Titanium(IV) Oxide with High Photocatalytic Activity, *Chem. Mater.* **2009**, *21*, 2601-2603.
- [72] X. G. Han, Q. Kuang, M. S. Jin, Z. X. Xie, L. S. Zheng, Synthesis of Titania Nanosheets with a High Percentage of Exposed (001) Facets and Related Photocatalytic Properties, *J. Am. Chem. Soc.* **2009**, *131*, 3152-3153.
- [73] D. Zhang, G. Li, X. Yang, J. C. Yu, A micrometer-size TiO₂ single-crystal photocatalyst with remarkable 80% level of reactive facets, *Chem. Commun.* **2009**, 4381-4383.
- [74] S. Liu, J. Yu, M. Jaroniec, Tunable Photocatalytic Selectivity of Hollow TiO₂ Microspheres Composed of Anatase Polyhedra with Exposed {001} Facets, *J. Am. Chem. Soc.* **2010**, *132*, 11914-11916.
- [75] J. A. Zhu, S. H. Wang, Z. F. Bian, S. H. Xie, C. L. Cai, J. G. Wang, H. G. Yang, H. X. Li, Solvothermally controllable synthesis of anatase TiO₂ nanocrystals with dominant {001} facets and enhanced photocatalytic activity, *Crystengcomm* **2010**, *12*, 2219-2224.
- [76] A. Wold, Photocatalytic properties of TiO₂, *Chem. Mater.* **1993**, *5*, 280-283.
- [77] J. K. Zhou, L. Lv, J. Q. Yu, H. L. Li, P. Z. Guo, H. Sun, X. S. Zhao, Synthesis of self-organized polycrystalline F-doped TiO₂ hollow microspheres and their photocatalytic activity under visible light, *J. Phys. Chem. C* **2008**, *112*, 5316-5321.
- [78] M. M. Ye, Q. Zhang, Y. X. Hu, J. P. Ge, Z. D. Lu, L. He, Z. L. Chen, Y. D. Yin, Magnetically Recoverable Core-Shell Nanocomposites with Enhanced Photocatalytic Activity, *Chem. Eur. J.* **2010**, *16*, 6243-6250.
- [79] M. Gratzel, Photoelectrochemical cells, *Nature* **2001**, *414*, 338-344.

- [80] Y. J. Kim, M. H. Lee, H. J. Kim, G. Lim, Y. S. Choi, N. G. Park, K. Kim, W. I. Lee, Formation of Highly Efficient Dye-Sensitized Solar Cells by Hierarchical Pore Generation with Nanoporous TiO₂ Spheres, *Adv. Mater.* **2009**, *21*, 3668-3673.
- [81] R. Li, Y. Gan, Q. L. Song, Z. H. Zhu, J. Shi, H. Yang, W. Wang, P. Chen, C. M. Li, Bidirectional mediation of TiO₂ nanowires field effect transistor by dipole moment from purple membrane, *Nanoscale* **2010**, *2*, 1474-1479.
- [82] S.J. Bao, C. M. Li, J.F. Zang, X.Q. Cui, Y. Qiao, J. Guo, Novel nanoporous TiO₂ electrode for direct electrochemistry of glucose oxidase, *Adv. Funct. Mater.* **2008**, *18*, 591-599.
- [83] J. W. Seo, H. Chung, M. Y. Kim, J. Lee, I. H. Choi, J. Cheon, Development of water-soluble single-crystalline TiO₂ nanoparticles for photocatalytic cancer-cell treatment, *Small* **2007**, *3*, 850-853.
- [84] X. W. Lou, L. A. Archer, A general route to nonspherical anatase TiO₂ hollow colloids and magnetic multifunctional particles, *Adv. Mater.* **2008**, *20*, 1853-1858.
- [85] M. Bousa, B. Laskova, M. Zukalova, J. Prochazka, A. Chou, L. Kavan, Polycrystalline TiO₂ Anatase with a Large Proportion of Crystal Facets (001): Lithium Insertion Electrochemistry, *J. Electrochem. Soc.* **2010**, *157*, A1108-A1112.
- [86] Y. G. Guo, Y. S. Hu, J. Maier, Synthesis of hierarchically mesoporous anatase spheres and their application in lithium batteries, *Chem. Comm.* **2006**, 2783-2785.
- [87] B. Song, S. W. Liu, J. K. Jian, M. Lei, X. J. Wang, H. Li, J. G. Yu, X. L. Chen, Electrochemical properties of TiO₂ hollow microspheres from a template-free and green wet-chemical route, *J. Power Sources* **2008**, *180*, 869-874.

- [88] S. K. Das, S. Darmakolla, A. J. Bhattacharyya, High lithium storage in micrometre sized mesoporous spherical self-assembly of anatase titania nanospheres and carbon, *J. Mater.Chem.* **2010**, *20*, 1600-1606.
- [89] C. H. Sun, X. H. Yang, J. S. Chen, Z. Li, X. W. Lou, C. Li, S. C. Smith, G. Q. Lu, H. G. Yang, Higher charge/discharge rates of lithium-ions across engineered TiO₂ surfaces leads to enhanced battery performance, *Chem. Comm.* **2010**, *46*, 6129-6131.
- [90] S. J. Bao, Q. L. Bao, C. M. Li, Z. L. Dong, Novel porous anatase TiO₂ nanorods and their high lithium electroactivity, *Electrochem. Comm.* **2007**, *9*, 1233-1238.
- [91] Y. G. Guo, Y. S. Hu, W. Sigle, J. Maier, Superior electrode performance of nanostructured mesoporous TiO₂ (anatase) through efficient hierarchical mixed conducting networks, *Adv. Mater.* **2007**, *19*, 2087-2091.
- [92] S. K. Cheah, E. Perre, M. Rooth, M. Fondell, A. Harsta, L. Nyholm, M. Boman, T. Gustafsson, J. Lu, P. Simon, K. Edstrom, Self-Supported Three-Dimensional Nanoelectrodes for Microbattery Applications, *Nano Lett.* **2009**, *9*, 3230-3233.
- [93] J. W. Xu, C. H. Ha, B. Cao, W. F. Zhang, Electrochemical properties of anatase TiO₂ nanotubes as an anode material for lithium-ion batteries, *Electrochim. Acta* **2007**, *52*, 8044-8047.
- [94] X. P. Gao, Y. Lan, H. Y. Zhu, J. W. Liu, Y. P. Ge, F. Wu, D. Y. Song, Electrochemical performance of anatase nanotubes converted from protonated titanate hydrate nanotubes, *Electrochem. Solid State Lett.* **2005**, *8*, A26-A29.
- [95] G. Binotto, D. Larcher, A. S. Prakash, R. H. Urbina, M. S. Hegde, J. M. Tarascon, Synthesis, characterization, and li-electrochemical performance of highly porous Co₃O₄ powders, *Chem. Mater.* **2007**, *19*, 3032-3040.

- [96] L. Aldon, P. Kubiak, A. Picard, J. C. Jumas, J. Olivier-Fourcade, Size particle effects on lithium insertion into Sn-doped TiO₂ anatase, *Chem. Mater.* **2006**, *18*, 1401-1406.
- [97] D. H. Wang, J. Liu, Q. S. Huo, Z. M. Nie, W. G. Lu, R. E. Williford, Y. B. Jiang, Surface-mediated growth of transparent, oriented, and well-defined nanocrystalline anatase titania films, *J. Am. Chem. Soc.* **2006**, *128*, 13670-13671.
- [98] A. Chemseddine, T. Moritz, Nanostructuring titania: Control over nanocrystal structure, size, shape, and organization, *Eur. J. Inorg. Chem.* **1999**, 235-245.
- [99] C. T. Dinh, T. D. Nguyen, F. Kleitz, T. O. Do, Shape-Controlled Synthesis of Highly Crystalline Titania Nanocrystals, *ACS Nano* **2009**, *3*, 3737-3743.
- [100] Y. W. Jun, M. F. Casula, J. H. Sim, S. Y. Kim, J. Cheon, A. P. Alivisatos, Surfactant-assisted elimination of a high energy facet as a means of controlling the shapes of TiO₂ nanocrystals, *J. Am. Chem. Soc.* **2003**, *125*, 15981-15985.
- [101] Y. Yin, A. P. Alivisatos, Colloidal nanocrystal synthesis and the organic-inorganic interface, *Nature* **2005**, *437*, 664-670.
- [102] H. G. Yang, G. Liu, S. Z. Qiao, C. H. Sun, Y. G. Jin, S. C. Smith, J. Zou, H. M. Cheng, G. Q. Lu, Solvothermal Synthesis and Photoreactivity of Anatase TiO₂ Nanosheets with Dominant {001} Facets, *J. Am. Chem. Soc.* **2009**, *131*, 4078-4083.
- [103] X. Y. Ma, Z. G. Chen, S. B. Hartono, H. B. Jiang, J. Zou, S. Z. Qiao, H. G. Yang, Fabrication of uniform anatase TiO₂ particles exposed by {001} facets, *Chem. Comm.* **2010**, *46*, 6608-6610.

- [104] Y. Alivov, Z. Y. Fan, A Method for Fabrication of Pyramid-Shaped TiO₂ Nanoparticles with a High {001} Facet Percentage, *J. Phys. Chem. C* **2009**, *113*, 12954-12957.
- [105] Y. Dai, C. M. Cobley, J. Zeng, Y. Sun, Y. Xia, Synthesis of Anatase TiO₂ Nanocrystals with Exposed {001} Facets, *Nano Lett.* **2009**, *9*, 2455-2459.
- [106] B. Wu, C. Guo, N. Zheng, Z. Xie, G. D. Stucky, Nonaqueous Production of Nanostructured Anatase with High-Energy Facets, *J. Am. Chem. Soc.* **2008**, *130*, 17563-17567.
- [107] R. Hengerer, L. Kavan, P. Krtil, M. Gratzel, Orientation dependence of charge-transfer processes on TiO₂ (anatase) single crystals, *J. Electrochem. Soc.* **2000**, *147*, 1467-1472.
- [108] S. Lunell, A. Stashans, L. Ojamae, H. Lindstrom, A. Hagfeldt, Li and Na Diffusion in TiO₂ from Quantum Chemical Theory versus Electrochemical Experiment, *J. Am. Chem. Soc.* **1997**, *119*, 7374-7380.
- [109] C. L. Olson, J. Nelson, M. S. Islam, Defect chemistry, surface structures, and lithium insertion in anatase TiO₂, *J. Phys. Chem. B* **2006**, *110*, 9995-10001.
- [110] J. S. Chen, L. A. Archer, X. Wen Lou, SnO₂ hollow structures and TiO₂ nanosheets for lithium-ion batteries, *J. Mater. Chem.* **2011**, *21*, 9912-9924.
- [111] A. Fujishima, K. Honda, Electrochemical photocatalysis of water at a semiconductor electrode, *Nature* **1972**, *238*, 37-38.
- [112] H. J. Snaith, L. Schmidt-Mende, Advances in liquid-electrolyte and solid-state dye-sensitized solar cells, *Adv. Mater.* **2007**, *19*, 3187-3200.
- [113] K. Yong Joo, L. Mi Hyeon, K. Hark Jin, L. Gooil, C. Young Sik, P. Nam-Gyu, K. Kyungkun, L. Wan In, Formation of Highly Efficient Dye-

Sensitized Solar Cells by Hierarchical Pore Generation with Nanoporous TiO₂ Spheres, *Adv. Mater.* **2009**, *21*, 3668-3673.

- [114] G. Nuspl, K. Yoshizawa, T. Yamabe, Lithium intercalation in TiO₂ modifications, *J. Mater. Chem.* **1997**, *7*, 2529-2536.
- [115] Y. Q. Dai, C. M. Cobley, J. Zeng, Y. M. Sun, Y. N. Xia, Synthesis of Anatase TiO₂ Nanocrystals with Exposed {001} Facets, *Nano Lett.* **2009**, *9*, 2455-2459.
- [116] X. Han, Q. Kuang, M. Jin, Z. Xie, L. Zheng, Synthesis of Titania Nanosheets with a High Percentage of Exposed (001) Facets and Related Photocatalytic Properties, *J. Am. Chem. Soc.* **2009**, *131*, 3152-3153.
- [117] B. H. Wu, C. Y. Guo, N. F. Zheng, Z. X. Xie, G. D. Stucky, Nonaqueous Production of Nanostructured Anatase with High-Energy Facets, *J. Am. Chem. Soc.* **2008**, *130*, 17563-17567.
- [118] D. Q. Zhang, G. S. Li, X. F. Yang, J. C. Yu, A micrometer-size TiO₂ single-crystal photocatalyst with remarkable 80% level of reactive facets, *Chem. Comm.* **2009**, 4381-4383.
- [119] K. F. Zmbov, J. L. Margrave, Mass spectrometric studies at high temperatures. XVI. Sublimation pressures for titanium(III)fluoride and the stabilities of TiF₂(g) and TiF(g), *J. Phys. Chem.* **1967**, *71*, 2893-2895.
- [120] G. Liu, H. G. Yang, X. Wang, L. Cheng, J. Pan, G. Q. Lu, H.-M. Cheng, Visible Light Responsive Nitrogen Doped Anatase TiO₂ Sheets with Dominant {001} Facets Derived from TiN, *J. Am. Chem. Soc.* **2009**, *131*, 12868-12869.
- [121] L. C. Zhang, Q. Zhou, Z. H. Liu, X. D. Hou, Y. B. Li, Y. Lv, Novel Mn₃O₄ Micro-octahedra: Promising Cataluminescence Sensing Material for Acetone, *Chem. Mater.* **2009**, *21*, 5066-5071.

- [122] Y. J. Kim, M. H. Lee, H. J. Kim, G. Lim, Y. S. Choi, N.-G. Park, K. Kim, W. I. Lee, Formation of Highly Efficient Dye-Sensitized Solar Cells by Hierarchical Pore Generation with Nanoporous TiO₂ Spheres, *Adv. Mater.* **2009**, *21*, 3668-3673.
- [123] B. Song, S. Liu, J. Jian, M. Lei, X. Wang, H. Li, J. Yu, X. Chen, Electrochemical properties of TiO₂ hollow microspheres from a template-free and green wet-chemical route, *J. Power Sources* **2008**, *180*, 869-874.
- [124] J. Xu, C. Jia, B. Cao, W. F. Zhang, Electrochemical properties of anatase TiO₂ nanotubes as an anode material for lithium-ion batteries, *Electrochim. Acta* **2007**, *52*, 8044-8047.
- [125] X. P. Gao, Y. Lan, H. Y. Zhu, J. W. Liu, Y. P. Ge, F. Wu, D. Y. Song, Electrochemical Performance of Anatase Nanotubes Converted from Protonated Titanate Hydrate Nanotubes, *Electrochem. Solid-state Lett.* **2005**, *8*, A26-A29.
- [126] J. C. Yu, Yu, Ho, Jiang, Zhang, Effects of F⁻ Doping on the Photocatalytic Activity and Microstructures of Nanocrystalline TiO₂ Powders, *Chem. Mater.* **2002**, *14*, 3808-3816.
- [127] B. Lim, M. J. Jiang, P. H. C. Camargo, E. C. Cho, J. Tao, X. M. Lu, Y. M. Zhu, Y. N. Xia, Pd-Pt Bimetallic Nanodendrites with High Activity for Oxygen Reduction, *Science* **2009**, *324*, 1302-1305.
- [128] N. Tian, Z. Y. Zhou, S. G. Sun, Y. Ding, Z. L. Wang, Synthesis of tetrahedral platinum nanocrystals with high-index facets and high electro-oxidation activity, *Science* **2007**, *316*, 732-735.
- [129] M. Schrunner, M. Ballauff, Y. Talmon, Y. Kauffmann, J. Thun, M. Moller, J. Breu, Single Nanocrystals of Platinum Prepared by Partial Dissolution of Au-Pt Nanoalloys, *Science* **2009**, *323*, 617-620.

- [130] L. H. Hu, Q. Peng, Y. D. Li, Selective Synthesis of Co_3O_4 Nanocrystal with Different Shape and Crystal Plane Effect on Catalytic Property for Methane Combustion, *J. Am. Chem. Soc.* **2008**, *130*, 16136-16137.
- [131] H. Lee, S. E. Habas, S. Kveskin, D. Butcher, G. A. Somorjai, P. D. Yang, Morphological control of catalytically active platinum nanocrystals, *Angew. Chem. Int. Ed.* **2006**, *45*, 7824-7828.
- [132] J. Zhu, S. H. Wang, Z. F. Bian, C. L. Cai, H. X. Li, A facile synthesis of hierarchical flower-like TiO_2 with enhanced photocatalytic activity, *Res. Chem. Intermediat.* **2009**, *35*, 769-777.
- [133] R. Schloegl, Energy - Fuel for thought, *Nat. Mater.* **2008**, *7*, 772-774.
- [134] H. G. Yang, H. C. Zeng, Creation of intestine-like interior space for metal-oxide nanostructures with a quasi-reverse emulsion, *Angew. Chem. Int. Ed.* **2004**, *43*, 5206-5209.
- [135] R. L. Penn, J. F. Banfield, Morphology development and crystal growth in nanocrystalline aggregates under hydrothermal conditions: Insights from titania, *Geochim. Cosmochim. Acta* **1999**, *63*, 1549-1557.
- [136] G. Liu, H. G. Yang, X. Wang, L. Cheng, J. Pan, G. Q. Lu, H.-M. Cheng, Visible Light Responsive Nitrogen Doped Anatase TiO_2 Sheets with Dominant {001} Facets Derived from TiN, *J. Am. Chem. Soc.* **2009**, *131*, 12868-12869.
- [137] M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki, R. Ryoo, Stable single-unit-cell nanosheets of zeolite MFI as active and long-lived catalysts, *Nature* **2009**, *461*, 246-U120.
- [138] A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon, W. Van Schalkwijk, Nanostructured materials for advanced energy conversion and storage devices, *Nat. Mater.* **2005**, *4*, 366-377.

- [139] B. Kang, G. Ceder, Battery materials for ultrafast charging and discharging, *Nature* **2009**, *458*, 190-193.
- [140] M. Kruk, M. Jaroniec, Gas adsorption characterization of ordered organic-inorganic nanocomposite materials, *Chem. Mater.* **2001**, *13*, 3169-3183.
- [141] A. R. Armstrong, G. Armstrong, J. Canales, R. Garcia, P. G. Bruce, Lithium-ion intercalation into TiO₂-B nanowires, *Adv. Mater.* **2005**, *17*, 862-865.
- [142] M. Wagemaker, A. P. M. Kentgens, F. M. Mulder, Equilibrium lithium transport between nanocrystalline phases in intercalated TiO₂ anatase, *Nature* **2002**, *418*, 397.
- [143] G. Armstrong, A. R. Armstrong, P. G. Bruce, P. Reale, B. Scrosati, TiO₂(B) nanowires as an improved anode material for lithium-ion batteries containing LiFePO₄ or LiNi_{0.5}Mn_{1.5}O₄ cathodes and a polymer electrolyte, *Adv. Mater.* **2006**, *18*, 2597-2600.
- [144] G. F. Ortiz, I. Hanzu, T. Djenizian, P. Lavela, J. L. Tirado, P. Knauth, Alternative Li-Ion Battery Electrode Based on Self-Organized Titania Nanotubes, *Chem. Mater.* **2009**, *21*, 63-67.
- [145] L. Kavan, M. Kalbac, M. Zukalova, I. Exnar, V. Lorenzen, R. Nesper, M. Graetzel, Lithium storage in nanostructured TiO₂ made by hydrothermal growth, *Chem. Mater.* **2004**, *16*, 477-485.
- [146] R. J. Cava, D. W. Murphy, S. Zahurak, A. Santoro, R. S. Roth, The crystal structures of the lithium-inserted metal oxides Li_{0.5}TiO₂ anatase, LiTi₂O₄ spinel, and Li₂Ti₂O₄, *J. Solid State Chem.* **1984**, *53*, 64-75.
- [147] T. Ohzuku, T. Kodama, T. Hirai, Electrochemistry of anatase titanium-dioxide in lithium nonaqueous cells, *J. Power Sources* **1985**, *14*, 153-166.

- [148] L. Kavan, M. Gratzel, J. Rathousky, A. Zukal, Nanocrystalline TiO₂ (anatase) electrodes: Surface morphology, adsorption, and electrochemical properties, *J. Electrochem. Soc.* **1996**, *143*, 394-400.
- [149] H. Lindstrom, S. Sodergren, A. Solbrand, H. Rensmo, J. Hjelm, A. Hagfeldt, S. E. Lindquist, Li⁺ ion insertion in TiO₂ (anatase) .2. Voltammetry on nanoporous films, *J. Phys. Chem. B* **1997**, *101*, 7717-7722.
- [150] J. S. Chen, X. W. Lou, Anatase TiO₂ nanosheet: An ideal host structure for fast and efficient lithium insertion/extraction, *Electrochem. Comm.* **2009**, *11*, 2332-2335.
- [151] G. Sudant, E. Baudrin, D. Larcher, J. M. Tarascon, Electrochemical lithium reactivity with nanotextured anatase-type TiO₂, *J. Mater. Chem.* **2005**, *15*, 1263-1269.
- [152] F. Caruso, R. A. Caruso, H. Mohwald, Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating, *Science* **1998**, *282*, 1111-1114.
- [153] Y. G. Sun, Y. N. Xia, Shape-controlled synthesis of gold and silver nanoparticles, *Science* **2002**, *298*, 2176-2179.
- [154] Y. D. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somorjai, A. P. Alivisatos, Formation of hollow nanocrystals through the nanoscale Kirkendall Effect, *Science* **2004**, *304*, 711-714.
- [155] X. W. Lou, Y. Wang, C. Yuan, J. Y. Lee, L. A. Archer, Template-free synthesis of SnO₂ hollow nanostructures with high lithium storage capacity, *Adv. Mater.* **2006**, *18*, 2325-2329.
- [156] B. X. Li, Y. Xie, M. Jing, G. X. Rong, Y. C. Tang, G. Z. Zhang, In₂O₃ hollow microspheres: Synthesis from designed in (OH)(3) precursors and applications in gas sensors and photocatalysis, *Langmuir* **2006**, *22*, 9380-9385.

- [157] H. P. Liang, H. M. Zhang, J. S. Hu, Y. G. Guo, L. J. Wan, C. L. Bai, Pt hollow nanospheres: Facile synthesis and enhanced electrocatalysts, *Angew. Chem. Int. Ed.* **2004**, *43*, 1540-1543.
- [158] Y. Piao, J. Kim, H. Bin Na, D. Kim, J. S. Baek, M. K. Ko, J. H. Lee, M. Shokouhimehr, T. Hyeon, Wrap-bake-peel process for nanostructural transformation from β -FeOOH nanorods to biocompatible iron oxide nanocapsules, *Nat. Mater.* **2008**, *7*, 242-247.
- [159] X. M. Sun, Y. D. Li, Ga₂O₃ and GaN semiconductor hollow spheres, *Angew. Chem. Int. Ed.* **2004**, *43*, 3827-3831.
- [160] Z. Z. Yang, Z. W. Niu, Y. F. Lu, Z. B. Hu, C. C. Han, Templated synthesis of inorganic hollow spheres with a tunable cavity size onto core-shell gel particles, *Angew. Chem. Int. Ed.* **2003**, *42*, 1943-1945.
- [161] J. Li, H. C. Zeng, Hollowing Sn-doped TiO₂ nanospheres via Ostwald ripening, *J. Am. Chem. Soc.* **2007**, *129*, 15839-15847.
- [162] J. G. Yu, H. T. Guo, S. A. Davis, S. Mann, Fabrication of hollow inorganic microspheres by chemically induced self-transformation, *Adv. Funct. Mater.* **2006**, *16*, 2035-2041.
- [163] P. Jiang, J. F. Bertone, V. L. Colvin, A lost-wax approach to monodisperse colloids and their crystals, *Science* **2001**, *291*, 453-457.
- [164] X. W. Lou, C. L. Yuan, L. A. Archer, Shell-by-shell synthesis of tin oxide hollow colloids with nanoarchitected walls: Cavity size tuning and functionalization, *Small* **2007**, *3*, 261-265.
- [165] X. W. Lou, C. L. Yuan, L. A. Archer, Double-walled SnO₂ nano-cocoons with movable magnetic cores, *Adv. Mater.* **2007**, *19*, 3328-3332.
- [166] Z. K. Zheng, B. B. Huang, X. Y. Qin, X. Y. Zhang, Y. Dai, M. H. Jiang, P. Wang, M. H. Whangbo, Highly Efficient Photocatalyst: TiO₂ Microspheres

Produced from TiO₂ Nanosheets with a High Percentage of Reactive {001} Facets, *Chem. Eur. J.* **2009**, *15*, 12576-12579.

- [167] P. M. Arnal, C. Weidenthaler, F. Schuth, Highly Monodisperse Zirconia-Coated Silica Spheres and Zirconia/Silica Hollow Spheres with Remarkable Textural Properties, *Chem. Mater.* **2006**, *18*, 2733-2739.
- [168] W. Stöber, A. Fink, E. Bohn, Controlled growth of monodisperse silica spheres in the micron size range, *J. Colloid Interf. Sci.* **1968**, *26*, 62-69.
- [169] D. H. Wang, D. W. Choi, J. Li, Z. G. Yang, Z. M. Nie, R. Kou, D. H. Hu, C. M. Wang, L. V. Saraf, J. G. Zhang, I. A. Aksay, J. Liu, Self-Assembled TiO₂-Graphene Hybrid Nanostructures for Enhanced Li-Ion Insertion, *ACS Nano* **2009**, *3*, 907-914.
- [170] C. H. Sun, X. H. Yang, J. S. Chen, Z. Li, X. W. Lou, C. Li, S. C. Smith, G. Q. Lu, H. G. Yang, Higher charge/discharge rates of lithium-ions across engineered TiO₂ surfaces leads to enhanced battery performance, *Chem. Comm.* **2010**, *46*, 6129-6131.
- [171] X. W. Lou, L. A. Archer, Z. C. Yang, Hollow Micro-/Nano-structures: Synthesis and Applications, *Adv. Mater.* **2008**, *20*, 3987-4019.
- [172] X. W. Lou, C. M. Li, L. A. Archer, Designed Synthesis of Coaxial SnO₂@carbon Hollow Nanospheres for highly reversible lithium storage, *Adv. Mater.* **2009**, *21*, 2536-2539.
- [173] J. B. Goodenough, Y. Kim, Challenges for Rechargeable Li Batteries†, *Chem. Mater.* **2009**, *22*, 587-603.
- [174] M. Winter, J. O. Besenhard, M. E. Spahr, P. Novak, Insertion electrode materials for rechargeable lithium batteries, *Adv. Mater.* **1998**, *10*, 725-763.

- [175] C. H. Jiang, I. Honma, T. Kudo, H. S. Zhou, Nanocrystalline rutile TiO₂ electrode for high-capacity and high-rate lithium storage, *Electrochem. Solid State Lett.* **2007**, *10*, A127-A129.
- [176] C. H. Sun, X. H. Yang, J. S. Chen, Z. Li, X. W. Lou, C. Z. Li, S. C. Smith, G. Q. Lu, H. G. Yang, Higher charge/discharge rates of lithium-ions across engineered TiO₂ surfaces leads to enhanced battery performance, *Chem. Comm.* **2010**, *46*, 6129-6131.
- [177] J. S. Chen, Y. L. Tan, C. M. Li, Y. L. Cheah, D. Luan, S. Madhavi, F. Y. C. Boey, L. A. Archer, X. W. Lou, Constructing Hierarchical Spheres from Large Ultrathin Anatase TiO₂ Nanosheets with Nearly 100% Exposed (001) Facets for Fast Reversible Lithium Storage, *J. Am. Chem. Soc.* **2010**, *132*, 6124-6130.
- [178] H. Liu, G. X. Wang, J. Z. Wang, D. Wexler, Magnetite/carbon core-shell nanorods as anode materials for lithium-ion batteries, *Electrochem. Comm.* **2008**, *10*, 1879-1882.
- [179] J. S. Zhou, H. H. Song, X. H. Chen, L. J. Zhi, S. Y. Yang, J. P. Huo, W. T. Yang, Carbon-Encapsulated Metal Oxide Hollow Nanoparticles and Metal Oxide Hollow Nanoparticles: A General Synthesis Strategy and Its Application to Lithium-Ion Batteries, *Chem. Mater.* **2009**, *21*, 2935-2940.
- [180] G. L. Cui, Y. S. Hu, L. J. Zhi, D. Q. Wu, I. Lieberwirth, J. Maier, K. Mullen, A one-step approach towards carbon-encapsulated hollow tin nanoparticles and their application in lithium batteries, *Small* **2007**, *3*, 2066-2069.
- [181] J. Fan, T. Wang, C. Z. Yu, B. Tu, Z. Y. Jiang, D. Y. Zhao, Ordered, nanostructured tin-based oxides/carbon composite as the negative-electrode material for lithium-ion batteries, *Adv. Mater.* **2004**, *16*, 1432-1436.
- [182] Y. Yu, L. Gu, C. L. Wang, A. Dhanabalan, P. A. van Aken, J. Maier, Encapsulation of Sn@carbon Nanoparticles in Bamboo-like Hollow Carbon

Nanofibers as an Anode Material in Lithium-Based Batteries, *Angew. Chem. Int. Ed.* **2009**, *48*, 6485-6489.

- [183] J. S. Chen, D. Luan, C. M. Li, F. Y. C. Boey, S. Qiao, X. W. Lou, TiO₂ and SnO₂@TiO₂ hollow spheres assembled from anatase TiO₂ nanosheets with enhanced lithium storage properties, *Chem. Comm.* **2010**, *46*, 8252-8254.
- [184] S. Ding, J. S. Chen, Z. Wang, Y. L. Cheah, S. Madhavi, X. Hu, X. W. Lou, TiO₂ hollow spheres with large amount of exposed (001) facets for fast reversible lithium storage, *J. Mater. Chem.* **2010**, *21*, 1677-1680.
- [185] M. Kruk, M. Jaroniec, Gas Adsorption Characterization of Ordered Organic-Inorganic Nanocomposite Materials, *Chem. Mater.* **2001**, *13*, 3169-3183.
- [186] J. Liu, J. S. Chen, X. Wei, X. W. Lou, X. W. Liu, Sandwich-like, stacked ultrathin titanate nanosheets for ultrafast lithium storage, *Adv. Mater.* **2010**, *23*, 998-1002.
- [187] A. K. Geim, K. S. Novoselov, The rise of graphene, *Nat. Mater.* **2007**, *6*, 183-191.
- [188] C. Rao, A. Sood, K. Subrahmanyam, A. Govindaraj, Graphene: The New Two-Dimensional Nanomaterial, *Angew. Chem. Int. Ed.* **2009**, *48*, 7752-7777.
- [189] H. Chen, M. B. Muller, K. J. Gilmore, G. G. Wallace, D. Li, Mechanically strong, electrically conductive, and biocompatible graphene paper, *Adv. Mater.* **2008**, *20*, 3557-3561.
- [190] D. Pan, J. Zhang, Z. Li, M. Wu, Hydrothermal Route for Cutting Graphene Sheets into Blue-Luminescent Graphene Quantum Dots, *Adv. Mater.* **2010**, *22*, 734-738.

- [191] Y. Y. Liang, H. L. Wang, H. S. Casalongue, Z. Chen, H. J. Dai, TiO₂ Nanocrystals Grown on Graphene as Advanced Photocatalytic Hybrid Materials, *Nano Res.* **2010**, 3, 701-705.
- [192] C. X. Guo, H. B. Yang, Z. M. Sheng, Z. S. Lu, Q. L. Song, C. M. Li, Layered Graphene/Quantum Dots for Photovoltaic Devices, *Angew. Chem. Int. Ed.* **2010**, 49, 3014-3017.
- [193] Z. Liu, J. T. Robinson, X. Sun, H. Dai, PEGylated Nanographene Oxide for Delivery of Water-Insoluble Cancer Drugs, *J. Am. Chem. Soc.* **2008**, 130, 10876-10877.
- [194] X. C. Dong, Y. M. Shi, W. Huang, P. Chen, L. J. Li, Electrical Detection of DNA Hybridization with Single-Base Specificity Using Transistors Based on CVD-Grown Graphene Sheets, *Adv. Mater.* **2010**, 22, 1649-1653.
- [195] M. Pumera, Graphene-based nanomaterials for energy storage, *Energy Environ. Sci.* **2011**, 4, 668-674.
- [196] G. Liu, L. Wang, H. G. Yang, H.-M. Cheng, G. Q. Lu, Titania-based photocatalysts-crystal growth, doping and heterostructuring, *J. Mater. Chem.* **2010**, 20, 831-843.
- [197] S. L. Chou, J. Z. Wang, M. Choucair, H. K. Liu, J. A. Stride, S. X. Dou, Enhanced reversible lithium storage in a nanosize silicon/graphene composite, *Electrochem. Comm.* **2010**, 12, 303-306.
- [198] J. K. Lee, K. B. Smith, C. M. Hayner, H. H. Kung, Silicon nanoparticles-graphene paper composites for Li ion battery anodes, *Chem. Comm.* **2010**, 46, 2025-2027.
- [199] S. M. Paek, E. Yoo, I. Honma, Enhanced Cyclic Performance and Lithium Storage Capacity of SnO₂/Graphene Nanoporous Electrodes with Three-Dimensionally Delaminated Flexible Structure, *Nano Lett.* **2009**, 9, 72-75.

- [200] L. Shen, C. Yuan, H. Luo, X. Zhang, S. Yang, X. Lu, In situ synthesis of high-loading $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -graphene hybrid nanostructures for high rate lithium ion batteries, *Nanoscale* **2011**, 3, 572-574.
- [201] M. Liu, L. Y. Piao, L. Zhao, S. T. Ju, Z. J. Yan, T. He, C. L. Zhou, W. J. Wang, Anatase TiO_2 single crystals with exposed {001} and {110} facets: facile synthesis and enhanced photocatalysis, *Chem. Comm.* **2010**, 46, 1664-1666.
- [202] J. Z. Wang, C. Zhong, S. L. Chou, H. K. Liu, Flexible free-standing graphene-silicon composite film for lithium-ion batteries, *Electrochem. Comm.* **2010**, 12, 1467-1470.
- [203] Z. S. Wu, W. C. Ren, L. Wen, L. B. Gao, J. P. Zhao, Z. P. Chen, G. M. Zhou, F. Li, H. M. Cheng, Graphene Anchored with Co_3O_4 Nanoparticles as Anode of Lithium Ion Batteries with Enhanced Reversible Capacity and Cyclic Performance, *ACS Nano* **2010**, 4, 3187-3194.
- [204] S. Yang, X. Feng, S. Ivanovici, K. Müllen, Fabrication of Graphene-Encapsulated Oxide Nanoparticles: Towards High-Performance Anode Materials for Lithium Storage, *Angew. Chem. Int. Ed.* **2010**, 49, 8408-8411.
- [205] J. Yao, X. P. Shen, B. Wang, H. K. Liu, G. X. Wang, In situ chemical synthesis of SnO_2 -graphene nanocomposite as anode materials for lithium-ion batteries, *Electrochem. Comm.* **2009**, 11, 1849-1852.
- [206] Z. Y. Wang, H. Zhang, N. Li, Z. J. Shi, Z. N. Gu, G. P. Cao, Laterally Confined Graphene Nanosheets and Graphene/ SnO_2 Composites as High-Rate Anode Materials for Lithium-Ion Batteries, *Nano Res.* **2010**, 3, 748-756.
- [207] G. Zhou, D.-W. Wang, F. Li, L. Zhang, N. Li, Z.-S. Wu, L. Wen, G. Q. Lu, H.-M. Cheng, Graphene-Wrapped Fe_3O_4 Anode Material with Improved

- Reversible Capacity and Cyclic Stability for Lithium Ion Batteries, *Chem. Mater.* **2010**, 22, 5306-5313.
- [208] J. Zhu, T. Zhu, X. Zhou, Y. Zhang, X. W. Lou, X. Chen, H. Zhang, H. H. Hng, Q. Yan, Facile synthesis of metal oxide/reduced graphene oxide hybrids with high lithium storage capacity and stable cyclability, *Nanoscale* **2011**, 3, 1084-1089.
- [209] B. S. Kong, J. X. Geng, H. T. Jung, Layer-by-layer assembly of graphene and gold nanoparticles by vacuum filtration and spontaneous reduction of gold ions, *Chem. Comm.* **2009**, 2174-2176.
- [210] H. Chang, Z. Sun, K. Y.-F. Ho, X. Tao, F. Yan, W.-M. Kwok, Z. Zheng, A highly sensitive ultraviolet sensor based on a facile in situ solution-grown ZnO nanorod/graphene heterostructure, *Nanoscale* **2011**, 3, 258-264.
- [211] S. Ansari, A. Kellarakis, L. Estevez, E. P. Giannelis, Oriented Arrays of Graphene in a Polymer Matrix by in situ Reduction of Graphite Oxide Nanosheets, *Small* **2010**, 6, 205-209.
- [212] Y. Qiu, K. Yan, S. Yang, L. Jin, H. Deng, W. Li, Synthesis of Size-Tunable Anatase TiO₂ Nanospindles and Their Assembly into Anatase@Titanium Oxynitride/Titanium Nitride-Graphene Nanocomposites for Rechargeable Lithium Ion Batteries with High Cycling Performance, *ACS Nano* **2010**, 4, 6515-6526.
- [213] S. Ding, J. S. Chen, G. Qi, X. Duan, Z. Wang, E. P. Giannelis, L. A. Archer, X. W. Lou, Formation of SnO₂ Hollow Nanospheres inside Mesoporous Silica Nanoreactors, *J. Am. Chem. Soc.* **2011**, 133, 21-23.
- [214] J. S. Chen, C. M. Li, W. W. Zhou, Q. Y. Yan, L. A. Archer, X. W. Lou, One-pot formation of SnO₂ hollow nanospheres and α -Fe₂O₃@SnO₂ nanorattles with large void space and their lithium storage properties, *Nanoscale* **2009**, 1, 280-285.

- [215] W. S. Hummers, R. E. Offeman, Preparation of graphitic oxide, *J. Am. Chem. Soc.* **1958**, 80, 1339-1339.

Complete List of Publications

1. **J. S. Chen**, T. Zhu, C. M. Li, X. W. Lou,* Building Hematite Nanostructures by Oriented Attachment, *Angew. Chem. Int. Ed.*, (as VIP), 50, 650 – 653 (2011).
2. **J. S. Chen**, Y. L. Tan, C. M. Li, Y. L. Cheah, D. Luan, S. Madhavi, F. Y. C. Boey, L. A. Archer,* X. W. Lou,* Constructing Hierarchical Spheres from Large Ultrathin Anatase TiO₂ Nanosheets with Nearly 100% Exposed (001) Facets for Fast Reversible Lithium Storage, *J. Am. Chem. Soc.*, 132, 6124 – 6130 (2010). (cited 75 times)
3. **J. S. Chen**, T. Zhu, X. H. Yang, H. G. Yang, X. W. Lou,* Top-down Fabrication of α -Fe₂O₃ Single-crystal Nanodiscs and Polycrystal Microstructures with Controlled Porosity for Enhanced Lithium Storage Capabilities, *J. Am. Chem. Soc.*, 132, 13162 – 13164 (2010).
4. B. Wang†, **J. S. Chen**†, H. B. Wu, Z. Y. Wang, X. W. Lou*, Quasiemulsion Templated Formation of α -Fe₂O₃ Hollow Spheres with Enhanced Lithium Storage Properties, *J. Am. Chem. Soc.*, 133, 17146 – 17148 (2011). (†Co-first author)
5. S. J. Ding†, **J. S. Chen**†, G. G. Qi, X. N. Duan, Z. Y. Wang, E. P. Giannelis, L. A. Archer,* X. W. Lou,* Formation of SnO₂ Hollow Spheres Inside Silica Nanoreactors, *J. Am. Chem. Soc.*, 133, 21 – 23 (2011). (†Co-first author)
6. S. J. Ding†, **J. S. Chen**†, X. W. Lou,* One Dimensional Hierarchical Structures Composed of Metal Oxide Nanosheets on CNT Backbone and Their Lithium Storage Properties, *Adv. Funct. Mater.*, 21, 4120 – 4125 (2011). (†Co-first author)
7. **J. S. Chen**, and X. W. Lou*, Unusual Rutile TiO₂ Nanosheets with Exposed (001) Facets, *Chem. Sci.*, 2, 2219 – 2223 (2011).

8. **J. S. Chen**, J. Liu, S. Z. Qiao, R. Xu* and X. W. Lou*, Formation of Large 2D Nanosheets via PVP-assisted Assembly of Anatase TiO₂ Nanomosaics, *Chem. Comm.*, 47, 10443 – 10445 (2011).
9. **J. S. Chen**, Y. M. Zhang, X. W. Lou,* One-pot Synthesis of Uniform Fe₃O₄@C Nanospheres with Carbon Matrix Support for Improved Lithium Storage Capabilities, *ACS Appl. Mater. Interfaces*, 3, 3276 – 3279 (2011).
10. **J. S. Chen**, Z. Y. Wang, X. C. Dong, P. Chen, X. W. Lou,* Graphene-wrapped TiO₂ Hollow Structures with Enhanced Lithium Storage Capabilities, *Nanoscale*, 3, 2158 – 2161 (2011).
11. **J. S. Chen**, H. Liu, S. Z. Qiao, X. W. Lou,* Carbon-supported Ultra-thin Anatase TiO₂ Nanosheets for Fast Reversible Lithium Storage, *J. Mater. Chem.*, 21, 5687 – 5692 (2011).
12. **J. S. Chen**, L. A. Archer,* X. W. Lou,* SnO₂ Hollow Structures and TiO₂ Nanosheets for Lithium-ion Batteries, *J. Mater. Chem.*, invited Feature Article, 21, 9912 – 9924 (2011).
13. **J. S. Chen**, C. P. Chen, J. Liu, R. Xu, S. Z. Qiao,* X. W. Lou,* Ellipsoidal Hollow Nanostructures Assembled from Anatase TiO₂ Nanosheets as Magnetically Separable Photocatalyst, *Chem. Comm.*, 47, 2631 – 2633 (2011).
14. **J. S. Chen**, D. Y. Luan, C. M. Li, F. Y. C. Boey, S. Z. Qiao,* X. W. Lou,* TiO₂ and SnO₂@TiO₂ Hollow Spheres Assembled from Anatase TiO₂ Nanosheets with Enhanced Lithium Storage Properties, *Chem. Comm.*, 46, 8252 – 8254 (2010).
15. **J. S. Chen**, Y. L. Cheah, S. Madhavi, X. W. Lou,* Fast Synthesis of α -MoO₃ Nanorods with Controlled Aspect Ratios and Their Lithium Storage Capabilities, *J. Phys. Chem. C*, 114, 8675 – 8678 (2010).
16. **J. S. Chen**, X. W. Lou,* The Superior Lithium Storage Capabilities of Ultra-fine Rutile TiO₂ Nanoparticles, *J. Power Sources*, 195, 2905 – 2908 (2010).

17. **J. S. Chen**, X. W. Lou,* Anatase TiO₂ Nanosheet: An Ideal Host Structure for Fast and Efficient Lithium Insertion/extraction, *Electrochem. Comm.*, 11, 2332 – 2335 (2009).
18. **J. S. Chen**, Y. L. Cheah, Y. T. Chen, N. Jayaprakash, S. Madhavi, Y. H. Yang, X. W. Lou,* SnO₂ Nanoparticles with Controlled Carbon Nanocoating as High-capacity Anode Materials for Lithium-ion Batteries, *J. Phys. Chem. C*, 113, 20504 – 20508 (2009).
19. **J. S. Chen**, C. M. Li, W. W. Zhou, Q. Y. Yan, L. A. Archer, X. W. Lou,* One-pot Formation of Hollow Nanospheres and Nanorattles with Large Void Space and Their Lithium Storage Properties, *Nanoscale*, 1, 280 – 285 (2009).
20. **J. S. Chen**, T. Zhu, Q. H. Hu, J. J. Gao, F. B. Su, S. Z. Qiao,* X. W. Lou,* Shape-controlled Synthesis of Co₃O₄ Nanostructures and Their Comparative Lithium Storage Properties, *ACS Appl. Mater. & Interfaces*, 2, 3628 – 3635 (2010).
21. W. Xiao†, **J. S. Chen**†, X. W. Lou,* Formation of Mn₃O₄-MnO₂ Heterostructures via Oriented Growth, *CrystEngComm*, 13, 5685 – 5687 (2011). (†Co-first author)
22. S. Ding†, **J. S. Chen**†, D. Y. Luan, F. Y. C. Boey, S. Madhavi, X. W. Lou,* Graphene Supported TiO₂ Nanosheets for Fast Lithium Storage, *Chem. Comm.*, 47, 5780 – 5782 (2011). (†Co-first author)
23. J. Liu, **J. S. Chen**, X. Wei, X. W. Lou,* X. W. Liu,* Sandwich-like, Stacked Ultrathin Titanate Nanosheets for Ultrafast Lithium Storage, *Adv. Mater.*, 23, 998 – 1002 (2011).
24. S. L. Xiong, **J. S. Chen**, X. W. Lou, H. C. Zeng,* Mesoporous Co₃O₄ and CoO@C Transformed from Chrysanthemum-like Co(CO₃)_{0.5}(OH)·0.11H₂O and Their Lithium-Ion Battery Application, *Adv. Funct. Mater.*, accepted (2012).

25. S. J. Ding, D. Y. Zhang, **J. S. Chen**, X. W. Lou,* Facile Synthesis of Hierarchical MoS₂ Microspheres Composed of Few-layered Nanosheets and Their Lithium Storage Properties, *Nanoscale*, DOI: 10.1039/C1NR11552A (2012).
26. H. B. Wu, **J. S. Chen**, X. W. Lou,* H. H. Hng, Asymmetric TiO₂ Nanocrystals with Exposed High-index Facets and Their Excellent Lithium Storage Properties, *Nanoscale*, 2, 4082 – 4084 (2011).
27. S. J. Ding, **J. S. Chen**, X. W. Lou,* Growth of MoS₂ Nanosheets on CNTs for Lithium Storage, *Chem. Euro. J.*, 17, 13142 – 13145 (2011).
28. S. J. Ding, **J. S. Chen**, X. W. Lou,* Sandwich-structured CNT@SnO₂@carbon Coaxial Nanocables for Lithium Storage, *Chem. Asian J.*, 6, 2278 – 2281 (2011).
29. T. Zhu, **J. S. Chen**, X. W. Lou,* Fe₃O₄@carbon Nanorods for Lithium Storage, *J. Phys. Chem. C*, 115, 9814 - 9820 (2011).
30. S. J. Ding, **J. S. Chen**, Z. Y. Wang, Y. L. Cheah, S. Madhavi, X. Hu, X. W. Lou,* TiO₂ Hollow spheres with Large Amount of Exposed (001) Facets for Fast Reversible Lithium Storage, *J. Mater. Chem.*, 21, 1677 – 1680 (2011).
31. W. Xiao, **J. S. Chen**, Q. Lu, X. W. Lou,* Porous Spheres Assembled from Polythiophene (PTh)-coated Ultrathin MnO₂ Nanosheets with Enhanced Lithium Storage Capabilities, *J. Phys. Chem. C*, 114, 12048 – 12051 (2010).
32. T. Zhu, **J. S. Chen**, X. W. Lou,* Shape-controlled Synthesis of Porous Co₃O₄ Nanostructures for Application in Supercapacitors, *J. Mater. Chem.*, 20, 7015 – 7020 (2010).
33. W. Xiao, **J. S. Chen**, C. M. Li, R. Xu, X. W. Lou,* Synthesis, Characterization and Lithium Storage Capability of AMoO₄ (A=Ni, Co) Nanorods, *Chem. Mater.*, 22, 746 – 754 (2009).

34. X. W. Lou,* **J. S. Chen**, P. Chen, L. A. Archer,* One-pot Synthesis of Carbon-coated SnO₂ Nano-colloids with Improved Reversible Lithium Storage Properties, *Chem. Mater.*, 21, 2868 – 2874 (2009).
35. T. Zhu, Z. Y. Wang, S. J. Ding, **J. S. Chen**,* X. W. Lou,* Hierarchical Nickel Sulfide Hollow Spheres for Supercapacitors, *RSC Adv.*, 1, 397 – 400 (2011).
36. J. Liu, S. Z. Qiao,* **J. S. Chen**, X. W. Lou,* X. R. Xing, G. Q. Lu,* Yolk/shell Nanoparticles: New Svenues for Developing Nanoreactors, Delivery Vehicles and Lithium-ion Batteries, *Chem. Comm.*, DOI: 10.1039/c1cc13658e (2011).
37. S. Ding, D. Y. Luan, F. Y. C. Boey, **J. S. Chen**,* and X. W. Lou*, SnO₂ Nanosheets Grown on Graphene Sheets with Enhanced Lithium Storage Properties, *Chem. Comm.*, 47, 7155 – 7157 (2011).
38. Y. Hu,* X. T. Zheng, **J. S. Chen**, M. Zhou, C. M. Li, X. W. Lou,* Silica-based Complex Nanorattles as Multifunctional Carrier for Anticancer Drug, *J. Mater. Chem.*, 21, 8052 – 8056 (2011).
39. S. J. Ding, T. Zhu, **J. S. Chen**, Z. Y. Wang, C. Yuan,* X. W. Lou,* Synthesis of Hierarchical NiO Nanosheet Hollow Spheres and Their Supercapacitive Properties, *J. Mater. Chem.*, 21, 6602 – 6606 (2011).
40. F. B. Su,* C. K. Poh, **J. S. Chen**, G. Xu, D. Wang, Q. Li, J. Y. Lin, X. W. Lou,* N-containing Microporous Carbon Nanospheres with Improved Capacitive Properties, *Energy Environ. Sci.*, 4, 717 – 724 (2011).
41. J. X. Zhu, T. Sun, **J. S. Chen**, W. Shi, X. J. Zhang, X. W. Lou, H. H. Hng, F. Boey, J. Ma, Q. Y. Yan,* Controlled Synthesis of Sb Nanostructures and Their Conversion to CoSb₃ Nanoparticle Chains for Li Ion Battery Electrodes, *Chem. Mater.*, 22, 5333 – 5339 (2010).