Nanostructured Thin Film Synthesis by Aerosol Chemical Vapor Deposition for Energy Storage Applications

Tandeep Singh Chadha
Washington University in St. Louis

Follow this and additional works at: https://openscholarship.wustl.edu/eng_etds

Part of the Chemical Engineering Commons, Environmental Engineering Commons, and the Oil, Gas, and Energy Commons

Recommended Citation
https://openscholarship.wustl.edu/eng_etds/185

This Dissertation is brought to you for free and open access by the Engineering and Applied Science at Washington University Open Scholarship. It has been accepted for inclusion in Engineering and Applied Science Theses & Dissertations by an authorized administrator of Washington University Open Scholarship. For more information, please contact digital@wumail.wustl.edu.
Nanostructured Thin Film Synthesis by Aerosol Chemical Vapor Deposition for Energy Storage Applications

By

Tandeep S. Chadha

A dissertation presented to the Graduate School of Washington University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

August 2016
St. Louis, Missouri
# Table of Contents

List of Figures ...................................................................................................................... vii  
List of Tables ......................................................................................................................... xiii 
Acknowledgments ................................................................................................................ xiv  
Abstract of the Dissertation .................................................................................................. xviii  

## Chapter 1 Introduction ..................................................................................................... 1  
1.1 Background and Motivation .......................................................................................... 2  
1.2 Solar to Fuel Conversion ............................................................................................... 6  
1.3 Metal-ion Batteries ........................................................................................................ 8  
  1.3.1 Alternative anode materials for lithium-ion batteries ............................................. 11  
  1.3.2 Beyond lithium-ion batteries .................................................................................. 12  
  1.3.3 Nanostructured materials as anodes ...................................................................... 14  
  1.3.4 Fabrication of battery electrodes and limitations .................................................... 16  
1.4 Synthesis of nanostructured thin films ......................................................................... 17  
1.5 Objectives ..................................................................................................................... 20  
1.6 Outline of the dissertation ........................................................................................... 21  
1.7 References ..................................................................................................................... 24  

## Chapter 2 Model based Prediction of Nanostructured Thin Film Morphology in an Aerosol Chemical Vapor Deposition Process ........................................................................ 34  
2.1 Abstract ....................................................................................................................... 35  
2.2 Introduction .................................................................................................................. 36  
2.3 Methods ....................................................................................................................... 39  
  2.3.1 Experimental process description .......................................................................... 39  
  2.3.2 Simulation of temperature and fluid flow ............................................................... 41  
  2.3.3 Implementation of aerosol dynamics .................................................................... 42  
  2.3.4 Experimental validation: ....................................................................................... 48  
2.4 Results and Discussion ............................................................................................... 49  
  2.4.1 CFD results for the reaction zone ......................................................................... 49  
  2.4.2 Simulation results for data in literature: ................................................................. 50
2.4.3 The influence of process parameters on particle size distribution and morphology 53
2.5 Conclusions: ........................................................................................................... 61
2.6 Acknowledgments: ............................................................................................... 62
2.7 References ............................................................................................................. 63

Chapter 3 Gold Nanocage Coupled Single Crystal TiO$_2$ Nanostructures for Near-Infrared Water Photolysis ......................................................... 68
  3.1 Abstract: ............................................................................................................... 69
  3.2 Introduction .......................................................................................................... 70
  3.3 Experimental Methods: ...................................................................................... 72
  3.4 Results and Discussion ....................................................................................... 74
  3.5 Conclusions ......................................................................................................... 83
  3.6 Acknowledgements ............................................................................................. 83
  3.7 References .......................................................................................................... 84

Chapter 4 One-Step Aerosol Route Synthesis of Oriented One-Dimensional Additive-Free Single Crystal TiO$_2$ Nanostructured Anodes for High Rate Lithium Ion Batteries .......... 90
  4.1 Abstract ............................................................................................................... 91
  4.2 Introduction .......................................................................................................... 92
  4.3 Experimental Methods: ...................................................................................... 94
    4.3.1 Thin film synthesis and electrode preparation .............................................. 94
    4.3.2 Structure and morphology characterization ................................................. 95
    4.3.3 Electrochemical measurements ................................................................... 95
  4.4 Results and Discussion ....................................................................................... 96
  4.5 Conclusions: ........................................................................................................ 102
  4.6 Acknowledgements ............................................................................................. 103
  4.7 References: ......................................................................................................... 104
  4.8 Supplementary Information .............................................................................. 109

Chapter 5 Model based analysis of one-dimensional oriented lithium ion battery electrodes ........................................................................................................... 113
  5.1 Abstract ............................................................................................................... 114
  5.2 Introduction .......................................................................................................... 115
  5.3 Model description ............................................................................................... 117
  5.4 Experimental Methods: .................................................................................... 122
5.4.1 1D Nanostructure synthesis, and cell fabrication ........................................... 122
5.4.2 Electrochemical Testing ..................................................................................... 122
5.4.3 Structural Characterization .............................................................................. 123
5.5 Results and Discussion: ...................................................................................... 123
  5.5.1 Experimental Results....................................................................................... 123
  5.5.2 Model input and validation: ............................................................................ 126
  5.5.3 Understanding the role of transport parameters ............................................ 128
  5.5.4 Prediction of optimal electrode structures .................................................... 129
5.6 Conclusions .......................................................................................................... 132
5.7 List of symbols .................................................................................................... 133
5.8 Acknowledgments ............................................................................................... 134
5.9 References ........................................................................................................... 134

Chapter 6 Additive-free Anatase Dendrites as Ultra-stable Anodes for Sodium-ion Batteries
........................................................................................................................................... 138
  6.1 Abstract ................................................................................................................ 139
  6.2 Introduction ........................................................................................................... 140
  6.3 Experimental Section .......................................................................................... 141
    6.3.1 Nanostructured TiO$_2$ thin films synthesis: ............................................... 141
    6.3.2 Material Characterization: ........................................................................... 142
    6.3.3 Electrochemical Cell Fabrication and Measurements: ............................... 142
    6.3.4 Ex-situ analysis ............................................................................................. 143
  6.4 Results and Discussion ....................................................................................... 144
    6.4.1 Structural Characterization: ........................................................................ 144
    6.4.2 Electrochemical Performance: .................................................................... 146
    6.4.3 In-situ Potentiostatic Electrochemical Impedance Spectroscopy: ............... 148
    6.4.4 Ex-situ analyses: ......................................................................................... 151
  6.5 Conclusions ......................................................................................................... 159
  6.6 Acknowledgments ............................................................................................... 160
  6.7 References ........................................................................................................... 160
  6.8 Supplementary Information ................................................................................ 165
    6.8.1 Material Characterization: ........................................................................... 165
6.8.2 Electrochemical Performance and HR-TEM analysis: ........................................ 165
6.8.3 1000 Cycles Extended Performance: ................................................................. 166
6.8.4 FEG-SEM Analysis (with EDS Line Scan on 1000th Cycle): .......................... 167
6.8.5 Diffusion Co-efficient Calculation: .................................................................. 167
6.8.6 Elemental Analysis (STEM-EDS): ................................................................. 168
6.8.7 Ex-situ HR-TEM analysis ............................................................................. 169
6.8.8 Supplementary References: ......................................................................... 170

Chapter 7 Single Step Synthesis of Nb doped TiO₂ nanostructured electrodes as high capacity
anodes for sodium ion batteries ............................................................................. 171

7.1 Abstract .................................................................................................................. 172
7.2 Introduction ............................................................................................................ 173
7.3 Experimental Methods: ....................................................................................... 174
  7.3.1 Synthesis of Nb doped TiO₂ using the ACVD process ................................. 174
  7.3.2 Nanostructure characterization ...................................................................... 175
  7.3.3 Electrochemical measurements .................................................................... 176
7.4 Results and Discussion: ....................................................................................... 176
7.5 Conclusions: ......................................................................................................... 185
7.6 Acknowledgments ............................................................................................... 185
7.7 References ............................................................................................................ 186

Chapter 8 Conclusions and Future Directions ............................................................ 189

8.1 Conclusions .......................................................................................................... 190
8.2 Future Directions .................................................................................................. 192
8.3 References ............................................................................................................ 195

Appendix A Design and operation of the multicomponent Aerosol Chemical Vapor
Deposition (ACVD) Reactor ..................................................................................... 196

A.1 Process Design ..................................................................................................... 197
  A.1.1 The precursor delivery system ...................................................................... 197
  A.1.2 The Reactor ..................................................................................................... 198
  A.1.3 The Control System ...................................................................................... 200
A.2 Standard Operating Procedure .......................................................................... 213
  A.2.1 Scope and Applicability ............................................................................... 213
A.2.2 Summary of the Method ........................................................................................................ 213
A.2.3 Definitions ............................................................................................................................. 213
A.2.4 Health and Safety Warnings ............................................................................................... 214
A.2.5 Equipment and Supplies ....................................................................................................... 214
A.2.6 Apparatus and Materials ...................................................................................................... 215
A.2.7 Procedures ............................................................................................................................ 217

Appendix B COMSOL model setup for simulating fluid dynamics and heat transfer in the
ACVD Reactor ................................................................................................................................ 220
B.1 Global Definitions ..................................................................................................................... 221
  B.1.1 Parameters ........................................................................................................................... 221
B.2 Model 1 (mod1) ....................................................................................................................... 222
  B.2.1 Geometry 1 .......................................................................................................................... 222
B.3 Materials ...................................................................................................................................... 223
  B.3.1 Air ........................................................................................................................................ 223
  B.3.2 Steel AISI 4340 .................................................................................................................. 224
  B.3.3 Silica glass .......................................................................................................................... 225
B.4 Heat Transfer (ht) ..................................................................................................................... 226
B.5 Laminar Flow (spf) .................................................................................................................... 227
B.6 Transport of Diluted Species (chds) ....................................................................................... 228
B.7 Mesh 1 ....................................................................................................................................... 229
B.8 Study1 ....................................................................................................................................... 229
  B.8.1 Stationary ............................................................................................................................ 229

Curriculum Vitae .............................................................................................................................. 230
List of Figures

Figure 1-1: Global energy consumption by fuel source from 2000 to 2014. Growth rates indicated for the 2010–2014 period. Figure reprinted by the permission of Nature publishing group from Jackson et al. [5], copyright 2015. .........................3

Figure 1-2: Possible strategies for addressing the challenge of energy storage ........................................5

Figure 1-3: Schematic of a photoelectrochemical cell with an n-type semiconductor as the photoanode and (b) solar radiation spectrum from the sun to earth's sea level (figure reproduced from Wikipedia article “Sunlight” [23], released under the Creative Commons Attribution-Share-Alike License 3.0). .............................6

Figure 1-4: Ragone Plot for various electrochemical storage technologies (figure adapted from Scrosati et. al. [26]). .........................................................................................8

Figure 1-5: Schematic of charging and discharging process in a lithium-ion battery using lithium cobalt oxide as the cathode and graphite as the anode. ......................................................10

Figure 1-6: Abundance of elements in the earth's crust (figure reproduced from Wikipedia article “Abundance of elements in Earth's crust” [43], released under the Creative Commons Attribution-Share-Alike License 3.0). .................................13

Figure 1-7: Schematic of electron transfer pathways and fate of nanostructures upon cycling in different electrode architectures. ...............................................................15

Figure 1-8: Schematic of the current battery fabrication process. Figure reproduced by the permission of Fraunhofer IKTS from Wolter et. al. [62], copyright 2013). .............16

Figure 1-9: Schematic of the ACVD process for the synthesis of nanostructured thin films (figure reprinted by the permission of The American Chemical Society from An. et. al. [78], copyright 2010). .................................................................19

Figure 2-1: Graphical abstract for the work presented in Chapter 2..........................................................35

Figure 2-2: Schematic of the (a) ACVD process and (b) 2D axisymmetric setup of the ACVD reactor for the finite element modelling .................................................................40

Figure 2-3: Overview of aerosol dynamics simulated by the discrete sectional model, the Brownian dynamics model and the sintering model to predict film morphology synthesized by the ACVD process .................................................................44

Figure 2-4: (a) Temperature, (b) velocity profile, (c) velocity streamlines depicting flow pattern in the ACVD reactor, and (d) velocity and temperature profile above the center of the substrate obtained from the finite element simulation ............50
Figure 2-5: (a) Simulated and (b) experimentally measured particle size distribution corresponding to the three different morphologies. Results reported are obtained from simulation and experiments performed at operating conditions described by An et. al [1] ........................................................................................................52

Figure 2-6: Effect of substrate temperature on (a) the particle size distribution (b) the time averaged temperature and (c) characteristic time ratio. The dotted lines indicate the value of the characteristic time ratio (\(\tau_{arr}/\tau_{sin}\)) for different morphologies observed experimentally by An et. al. [1] (d) SEM images depicting the morphology of the thin films synthesized at various temperatures..............................................................................................55

Figure 2-7: Effect of feeder-substrate distance on (a) the particle size distribution (b) the time averaged temperature and (c) characteristic time ratio........................................57

Figure 2-8: Effect of total inflow flow rate on (a) the particle size distribution, (b) the time averaged temperature, and (c) the characteristic time ratio with the SEM images for the corresponding experimental measurements............................................58

Figure 2-9: Effect of precursor concentration in the inlet flow on (a) the particle size distribution and (b) the characteristic time ratio.........................................................59

Figure 2-10: Effect of precursor inlet temperature on (a) the particle size distribution (b) the time averaged temperature and (c) the characteristic time ratio ......................61

Figure 3-1: Graphical abstract of the work presented in Chapter 3..........................................................69

Figure 3-2: (a) Cross section SEM image and (b) XRD spectra of the columnar TiO\(_2\) thin films synthesized by the ACVD process. ..................................................................................74

Figure 3-3: TEM image of the (a) SS Au-TiO\(_2\) (b) LS Au-TiO\(_2\) (c) NC Au-TiO\(_2\) nanocomposite films. Inset shows the TEM image of the Au nanoparticles prior to deposition............................................................75

Figure 3-4: UV-Vis absorption spectra of the different gold nanoparticles in solution. ........75

Figure 3-5: (a) Absolute UV-Vis absorption spectra of the Au-TiO\(_2\) nanocomposite films; Inset shows the Tauc plot for the pristine TiO\(_2\) film and (b) UV-Vis absorption spectra of the Au-TiO\(_2\) nanocomposite films relative to the pristine TiO\(_2\) thin films. ........................................................................................................76

Figure 3-6: (a) Photocurrent density versus voltage and (b) corresponding squared photocurrent density versus voltage curves of the Au-TiO\(_2\) nanocomposite films under broad wavelength illumination (\(\lambda > 250\) nm) (c) Photocurrent density versus voltage of the Au-TiO\(_2\) nanocomposite films under visible light illumination (\(\lambda > 400\) nm)....................................................................................78

Figure 3-7: Photocurrent action spectra (IPCE) of the Au-TiO\(_2\) nanocomposite films.............80
Figure 3-8: (a) Mechanism of hot electron injection from Au nanoparticle into the TiO$_2$ column and (b) schematic of plasmon wave around Au nanoparticles of different size and shape. .................................................................81

Figure 4-1: Graphical abstract for the work presented in Chapter 4 .................................................................91

Figure 4-2: (a) Overview of the nanostructure fabrication by the ACVD process. TiO$_2$ nanostructures are synthesized directly on the stainless steel current collector and are assembled as anodes in a lithium ion battery. SEM images of the (b) columnar and (d) granular nanostructures. (c) XRD spectra of the different TiO$_2$ nanostructures synthesized by the ACVD process. Anatase standard diffraction data is from JCPDS No. 071-1166. (d) HR-TEM image of the columnar structure. Inset shows the crystal lattice at the tip of the column. (e) SAED pattern at the tip of the column. ........................................97

Figure 4-3: (a) Cyclic voltammogram of the columnar nanostructures for 5 cycles at a scan rate of 1 mV/sec. The voltammogram for the 5 cycles is overlapping at most of the points. Galvanostatic charge-discharge voltage profiles of the (b) columnar nanostructure for selected cycle numbers as shown at 1 C rate (=335 mA g$^{-1}$) (c) columnar nanostructures at varying rates (1 C - 10 C) for the third cycle and (d) granular nanostructure at 1 C rate for selected cycle numbers as shown. The regions mentioned in (b) are marked for the first discharge cycle. .................................................................................99

Figure 4-4: (a) Cycle performance of the columnar nanostructures at varying cycling rates (1 C-10 C rate) and granular nanostructures at 1 C rate for 100 cycles. TEM image of the columnar nanostructure (b) before cycling and (c) after 100 cycles. Inset shows the amorphous SEI layer formed on the TiO$_2$ nanostructure after cycling. (d) Rate capability of the columnar and the granular nanostructures. The charge rate was varied from 1 C to 50 C while the discharge rate was kept constant at 1 C. (e) Structural uniqueness of the dendritic columnar structure over the granular structure and its benefits to battery operation. .........................................................................................101

Figure 5-1: Graphical Abstract for the work presented in Chapter 5 .................................................................114

Figure 5-2: Schematic of the P2D type model for a lithium-ion half-cell with 1D oriented TiO$_2$ columnar electrode. ..........................................................................................117

Figure 5-3: (a) SEM image and (b) XRD spectra of the TiO$_2$ columnar nanostructures of the different heights. ............................................................................................................123

Figure 5-4: (a) Galvanostatic charge-discharge voltage profiles of columnar nanostructures of varying heights at a 1C rate of charge and discharge. (b) Cycling performance represented in terms of specific capacity and (c) areal capacity of the columnar structures of varying heights at 1C rate of charge and discharge ........................................................................................................125
Figure 5-5: Galvanostatic charge-discharge voltage profile from experimental measurements and modeling of (a) the 0.8 µm columnar nanostructures at varying rates (1C-10C) of discharge (intercalation) and (b) the columnar nanostructures of varying heights at 1C rate of discharge (intercalation). ........127

Figure 5-6: Predicted effect of (a) diffusivity of the lithium in the TiO₂ column and (b) electronic conductivity of the TiO₂ column on the performance of 0.8 µm tall columnar nanostructures. The dashed line indicates the experimentally measured values of the parameters. ........................................................................128

Figure 5-7: Predicted areal capacity for columnar structures of varying heights at varying rates of discharge. .....................................................................................................................129

Figure 5-8: Simulated voltage-time profile at different axial locations in the TiO₂ column for 3µm tall columns with electronic conductivity of (a) 2.35×10⁻⁶ S/m (as prepared) and (b) 59 S/m (hypothetical carbon coated electrodes). The different curves are equally spaced on the column in the axial direction........130

Figure 5-9: Predicted areal capacity for hypothetical carbon coated columnar structures of (a) varying heights at varying rates of discharge and (b) 10 µm carbon coated columnar structures with varying column spacing (porosity) .................131

Figure 6-1: Graphical abstract of the work presented in Chapter 6........................................139

Figure 6-2: (a) Galvanostatic cycling at different current rates, (b) charge-discharge plots for different cycles, (c) TEM and (d) cross-sectional SEM images of the TiO₂ columns before and after 1000 cycles .................................................................145

Figure 6-3: dQ/dV plots (a) at different current rates during the power cycles and (b) at 100 mA g⁻¹ during the long term cycling . (c) Charge discharge curves for selected cycles during the long term cycling at 100 mA g⁻¹. (d) GITT at 2nd cycle at a current rate of 50 mA g⁻¹ ..................................................147

Figure 6-4: (a) Potentiostatic electrochemical impedance spectroscopy at different states of charge during the (d) first discharge cycle at 50 mA g⁻¹; FEG-SEM top view of the TiO₂ columns (b) before and (e) after 1st discharge; (c) equivalent circuit for the cell and (f) zoomed fitted impedance curves for four voltage points.........................................................................................................................149

Figure 6-5: (a) Charge-discharge profiles at a 50 mA g⁻¹ current rate, (b) Raman spectra of the pristine TiO₂ and the cycled TiO₂ samples, (c) XRD pattern, (d) Lattice constants of the tetragonal crystal structure (I41/amd) obtained via Rietveld refinement of the XRD spectra of pristine TiO₂ and cycled TiO₂ samples. Anatase standard diffraction pattern was taken from ICSD PDF No. 01-071-1166 and the rutile standard diffraction pattern was taken from ICSD PDF No. 04-001-7096. ........................................................................................................152
Figure 6-6: XPS spectra of the cycled electrodes: after (a) 1st discharge, (b) 1st charge, (c) 2nd discharge and (d) 2nd charge at a current rate of 50 mA g⁻¹. .................................................154

Figure 6-7: STEM-EDX mapping of TiO₂ columns after (a) 1st discharge, (b) 1st charge along with line scan data for the same columns with the (c) SAED pattern and HR-TEM image to evaluate the Na-ion storage mechanism. .........................155

Figure 6-8: Raman spectra on (a) the SEI lumps formed on the TiO₂ nanostructure (b) the TiO₂ nanostructure at low magnification and (c) the TiO₂ nanostructure at different penetration depth. All spectra and images are for the electrode post 1000 cycles. The pristine TiO₂ spectra is for the as synthesized pure anatase TiO₂ electrode for reference...............................................................157

Figure 7-1: Graphical abstract of the work presented in Chapter 7........................................172

Figure 7-2: Schematic of the multicomponent ACVD process for the synthesis of doped nanostructured thin films. ........................................................................................................177

Figure 7-3: (a) Cross-section view and (b) Top view SEM image of the one-dimensional Nb doped TiO₂ thin film with 15.3% Nb doping. (c) SEM-EDX spectra of the doped and undoped thin films. .................................................................179

Figure 7-4: (a) XRD spectra of the Nb doped TiO₂ thin films with the (b) 25–26° two theta range zoomed in. Change in (c) unit cell lattice parameters and (d) the cell volume of the tetragonal crystal structure (I41/amd) obtained via Rietveld refinement of the measured XRD spectra..................................................180

Figure 7-5: XPS spectra of the Nb doped TiO₂ thin films showing the (a) Ti (b) Nb and (c) O peaks. Curve fitting of the spectra peaks was used to deconvolution the peaks and observe the peak shifts. .................................................................181

Figure 7-6: Galvanostatic charge discharge voltage profiles of the Nb doped TiO₂ anodes for the 5th cycle at a current rate of 20 mA.g⁻¹............................................................182

Figure 7-7: Rate Capability of the Nb doped TiO₂ anodes in a sodium-ion system. Inset shows the 5th cycle discharge capacity as a function of the Nb doping %. ..........183

Figure 8-1: Schematic representation of the proposed R2R ACVD system for thin film deposition..........................................................................................................................193

Figure 8-2: Utilization of the ACVD process for direct fabrication of binder free oriented one-dimensional nanostructured electrodes directly on current collectors for lithium and sodium-ion batteries. Figure reprinted by the permission of John Wiley and Sons from Chadha et. al [1], copyright 2014. ..................................................194

Figure A-1: Design of the precursor feed system for the multicomponent ACVD system........197

Figure A-2: Design of the reactor system..............................................................................198
Figure A-3: Design of the substrate holder.............................................................................................................199
Figure A-4: Design of the substrate holder base which mounts the heater cartridges..................199
Figure A-5: Substrate holder design (left: sideview, right: topview) .........................................................200
Figure A-6: Possible film configurations which can be synthesized by the ACVD system.........201
Figure A-7: Overview of the Labview main vi ..................................................................................................202
Figure A-8: Block diagram of a mass flow controller sub vi. .................................................................210
Figure A-9: Block diagram of heater control sub vi implemented via pulse-width modulation and PID control..............................................................................................................211
Figure A-10: Front Panel of the Labview program for the ACVD system .................................212
Figure A-11: Photograph of the ACVD process reactor ...........................................................................216
Figure B-1: Setup of the geometry of the ACVD reactor in COMSOL .................................................222
Figure B-2: Setup of simulation domains in COMSOL. The domain highlighted in blue is air. ..............................................................................................................................................223
Figure B-3: Setup of simulation domains in COMSOL. The domains highlighted in blue are steel. ...........................................................................................................................................224
Figure B-4: Setup of simulation domains in COMSOL. The domain highlighted in blue is silica glass. ...........................................................................................................................................225
Figure B-5: Setup of the heat transfer module for the ACVD reactor. Domains for which the heat transfer simulation was carried out are highlighted in blue. ........................226
Figure B-6: Setup of the heat transfer module for the ACVD reactor. Domains for which the laminar flow simulation was carried out are highlighted in blue. ......................227
Figure B-7: Setup of the transport of diluted species module for the ACVD reactor. Domains for which the transport of diluted species simulation was carried out are highlighted in blue. ........................................................................................................228
Figure B-8: Mesh formulation for the ACVD reactor simulation in COMSOL.................................229
List of Tables

Table 1-1: Comparison of sodium and lithium elemental characteristics........................................13
Table 1-2: Examples of one-dimensional nanostructures synthesized by various methods and their limitations ..........................................................18
Table 2-1: List of process parameters and their values used in the simulation study..................41
Table 3-1: Summary of light absorption characteristics and photoelectrochemical performance of the various Au-TiO₂ samples .................................................77
Table 4-1: Process parameters for the synthesis of columnar and granular nanostructures by the ACVD process ........................................................................94
Table 5-1: Values of parameters used for the modeling study ....................................................118
Table 6-2: Non-linear least square fit to the experimental EIS spectra and fitted parameters for four different voltage points .........................................................150
Table 7-1: Feed flow rates of carrier nitrogen bubbled the niobium and titanium precursor in the ACVD process. The calculated molar feed percentage of Nb and the doping percentage of Nb in the TiO₂ as measured by SEM-EDX and XPS........175
Acknowledgments

Over the past several years, there have been a lot of individuals who have provided the support and encouragement that made the existence of this dissertation possible. First and foremost, a dissertation simply cannot exist without an advisor. I have been extremely fortunate and honored to have Prof. Pratim Biswas as my dissertation advisor and I cannot thank him enough for giving me the opportunity to join his research group. He provided me with the freedom of exploring my own research focus and; the guidance and motivation when goals started to seem like a distant possibility. His mentorship has spanned beyond academia, providing me with the opportunities and skillset to be better prepared for a professional career. His critical thinking, teaching and time management skills have always left me awestruck. If there was any doubt in my mind about pursuing my research in the field of aerosol science, his graduate course certainly left no trace of it. He has, and will continue to serve as an inspiration for excellence for me. I would also like to thank my other committee members, Prof. Richard Axelbaum, Prof. Palghat Ramachandran, Prof. Elijah Thimsen, Prof. Parag Banerjee, Dr.Srikanth Kommu and Dr. David S. Ginley for guiding me through my doctoral research and providing valuable inputs to improving this dissertation. I express my sincere gratitude to Prof. Sagar Mitra, Dr. Alok Mani Tripathi and Prasit Dutta from IIT Bombay, Dr. Mengmeng Yang and Prof. Shuiqing Li from Tsinghua University, Dr. Bharat Suthar from Washington University in St. Louis, and Prof. Venkat Subramanian from University of Washington, Seattle for the extremely productive collaborative research presented in this dissertation.

I graciously acknowledge the funding agency for making the research presented in the dissertation feasible and for the financial support as a graduate student. The work in the dissertation was
supported by the Solar Energy Research Institute for India and the U.S. (SERIIUS) funded jointly by the U.S. Department of Energy subcontract DE AC36-08G028308 (Office of Science, Office of Basic Energy Sciences, and Energy Efficiency and Renewable Energy, Solar Energy Technology Program, with support from the Office of International Affairs) and the Government of India subcontract IUSSTF/JCERDC-SERIIUS/2012 dated 22nd Nov. 2012.

I thank all the present and past members of the Aerosol and Air Quality Research Laboratory (AAQRL) for making my graduate school experience wonderful and one which will be cherished by me forever. I am proud to share this bond with the alumni, current and future members of AAQRL (Aerosol Mafia). I would like to especially thank Dr. Woo-Jin An and Dr. Vivek Shah for mentoring me through the initial phases of my graduate research. Apart from being a great mentor, Vivek has also been a very good friend since my very first days in St. Louis. I thank Dr. Weining Wang for teaching me aerosol instrumentation, material characterization and design of experiments. I thank current AAQRL lab members and my friends, Dr. Ramesh Raliya, Jiaxi Fang, Yi Jiang, Shalinee Kavadiya, Sameer Patel, Yang Wang, Miguel Vazquez Pufleau, Kelsey Haddad, Ahmed Abokifa, Bedia Begüm Karakoçak, Yao Nie and Girish Sharma for the hangouts and fruitful discussions on research and topics way beyond it. Perhaps, one of the most exciting experience of being in the AAQRL group (outside of research) is the international diversity in the group through which I have learnt about different cultures and of course, food! I also thank my friends in the EECE department for making graduate school an enjoyable experience. I would also like to thank the EECE staff, Rose Baxter, for the paperwork related to my graduate studies, Trisha Sutton, for helping with purchasing, Beth Mehringer, for reimbursements, Lesley Smith and Christine Tilley, for administrative help and Kim Coleman, for setting up meetings.
I thank all my friends here for making my experience of St. Louis a memorable one. A special thanks to Sriya for her friendship, continued support and motivation through all these years. I would also like to thank my undergraduate college friends who have been with me all these years and have kept me motivated.

I express my gratitude to Prof. K. Uma Maheswari, SASTRA University and Prof. Chandra Venkataraman, IIT Bombay for undergraduate research opportunities, which eventually inspired me to pursue my PhD. Finally, I would like to thank my parents and brothers, for their unconditional love and support throughout my life and for making me what I am today.

Tandeep S. Chadha

Washington University in St. Louis, 

August 2016
Dedicated to my family
ABSTRACT OF THE DISSERTATION

Nanostructured Thin Film Synthesis by Aerosol Chemical Vapor Deposition for Energy Storage Applications

by

Tandeep S. Chadha

Doctor of Philosophy in Energy, Environmental, and Chemical Engineering

Washington University in St. Louis, 2016

Professor Pratim Biswas, Chair

Renewable energy sources offer a viable solution to the growing energy demand while mitigating concerns for greenhouse gas emissions and climate change. This has led to a tremendous momentum towards solar and wind-based energy harvesting technologies driving efficiencies higher and costs lower. However, the intermittent nature of these energy sources necessitates energy storage technologies, which remain the Achilles heel in meeting the renewable energy goals. This dissertation focusses on two approaches for addressing the needs of energy storage: first, targeting direct solar to fuel conversion via photoelectrochemical water-splitting and second, improving the performance of current rechargeable batteries by developing new electrode architectures and synthesis processes.

The aerosol chemical vapor deposition (ACVD) process has emerged as a promising single-step approach for nanostructured thin film synthesis directly on substrates. The relationship between the morphology and the operating parameters in the process is complex. In this work, a simulation based approach has been developed to understand the relationship and acquire the ability of predicting the morphology. These controlled nanostructured morphologies of TiO₂, compounded with gold nanoparticles of various shapes, are used for solar water-splitting applications. Tuning
of light absorption in the visible-light range along with reduced electron-hole recombination in the composite structures has been demonstrated.

The ACVD process is further extended to a novel single-step synthesis of nanostructured TiO$_2$ electrodes directly on the current collector for applications as anodes in lithium-ion batteries, mainly for electric vehicles and hybrid electric vehicles. The effect of morphology of the nanostructures has been investigated via experimental studies and electrochemical transport modelling. Results demonstrate the exceptional performance of the single crystal one-dimensional nanostructures over granular structures, due to a combination of high surface area, improved lithium diffusivity and electronic conductivity. The model developed allows for the prediction of optimized nanostructure geometry depending on the end-use application.

Increasing demand for lithium-ion batteries, posing concerns for lithium supply and costs in future, have motivated research in sodium-ion batteries as alternatives. In this work, the nanostructured TiO$_2$ electrodes have been studied as anodes for sodium ion batteries. To improve the performance, a new multi-component ACVD process has been developed to achieve single-step synthesis of doped nanostructured thin films. One-dimensional niobium doped TiO$_2$ thin films have been synthesized and characterized as a novel anode material for sodium-ion batteries. The doped nanostructured thin films deliver significant improvements on capacity over their undoped counterparts and demonstrate feasibility of sodium-ion batteries. In summary, the studies conducted in this dissertation develop a detailed understanding of the ACVD process and demonstrate its ability to synthesize superior nanostructured thin films for energy storage applications, thereby motivating process scalability for commercial applications.
Chapter 1

Introduction
1.1 Background and Motivation

The global energy consumption is rapidly increasing each day, accelerated by the improvement in living conditions and growth surges in developing nations. The annual rate of global energy consumption was estimated at 13 TW in 2001 [1]. The global population is projected to increase from 7.4 billion in 2015 to 9.7 billion in 2050 and 11.2 billion in 2100 [2], thus leading to an increase in energy demand from 14 TW to 28 TW by 2050 [3]. 86% of this energy comes from fossil fuels as of 2008 [1]. Although estimated fossil fuel reserves show that it can sustain a 25-30 TW annual consumption rate for several centuries [4], their prolonged use can lead to severe environmental problems. Burning of fossil fuels like coal and oil leads to the production of carbon dioxide. The global carbon dioxide emissions from fossil fuel use was 35.9 Gt in 2014 [5]. The accumulation of carbon dioxide in the atmosphere has severe environmental implications. Studies from Dome Concordia ice cores have shown that the amount of CO₂ in the atmosphere had been less than 300 ppm for the past 650,000 years [6]. However, the technological and economic advancement over the past 50 years has increased the CO₂ content to 380 ppm [4]. Carbon dioxide equilibration in the atmosphere occurs very slowly and takes around 10–30 years. Most of it enters the biosphere and the oceans. If no effort is made at reducing these levels, the amount of CO₂ in the atmosphere accumulated over the next half-century will remain in the atmosphere for the next 500–4000 years. High carbon dioxide content in the atmosphere is related to global warming and changes in the hydrological cycle. In this respect, the Copenhagen Accord (2009) and subsequently the 2015 UNFCCC meeting at Paris (COP21) reached a resolution to limit the maximum temperature increase due to global warming to 2°C. In order to achieve this target, a structured move towards renewable energy sources is necessary. The earth has an abundance of wind, solar,
and geothermal energy, which if tapped in the correct way can serve as the essential energy means in the future.

According to the US annual energy review of 2011, electricity accounts for 40% of the energy consumption and 46% of electricity is generated from coal [7]. Also the transportation sector accounts for 30% of the energy consumption and is fueled 96% by petroleum. Therefore a shift to renewables for generating electricity and using electric or battery powered vehicles would lead to a greener economy. This trend can be observed from the 15.9%/year increase in the annual energy consumption from renewables as shown in Figure 1-1. Of all the renewable energy sources solar has the highest potential for global adoption. This is because solar insolation is available everywhere and is not limited to certain geographic locations, as is in the case of tidal or hydroelectricity. The amount of solar energy striking the earth’s surface is approximately 120,000 TW [8] while the global energy consumption as of 2010 was 16 TW. Perhaps the success of solar energy is best demonstrated by plants which harness 100 TW of the energy, approximately 6 times the energy required by humans. Despite this, the use of solar energy has been limited to only 0.35%

![Figure 1-1: Global energy consumption by fuel source from 2000 to 2014. Growth rates indicated for the 2010–2014 period. Figure reprinted by the permission of Nature publishing group from Jackson at al. [5], copyright 2015.](image-url)
of the net global renewable electricity generation in 2008 [1]. The main obstacles in the harnessing and large scale utilization of solar energy are the low conversion efficiency of sunlight to electric power and the variation of sunlight with time of day, weather conditions and the season.

So far, silicon has been the main component in PV devices constituting the 1st generation solar cells. With the research and development in silicon solar photovoltaic modules, the present levelized cost of energy (LCOE) [9, 10] is comparable to that from conventional electricity mainly due to a lowering of module costs. The solar LCOE is $0.06-$0.32/KWh while conventional electricity cost is ~$0.07/KWh. However the main limitation for largescale solar energy use is in the intermittent nature of the energy generation due to fluctuations in insolation due to seasonal variations and external factors such as dust deposition or clouds. Therefore solar electricity with low LCOE, grid integration and a robust and low cost electrical energy storage system is required to make solar energy a reliable global energy source and overcome its problem of intermittency.

Out of the various approaches for addressing the challenge of energy storage, two approaches have been studied in this dissertation (Figure 1-2). The first is an integrated harvesting and storage approach to convert the solar energy directly into chemical energy in the form of fuels instead of conversion to electricity. Fuels can be readily stored and transported thus addressing both challenges of intermittency and availability of solar insolation. Several approaches including thermochemical CO$_2$ dissociation [11], photochemical CO$_2$ reduction [12] into syngas or methane, photoelectrochemical splitting of water into hydrogen and oxygen [13] are being considered. While efficiencies of CO$_2$ photoreduction are extremely low and far from commercialization, photoelectrochemical water splitting has attained good efficiencies at a lab-scale. The highest solar-to-hydrogen (STH) efficiency reported for a research scale photoelectrochemical system is 14% [14] which is still less than the single-crystal silicon photovoltaic efficiency of 25% [15].
The second approach is to couple secondary energy storage devices to the existing PV devices. There are several electrical energy storage systems that are used presently [16]. Pumped hydroelectricity, compressed air energy storage and superconducting magnetic energy storage and flywheel each have their limitations [16]. All these systems are limited by location. Flywheel storage system is also limited by its applicability in high power low energy systems. On the other hand electrochemical energy storage systems based on batteries have the advantage of being installed anywhere. They can be used for energy storage ranging from kWh to MWh and can be deployed for power and energy management at the same time.

In addition, batteries can also be used to power hybrid vehicles, thus solving the problem of emissions and fossil fuel consumption from the transportation sector. Research has shown that electric and hybrid vehicles emit 50% less pounds of CO₂ equivalents compared to gasoline cars.
In 2014 transportation accounted for 26% of greenhouse gas emissions in USA, making it the second largest emission sector after electricity [18]. The present limiting factor for lithium ion batteries is the $1000/kWh cost. Tesla Motors has announced plans for the construction of a gigafactory with an annual battery production of 35 gigawatt-hours, which is expected to reduce the per kWh cost of lithium-ion batteries by 30% [19]. The DOE aims at reducing this cost to less than $250/kWh [20].

1.2 Solar to Fuel Conversion

Fujishima and Honda first showed the ability to split water under illumination using $n$-type TiO$_2$ [21]. Since then solar to hydrogen conversion efficiency of 14% has been reported using a integrated photovoltaic cell [14], and 18.3% using a multi-junction cell [22, 23]. Photoelectrochemical water splitting is a complex process since it combines the solar absorber and the electrolysis in a single device. A photoelectrochemical cell with an n-type semiconductor has been shown in Figure 1-3a. When an n-type semiconductor is brought in contact with the electrolyte, whose redox potential is more negative than the Fermi level of the semiconductor,
electrons are transferred from the semiconductor to the electrolyte to equilibrate the Fermi level at the semiconductor electrolyte interface. This results in a bending of the conduction and valence band edge upwards until the chemical potential of electrons across the interface is the same. At this point, a space charge region is created at the semiconductor liquid interface due to the depletion of the electrons, and a resulting potential barrier is formed which prevents further movement of electrons to the electrolyte. When light is incident on the semiconductor, electron-hole pairs are generated. The electron-hole pairs that are generated within the depletion region are quickly separated by the built in electric field. The holes move towards the electrolyte and help to oxidize water. The electrons are removed to the counter electrode through the external circuit and reduce water to hydrogen. The generated hydrogen can be stored and used as a fuel. The semiconductor in this case is called the photoanode. If a p-type semiconductor was used, hydrogen evolution would occur at the semiconductor electrolyte interface, and the semiconductor then behaves as a photocathode.

Several factors that determine the how efficiently the material can electrolyze water under solar illumination. Combining all these factors, the ideal electrode should have the following properties:

i. The material’s band gap must lie within the visible part of the solar spectrum so that it can absorb a significant part of the incident solar energy. The spectral distribution of the solar energy has been shown in Figure 1-3b [24].

ii. The potential of the band edges must straddle the hydrogen and oxygen evolution potentials

iii. There should be facile charge transfer from the semiconductor to the electrolyte.

iv. The material should be stable in aqueous solution for relatively large periods of time.

v. The minority carrier diffusion lengths must be long compared to the penetration depth of light so that charge carriers generated, can be efficiently collected.
vi. The energy loses due to kinetic overpotential must be minimized and be selective for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), by a facile charge transfer from the surface of the semiconductor to the solution.

Tremendous research efforts have focused on the utilization of TiO$_2$ as a candidate for water-splitting due to its excellent chemical inertness and the strong oxidation potential of photogenerated holes. However, two major issues with TiO$_2$ that remain persistent are high electron hole pair recombination within the semiconductor and the large band gap of TiO$_2$ (3.2eV) which limits the light absorption to the ultraviolet region (≈4% of the solar spectrum). These issues have confined this technology to a research scale only.

1.3 Metal-ion Batteries

Metal-ion batteries dominated by lithium-ion batteries have seen exponential growth as secondary energy storage devices since their commercialization by Sony in 1991. Although introduced
primarily for portable electronic devices, lithium ion batteries are now being used for a wide variety of applications including electric and hybrid vehicles (EVs and HEVs) and grid scale energy storage. The primary reason for their success is the broad range of energy density (and power density offered by lithium-ion batteries compared to lead acid and nickel-metal hydride chemistries (Figure 1-4) [25, 26]. This high energy density and power density of lithium ion batteries has enabled the introduction of EVs such as the Tesla Model S, running on a 90kWh lithium ion battery system with a gravimetric energy density of 140 W.h.kg\(^{-1}\) and a gravimetric power density of 516 W.kg\(^{-1}\), providing a range of 294 miles [27].

Metal-ion batteries comprise of three primary components (defined by the role played during the discharge process) including a cathode, an anode and an electrolyte and is based on the transport of metal-ions in the electrolyte and storage at the electrodes (Figure 1-5). Initially, the battery is in a discharged stated and it is first charged via a reversible oxidation reaction releasing a metal cation at the positive electrode (cathode), which is transported via the electrolyte to the negative electrode (anode) where it is stored in a host material via a reversible reduction reaction. The electron flow during the charging process is driven by an external power source. During the discharge process, the oxidation and reduction electrodes and the flow of the metal cation is reverse generating current in the electrical circuit which can be used to operate a load.

In a metal-ion battery, the cathode serves as the initial source of the metal ions and hence an oxide of the metal-ion is used as the cathode. Typical materials used as cathodes in lithium-ion batteries are layered Li[M]O\(_2\) (M=Co, Ni, Mn), spinel Li[M’]\(_2\)O\(_4\) (M’=Ni, Mn), olivine-type Li[M’’]PO\(_4\) (M’’ = Fe, Mn) or their derivatives [28, 29]. The anode serves as the host of the metal-ion during the charged state. The most common commercially used cathode and anode materials for lithium
ion batteries, thus far, are lithium cobalt oxide and graphite respectively. The reactions for these materials are represented as follows:

Cathode: \( \text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}^+ + xe^- \)

Anode: \( \text{C} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C} \)

Overall reaction: \( \text{LiCoO}_2 + \text{C} \rightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C} \)

Lithium ions intercalate and are stored in the interstitial spaces between the graphite planes as LiC\(_6\) yielding a theoretical capacity of 372 mA.h.g\(^{-1}\). This intercalation process of lithium in the graphite takes place at potentials of less than 100 mV vs Li\(^+\)/Li, which if not controlled carefully leads to highly reactive lithium metal deposition on the graphite surface. This lithium metal deposition is a major safety concern and is often responsible for battery explosions via thermal runaway [30].

Figure 1-5: Schematic of charging and discharging process in a lithium-ion battery using lithium cobalt oxide as the cathode and graphite as the anode.
1.3.1 Alternative anode materials for lithium-ion batteries

The safety concerns and limited theoretical capacity of the graphite anode has prompted research into alternate materials as anodes for lithium-ion batteries. Ideally, an anode material should possess: (1) low redox potential for intercalation and de-intercalation of lithium ions into the anode material to achieve high working voltage, (2) highly reversible reaction with high capacity to host the lithium ion, (3) fast diffusion rate of lithium ion in the structure and good electronic conductivity, and (4) good structural stability to withstand the intercalated ions without damage. However, a single material does not possess all the above properties and thus, the search for an alternate anode material remains a challenge for lithium ion batteries. Anode materials are classified as insertion, alloying, or conversion electrodes depending on the storage chemistry of the lithium-ions in the material. Insertion anode materials are the most commonly used anode materials due to the high reversibility of the storage of lithium-ions in the material accompanied by good structural stability, but are often limited in their capacities since only a limited amount of lithium can be stored in the interstitial sites within the material. Examples of insertion anode materials include graphite [31], titanium dioxide [32], lithium titanate [33]. Alloying anodes are based on reversible alloy formation with Li forming LiₓM (M=Sn, Si) and often have high theoretical capacities (994 mAh.g⁻¹ for Sn [34] and 3579 mAh.g⁻¹ for Si [35]) but suffer from the disadvantage of high volume expansion leading to structural degradation. Conversion electrodes are based on a conversion reaction, Li+ MₓXₜ → aM+bLiₓX, where M is a transition metal (Cu, Ni, Co, Fe) and X is an anion (mostly O). Similar to alloying compounds exhibit high theoretical capacities but suffer from the disadvantage of large voltage hysteresis between charge and discharge leading to a decline in overall efficiency [36].
The absence of a single anode material which possesses high capacity as well as good structural stability high rates of cycling has led to the selection of anode materials depending on the desired application. While graphite is the most widespread anode materials currently in commercial use, new materials are being introduced for specific applications. Lithium titanates, due to their exceptional stability and safety, are finding applications in EV and HEV applications [37]; tin/cobalt alloy and silicon/carbon composites, due to their high specific capacity, are finding application in portable electronics [38]. Anatase titanium dioxide is a candidate anode material owing to its structural stability providing safe performance at high rate of charge and discharge [39, 40]. However, the material suffers from limitations such as the low diffusivity of lithium in the anatase crystal structure ($10^{-11}$ to $10^{-13}$ cm s$^{-1}$) [41, 42] and the low conductivity ($1.9 \times 10^{-12}$ S m$^{-1}$) [43] which limits the performance of the material.

1.3.2 Beyond lithium-ion batteries

With the incredible success of lithium-ion batteries, the demand for lithium has grown exponentially in the past few decades. This has raised concern over the lithium cost and supply in the future, owing to its low abundance in the earth’s crust [44] (Figure 1-6), largely limited to area in North and South America, China, Australia, Portugal and Zimbabwe [45]. This has motivated research into technologies beyond lithium-ion systems. Sodium-ion batteries are being considered as potential alternatives lithium-ion batteries due to the abundance of sodium in the earth’s crust and its similar properties with lithium [46] (Table 1-1). This has enabled the translation of research conducted on lithium-ion systems to sodium-ion batteries. However, sodium-ion batteries present a few challenges which include:
i. The lower ionization potential of Na than Li, leading to lower operating voltages and thus lower energy densities compared to lithium-ion systems.

ii. The higher mass and larger size of the Na\(^+\) ion which impedes sodium diffusion in the electrode and leads to higher volume expansion of the electrode material.

Table 1-1: Comparison of sodium and lithium elemental characteristics

<table>
<thead>
<tr>
<th>Property</th>
<th>Lithium</th>
<th>Sodium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation Radius</td>
<td>0.76 Å</td>
<td>1.06 Å</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>6.9 g.mol(^{-1})</td>
<td>23 g.mol(^{-1})</td>
</tr>
<tr>
<td>(E^0) (vs. SHE)</td>
<td>−3.04 V</td>
<td>−2.7 V</td>
</tr>
<tr>
<td>Melting Point</td>
<td>180.5 °C</td>
<td>97.7 °C</td>
</tr>
<tr>
<td>Capacity, metal</td>
<td>3829 mA.h.g(^{-1})</td>
<td>1165 mA.h.g(^{-1})</td>
</tr>
<tr>
<td>Cost, carbonates</td>
<td>$5000 per ton</td>
<td>$150 per ton</td>
</tr>
</tbody>
</table>

Traditionally used graphite anode for lithium ion batteries is electrochemically less active for sodium ion and hence is not a viable anode material for sodium ion batteries [47]. Other forms of carbon such as petroleum cokes, carbon microspheres, carbon black, carbon fibers and hard carbon
in addition to metal oxides have been investigated as anode materials for sodium ion systems [48]. Anatase TiO$_2$ has been investigated as a potential anode material and has been shown to exhibit a reversible charge capacity of approximately 150 mA.h.g$^{-1}$ up to current densities of 2A.g$^{-1}$ [49].

1.3.3 Nanostructured materials as anodes

As discussed, the performance of an electrode depends on the inherent physical and chemical properties of the electrode material. However, apart from the intrinsic properties, the size and shape of the material also influences its performance as electrodes in batteries. Nanostructuring the electrode has emerged as a promising pathway of improving the performance due to the following advantages:

i. It provides a shorter path for lithium-ion transport which significantly improves the rate of lithium intercalation and de-intercalation. The Li-ion diffusion in the material is related to the Li-ion diffusion coefficient and the diffusion length in the material given by:

\[ \tau = \frac{L_{ion}^2}{D_{Li}} \]

b. where $L_{ion}$ is the diffusion length and $D_{Li}$ is the diffusion coefficient of lithium in the material.

ii. It provides better electron transport similar to the effect on lithium transport.

iii. It provides a higher surface area which permits high lithium-ion flux across the interface. However, the increased surface area also possesses the disadvantage of higher side reactions with the electrolyte.

iv. They provide a higher range of composition over which the solid solutions exist accompanied by better strain relaxation.
Due to these reasons most of the research on materials for metal-ion batteries utilizes nanomaterials. Nanostructured materials can be made with different morphologies broadly classified as nanoparticles (0D), nanorods/nanotube/nanowires (1D), nanosheets (2D) and porous hierarchical nanostructures (3D) materials [50]. One dimensional nanostructuring, in particular, has received considerable attention due to the decoupling of electrode/electrolyte interface area and the diffusion path length in these structures accompanied by better strain relaxation in oriented one-dimensional nanostructures (Figure 1-7) [35]. One dimensional nanostructures of nearly all anode materials including carbon [51], silicon [35], cobalt oxide [52], copper oxide [53, 54], manganese oxide [55], titanium dioxide [56, 57], lithium titanate [58], iron oxide [59], tin oxide [60], and vanadium oxide [61] have been developed and tested. However, the advantages of

Figure 1-7: Schematic of electron transfer pathways and fate of nanostructures upon cycling in different electrode architectures.
nanostructured materials are limited due to the current battery fabrication process as shown in Figure 1-7.

1.3.4 Fabrication of battery electrodes and limitations

The current manufacturing of lithium ion battery electrodes is a multi-step process (Figure 1-8) [62]. First, the electrode material is synthesized as a dry powder (active material) which is then mixed with a conducting additive (for non-carbon based materials) and a binding agent to form a slurry. This slurry is then coated onto a current collector (copper foil for anode) by a slot die coating process, following which it is dried in an oven. This multi-step process presents several limitations and disadvantages:

i. The separate preparation of the active material and the coating onto the current collector requires the use of a binding agent to stick the active material powder together with the current collector. Binding agents are electrochemically inactive and thus lead to decrease in the gravimetric capacity of a battery. Further, decomposition of binding agents causes

---

Figure 1-8: Schematic of the current battery fabrication process. Figure reproduced by the permission of Fraunhofer IKTS from Wolter et. Al. [62], copyright 2013.)
loss of lithium, electrical connectivity, and mechanical stability leading to capacity fade [63].

ii. For nanomaterials, the multi-step process does not allow a good control over the final morphology of the nanostructure on the current collector. While multiple processes exist for the preparation of intricate nanostructures, the slot die coating process just stacks the nanostructure on each other with no control over their orientation or stacking (Figure 1-7). This limits the advantages of the nanostructures mentioned previously in terms of the better strain relaxation, control over the electrode/electrolyte interface area and the electronic conductivity [64].

Thus, new electrode fabrication processes must be explored which have the ability of synthesizing the nanostructured material directly onto the current collector. This would allow a control over the morphology of the nanostructure along with its orientation and arrangement on the current collector. Furthermore, the process needs to be scalable and low-cost in order to meet the massive demand of batteries in an economical manner.

1.4 Synthesis of nanostructured thin films

Nanostructured film synthesis has attracted enormous interest for both fundamental research as well as technical applications. Nanostructures offer a high surface area to volume ratio, excellent stability, and enhanced and tunable surface reactivity [65]. Specifically, one-dimensional (1-D) metal-oxide nanostructures, including wires, tubes, belts, and rods, have been studied extensively because of their superior electronic, optical, thermal, mechanical, and magnetic properties [66]. Compared to the bulk, the improved characteristics of 1-D nanostructured materials permit the use
of only a fraction of the material in functional devices, enabling the production of micro-
electromechanical systems.

Various thin film deposition methods to produce 1-D nanostructures are summarized in Table 1-2. While there are a number of film deposition methodologies, they all have limitations in control of the morphology (or require the use of templates, which are inherently slow and not readily scalable). Many of the processes only operate at low pressures, precluding larger area thin film deposition. Additional limitations in the use of multiple species make it difficult to deposit films with varying multicomponent and doped nanostructures.

Aerosol reactors have been established as a robust route for the scalable synthesis of nanomaterial. A promising example of this is the flame aerosol reactor technology which is currently utilized for the production of carbon black, pigmentary titania, fumed silica and optical fibers, a $15 billion annual market [73]. Flame aerosol deposition has been utilized for the synthesis of nanostructure films for various applications including dye sensitized solar cells [74], biomimetic solar cells [75], solar water-splitting [76] and gas sensing [77]. The morphology of the nanostructured thin film in the reactor is governed by the magnitudes of certain characteristic times in the reactor that leads

<table>
<thead>
<tr>
<th>Method</th>
<th>Materials</th>
<th>Morphology</th>
<th>Limitation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal CVD</td>
<td>ITO</td>
<td>Vertically aligned Nanowire</td>
<td>High Temp and low pressure</td>
<td>[67]</td>
</tr>
<tr>
<td>Aerosol CVD</td>
<td>TiO₂</td>
<td>Vertically aligned Column</td>
<td>Low growth rate</td>
<td>[68]</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>KNbO₃</td>
<td>Randomly oriented nanowires</td>
<td>Low growth rate</td>
<td>[69]</td>
</tr>
<tr>
<td>Template assisted</td>
<td>ZnO</td>
<td>Bundled nanowires</td>
<td>Multi step process</td>
<td>[70]</td>
</tr>
<tr>
<td>Electrochemical anodization</td>
<td>TiO₂</td>
<td>Nanotube arrays</td>
<td>Single component metal oxide</td>
<td>[71]</td>
</tr>
<tr>
<td>Etching</td>
<td>Si</td>
<td>Si@CN core-shell nanowire</td>
<td>Metal catalyzed and HF</td>
<td>[72]</td>
</tr>
</tbody>
</table>
to different deposition regimes and hence different morphologies in the reactor. These will be discussed further in Chapter 2.

Recent developments have demonstrated the aerosol chemical vapor deposition (ACVD) process as a novel method for the one-step synthesis of thin films of varying morphologies with a high degree of control [78]. This method involves the vaporization of the precursor followed by chemical reaction to form particles and their growth dynamics in the gas phase. The particles then deposit onto a substrate where the particle size and the sintering rates are used to control the film morphology (Figure 1-9). The main advantage of the ACVD method is that it is a one-step atmospheric pressure process for the synthesis of nanostructures in the form of thin films with excellent control over the morphology, crystallinity, and size. The advantage of the ACVD process

![Figure 1-9: Schematic of the ACVD process for the synthesis of nanostructured thin films (figure reprinted by the permission of The American Chemical Society from An. et. al. [78], copyright 2010).](image-url)
over spray pyrolysis, aerosol assisted CVD or aerosol printing is that it is independent of pressure, and very high temperatures are not required for synthesis. Unlike the other commonly used synthesis methods, the ACVD method does not require a template or a catalyst for the growth of 1-D structures. These features, in addition to the low cost of synthesis and ease of operation, make the ACVD method an ideal candidate for the synthesis of nanostructures.

The ACVD process has been successfully used for the synthesis of single crystal 1-D structures of TiO₂, and NiO in the form of thin films on a substrate. These single crystal 1-D TiO₂ structures have been synthesized directly on various substrates including quartz glass, and ITO coated glass for applications in solar watersplitting [78], dye sensitized solar cells [79], CO₂ photoreduction [12]. In all of the above applications, anatase single crystal films with a high (112) plane orientation and one dimensional columnar morphology have shown to have better performance as compared to the other morphologies.

1.5 Objectives

The intent of the work presented in the thesis is to investigate the application of nanostructured thin films as electrodes in energy storage devices. This dissertation focuses on the use of titanium dioxide based one dimensional nanostructures fabricated by single step aerosol chemical vapor deposition process as photo-anodes for solar to fuel conversion and as anodes for lithium-ion and sodium ion batteries. Detailed investigations into the mechanisms of performance improvements by the use of one-dimensional nanostructures has been carried out. The specific objectives of the research are to:

- Develop a simulation based understanding and prediction of nanostructured morphology synthesized by the ACVD process.
• Study tunability of visible light absorption wavelength by use of Au:TiO$_2$ composite nanostructures for increased water-splitting performance.

• Demonstrate single-step synthesis of carbon and binder free oriented TiO$_2$ nanostructures as anodes for lithium-ion batteries.

• Understand the relationship of nanostructure to performance in one-dimensional oriented nanostructures via modeling.

• Investigate the performance of single crystal oriented TiO$_2$ as anodes for sodium-ion batteries.

• Demonstrate single-step synthesis of one-dimensional niobium doped TiO$_2$ nanostructures via the ACVD process and to study their performance as anodes in sodium ion batteries.

1.6 Outline of the dissertation

Nanostructures of TiO$_2$ with various morphologies find applications in numerous fields including solar photovoltaics, photocatalysis, gas sensing, solar water splitting, lithium-ion batteries and sodium ion batteries. Aerosol chemical vapor deposition is a single-step, atmospheric pressure process to fabricate nanostructured metal oxide thin films with dense, columnar and granular morphologies. These nanostructures have thus far been used as electrodes for solar energy harvesting.

Chapter 2 aims at developing a simulation based understanding of the fluid dynamics, heat transfer and aerosol dynamics in the process to enable control and prediction nanostructured morphology synthesized by the process by tuning the process parameters. A finite element based computational fluid dynamics model coupled with a discrete sectional aerosol model and a boundary layer diffusion and sintering model has been formulated to predict the evolution of particle size
distribution and the morphology of the synthesized nanostructured film. The morphology predicted by the model was validated by experimental observations.

Chapter 3 utilizes the process for synthesizing controlled 1D nanostructures for applications in solar to fuel conversion. Due to the wide band gap of TiO$_2$, it absorbs a very small part ($<$4%) of the solar spectrum in the UV range. In order to enhance the performance in visible light, gold (Au) nanocages were deposited on single crystal TiO$_2$ columnar thin films and their effect on the photoelectrochemical performance for water oxidation was studied. The effect of shape of the Au nanoparticle has also been studied. The work demonstrates the feasibility of tuning the absorption spectra of these Au:TiO$_2$ nanocomposites by controlling the shape of the Au nanoparticles.

Chapter 4 transforms the application of the ACVD process to fabricate nanostructured electrodes for lithium-ion batteries in a single step, directly onto the current collector, obviating the need for any binding agents. This work utilizes the understanding developed in chapter 1 to synthesize oriented single crystal columnar and polycrystalline granular morphologies of TiO$_2$ onto stainless steel foils (current collector) for use as anode materials in lithium ion batteries. The single crystal columnar TiO$_2$ thin films exhibit exceptional performance with a high specific capacity and good rate capability, without the use of any conducting carbon.

The astonishing performance delivered by the oriented 1D nanostructured motivated the development of an understanding of the relationship between nanostructure and morphology in such electrodes. In chapter 5, an electrochemical transport model was formulated and validated with the experimental data. This model was used to understand the role of kinetic parameters including the diffusivity of lithium in the TiO$_2$ and the electronic conductivity of the TiO$_2$ columns and structural parameters including the height of the columns and the porosity of the electrode on
the areal capacity of a lithium ion battery at different rates of discharge. The model allows for the prediction of optimized electrode geometry based on the desired application of the battery.

As the demand for lithium ion batteries increases, the limited and depleting lithium resources on the earth are of concern. Sodium ion batteries are seen as a possible alternative for energy storage applications. Chapter 6 focuses on the study of one dimensional single crystal TiO$_2$ nanostructures for application as anodes for sodium ion batteries. The synthesized nanostructures exhibit a high specific capacity of 175 mAh g$^{-1}$ at 100 mA g$^{-1}$ and exceptional durability of 1000 cycles with 85% capacity retention. The mechanism of sodium-ion intercalation into the TiO$_2$ nanostructure is studied using *ex-situ* material characterization techniques and the kinetic parameter related to sodium-ion diffusion is estimated by electrochemical experiments.

A promising approach to improving the performance of TiO$_2$ as anode for sodium ion batteries is to improve the diffusivity of sodium in the TiO$_2$ nanostructure and to improve the electronic conductivity of the TiO$_2$ nanocolumns. Chapter 7 focuses on the synthesis of niobium doped titanium dioxide nanostructures using a novel multi component aerosol chemical vapor deposition process. Niobium and titanium precursors are co-fed into the ACVD process to form one-dimensional oriented doped thin films. Extensive material characterization of the synthesized nanostructures is performed. The synthesized nanostructures were used as binder and carbon free anodes for sodium ion batteries and the performance was studied. Electrochemical performance results demonstrate significant capacity and rate capability improvements with niobium doping with capacities and rate capability better than the graphite anode currently used in lithium ion systems.
Chapter 8 lists the conclusions of the present work and recommendations for future work towards scale-up of the process for large scale commercial production.

1.7 References


[37] A. Burke, M. Miller, Performance characteristics of lithium-ion batteries of various chemistries for plug-in hybrid vehicles, Institute of Transportation Studies, (2009).


Chapter 2

Model based Prediction of Nanostructured Thin Film Morphology in an Aerosol Chemical Vapor Deposition Process

Submitted to Chemical Engineering Journal, July 2016
2.1 Abstract

The aerosol chemical vapor deposition (ACVD) process has been demonstrated as a promising approach to the single step synthesis of nanostructured metal oxide thin films. Multiple process parameters control the nanostructure morphology and the growth of thin films. This work focuses on utilizing a simulation based approach to understand the role of these parameters in governing the morphology of the thin film. A finite element based computational fluid dynamics model, coupled with a discrete-sectional aerosol model, and a boundary layer diffusion and sintering model has been formulated to predict the evolution of particle size distribution and the morphology of the synthesized nanostructured film (Figure 2-1). The morphology predicted by the model was validated by experimental observations. The model enables scale up and wider application of the ACVD process and can be extended to other gas phase deposition systems.
2.2 Introduction

Nanostructured thin films synthesis has attracted enormous interest in the past several decades due to their wide array of applications including solar photovoltaics [2-4], solar water-splitting [1, 5-11], CO₂ photoreduction [12, 13], and lithium-ion batteries [14]. Various approaches have been used to synthesize these nanostructured films, such as, thermal oxidation [15], vapor-liquid solid (VLS) growth [16], template-based synthesis [17], electrochemical methods [18] and gas phase methods [1, 19, 20]. Among these methods, gas phase synthesis such as flame aerosol deposition [19], particle-precipitation chemical vapor deposition (PP-CVD) [21], and aerosol chemical vapor deposition (ACVD) [22] present a rapid, scalable and low-cost method of synthesizing nanostructured thin films. These gas phase methods utilize the direct deposition and sintering of particles onto substrates to form the desired thin film morphology. Three predominant morphologies, namely, dense, columnar, and granular have been reported in the literature [1, 2]. For applications in solar energy and energy storage, the columnar morphology has proven to be the most advantageous due to its oriented, single crystalline, one-dimensional structure, high surface area, and fast electron transfer [1, 2, 6, 14].

Increasing interest in the nanostructured thin films synthesized by the ACVD process and desire to scale-up the process for commercial application has prompted further research into understanding the effect of process parameters on the aerosol dynamics in the reactor and the synthesized morphology. While, the process is simple to operate, the intricate combination of fluid dynamics, heat transfer and aerosol dynamics needed to achieve control over the synthesized morphology is relatively complex. Understanding the relationship between process parameters and the morphology is crucial for scalability and commercial implementation of these processes. Efforts have been made to understand the factors that govern the morphology in such processes.
Thimsen and Biswas [19] studied the effect of precursor feed rate and the substrate temperature on the morphology, crystalline nature and photoactive performance of nanostructured TiO$_2$ thin films synthesized by a flame aerosol deposition process. The two parameters were linked to four characteristic times, the residence time ($\tau_{res}$), the reaction time ($\tau_{rxn}$), the collision time ($\tau_{col}$) and the sintering time ($\tau_{sin}$). Based on a qualitative comparison between these four characteristic times, three regimes in the deposition process were identified namely, chemical vapor deposition (CVD), individual particle deposition (IPD) and agglomerate particle deposition (APD), which yielded the three different morphologies stated above. An et. al. [1] utilized a similar empirical approach for understanding the link between the process parameters and the morphology in the aerosol chemical vapor deposition process (ACVD) utilizing the same characteristic times to identify three regimes — vapor only, vapor-particle mix and particle only regime. However, for the ACVD process, the process parameters often influence more than one characteristic time, making it difficult to correlate to the morphology of the synthesized films to characteristic times. As an example, increasing the substrate temperature leads to a decrease in $\tau_{rxn}$, $\tau_{col}$, and $\tau_{sin}$ but the effect on morphology would be dictated by the relative magnitude of decrease in each of these times, which cannot be determined by these qualitative approaches. This warrants the need for a quantitative approach, accounting for both the computational fluid dynamics (CFD) and the aerosol dynamics in the process.

Numerous studies have focused on coupling aerosol dynamics with CFD simulations for aerosol reactors [23, 24]. In order to do this coupling in a computationally efficient manner, approximations are often made on the CFD model and/or the aerosol dynamics model. Various aerosol dynamics models such as monodisperse, lognormal [25], modal [26], sectional [27], and discrete-sectional [28] have been developed to simulate aerosol dynamics in gas phase reactors.
[29], as well as in atmospheric processes [30]. The selection of the aerosol dynamics model and the coupling depends on a number of factors that characterize the system being modeled. Grohen et. al. [31] and Schild et al. [23] applied mono-disperse aerosol dynamics models interfacing with the fluid mechanics to simulate the particle production in a flame spray pyrolysis reactor and a premixed aerosol reactor, respectively. The mono-disperse assumption reduces the number of aerosol dynamics equations on each discretized node to one, which substantially lowers the computational requirement. However, this simplification leads to inaccuracies in the particle size distribution. Prior literature for the ACVD process suggests that the particles depositing on the substrate are smaller than 5 nm. This makes the particle size information extremely critical and higher accuracies are desired, especially in the lower size range close to the nucleation size (0.49 nm).

In order to address the issue of computational time and desired accuracies in the aerosol size distribution, this work utilizes a COMSOL® multiphysics finite element simulation coupled one way to an aerosol dynamics model to simulate particle formation and growth in the reactor. The discrete sectional model (DSM) is chosen for the simulation of aerosol dynamics due to its molecular size resolution in the lower size range and the computational efficiency in the higher size range. Finally, the particle size distribution arriving at the boundary layer of the deposition substrate is correlated to the nanostructured morphology by simulating Brownian diffusion in the boundary layer and sintering on the substrate. The findings from the simulation have been validated by experimental results reported by An et. al [1]. The influence of process conditions on the particle size distribution and the resulting film morphology has been reported and an understanding of the governing parameters is developed.
2.3 Methods

2.3.1 Experimental process description

The ACVD process is specifically designed for the synthesis of nanostructured thin films while maintaining precise control over the morphology and the crystallinity of the thin films. The process originates from the flame aerosol deposition reactor but, it exhibits certain distinguishing features which will be described later. The process (Figure 2-2a) is comprised of three parts: the precursor feed system, the reaction chamber, and the control system. The precursor feed system contains a volatile precursor in a bubbler maintained at a constant temperature. Carrier gas (N$_2$) is bubbled through the volatile precursor to feed the precursor vapors into the reactor system via a feeder tube accompanied by an optional dilution system. The precursor reaction and aerosol dynamics occur in the reaction chamber as a result of the heat flux from the heated substrate. The aerosol is transported via mass convection to the heated substrate, where the vapor-particle mix is then deposited through Brownian diffusion in the boundary layer above the substrate. On the substrate, the vapors react and the particles sinter to form nanostructured thin films. The control system (Appendix A) provides real-time control over various process parameters in the precursor feed system and the reaction chamber, leading to consistent and reliable operation of the process. These process parameters include the carrier gas flow rate ($Q_1$), the precursor temperature ($T_{wb}$), the dilution gas flow rate ($Q_2$), and the dilution gas temperature ($T_2$) in the precursor feed system. For the modeling study, the above process parameters can be translated into three parameters namely, the initial precursor concentration ($c_0$), the total flow rate ($Q_0$), and the initial precursor feed flow temperature ($T_0$). In the reaction chamber, the process parameters controlled are the substrate temperature ($T_{s0}$) and the feeder tube-substrate distance ($h_0$). In the present work, we investigate
Figure 2-2: Schematic of the (a) ACVD process and (b) 2D axisymmetric setup of the ACVD reactor for the finite element modelling
the influence of these five parameters ($c_0$, $Q_0$, $T_0$, $T_{s0}$, and $h_0$) on the aerosol particle size distribution and the morphology of the synthesized nanostructured thin film. In most cases, since the columnar morphology is desired, the process parameters reported by An et al. for columnar morphology growth is chosen as the reference case (base set of parameters) and the effect of each parameter is studied [1]. The details of these simulation cases are listed in Table 2-1. Although, the system has previously been used to synthesize thin films of various metal-oxides, the present work focuses on the synthesis of TiO$_2$ using titanium tetraisopropoxide (TTIP) as the precursor.

**2.3.2 Simulation of temperature and fluid flow**

The fluid dynamics and heat transfer simulation, together with the mass transport are implemented using COMSOL®, a commercial finite element software designed for solving problems of multi-physics. The simulation domain is shown in Figure 2-2b simulated as a 2D axisymmetric geometry in COMSOL®. The equations for the heat transfer in the reactor components and the fluid phase along with the fluid flow and the mass transport of the vapor species are solved simultaneously at steady state using the heat transfer, laminar flow, and transport of diluted species physics in the package. The simulation zone is discretized using a free triangular mesh with a finer mesh for the zone between the end of the feeder tube and the substrate (defined as the refined zone). Corner and boundary layer refinement of the mesh is carried out for regions close to any surface. A laminar
inflow boundary condition for the flow is used at the inlet of the reactor and a constant pressure boundary condition is used for the outflow. A no-slip boundary condition is applied to the flow interaction with the substrate. A convective cooling boundary condition with external natural convection is applied to the outside wall of the glass chamber. Details of the COMSOL® model are provided in Appendix B.

Outputs of the finite element simulation, including the velocity profile, the temperature profile and the reference vapor concentration are utilized as inputs to the aerosol dynamics model. This one-way coupling can be done under the assumption that the aerosols do not affect the fluid flow or the temperature profile within the reaction chamber. Further, since the Peclet number for particle transport is considerably high, in the range of 20 to $10^5$ for particle sizes ranging from 0.4 to 20 nm in the temperature range under consideration, the diffusion of particles in the reaction chamber has been ignored. The discrete sectional model provides the solution for the temporal evolution of the aerosol size distribution and is performed using a Lagrangian approach along the velocity streamlines obtained from the CFD simulation. The simulation is done on different streamlines at varying radial distance from the axisymmetric axis up to the entrance of the substrate boundary layer, which is defined as the region above the substrate at which the radial velocity of the flow reaches 99% of the velocity magnitude [32]. The Peclet number for particle transport in the boundary layer tends to 0 and hence the above simulation scheme can no longer be applied. Instead, a different simulation scheme that only considers Brownian diffusion should be implemented to describe the boundary layer.

2.3.3 Implementation of aerosol dynamics

Various mechanisms participate in the particle size evolution, including the precursor decomposition, vapor nucleation, condensation, coagulation and surface growth. The aerosol
dynamics simulated and the modeling approach for film morphology prediction is shown in Figure 2-3. These mechanisms are all considered in the aerosol dynamics equation [33]:

\[
\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial v} + \frac{\partial (Sn)}{\partial v} - I(v^*)\delta(v - v^*)
\]

\[=
\frac{1}{2} \int_0^v \beta(v - u, u)n(v - u, t)n(u, t)du - n(v, t) \int_0^\infty \beta(v, u)n(u, t)du
\]

where \(n\) is the particle size distribution function, a function of particle size and time \((t)\). The latter three terms on the left in Equation (2-1) represent the processes of condensation, surface growth, and nucleation respectively, while terms on the right side account for the coagulation process where \(\beta(v, u)\) is the kinetic coefficient of coagulation of two particles of volume \(v\) and \(u\). For TiO\(_2\) particles originating from the thermal decomposition of TTIP, the monomer volume of TiO\(_2\) exceeds the critical volume for nucleation and hence the formation rate of monomers can be directly calculated by the precursor decomposition rate, expressed by [34]:

\[R_g = k_g C_{TTIP}; k_g = 1.54 \times 10^6 [s^{-1}] \exp\left(-\frac{74.03 [kJ/mol]}{RT}\right)\]  (2-2)

where \(R_g\) [mol.m\(^{-3}\).s\(^{-1}\)] is the TTIP decomposition rate, \(k_g\) is the reaction rate constant and \(C_{TTIP}\) [mol.m\(^{-3}\)] is the concentration of the TTIP precursor in the gas phase. Surface growth is dictated by the reaction of TTIP on the TiO\(_2\) surface, and the surface growth rate is expressed by [35]:

\[R_s = k_s A C_{TTIP}; k_s \approx 1 \times 10^{11} [cm.s^{-1}] \exp\left(-\frac{15155.16[K]}{T}\right),\]  (2-3)

where \(R_s\) [mol.m\(^{-3}\).s\(^{-1}\)] and \(k_s\) are the surface growth rate and reaction constant respectively, and \(A\) [cm\(^2\).cm\(^{-3}\)] is the surface area concentration of TiO\(_2\) particles.
Figure 2-3: Overview of aerosol dynamics simulated by the discrete sectional model, the Brownian dynamics model and the sintering model to predict film morphology synthesized by the ACVD process
The discrete sectional method is a widely used approach for solving the aerosol general dynamics equation. The particle size distribution is discretized into several discrete sizes in the small size range and is sectionalized in the large size range. In this study, volume concentration is applied as the conserved aerosol moment, which is proven to produce the least numerical diffusion [36]. Based on the TTIP decomposition rate, surface growth rate and the aerosol dynamics equation (2-1), the DSM scheme proposed by Biswas et. al. [33], with modification to include surface growth, is used to calculate the change in aerosol moment for the discrete sizes and the sections. The number of discrete sizes is set to be 100, to better reflect the behavior of small TiO\textsubscript{2} clusters and to reduce the fluctuation brought by the transition from discrete sizes to sections. Therefore, the discrete sizes cover the volume from \(v_{d,1} (=v_1)\) to \(v_{d,100} (=100v_1)\), where \(v_1\) is the volume of a TiO\textsubscript{2} monomer. The first section starts from \(v_{s,1} (=100.5v_1)\) to \(v_{s,2} (=f_sv_{s,1})\), where \(f_s\) is the section spacing factor and is set at 1.08 in the simulations. The largest size covered by the sections is 20 nm.

Multiple size distributions are obtained at the substrate boundary layer depending on the streamline along which the simulation was performed. As discussed earlier, since the Peclet number is high, diffusion of the aerosols in the gas phase is neglected and hence it is assumed that no interaction takes place between the aerosols following different streamlines. The boundary layer can be divided into several annuluses based on the discretization of the space by the streamlines and the axisymmetric nature of the reaction chamber. Since, the axial velocity of the flow in every annulus is known, the flow rate through each annulus can be calculated using equation (2-4):

\[
Q_i = v_i A_i; \quad A_i = \left( \pi (r_i + \frac{\Delta r}{2})^2 - \left( r_i - \frac{\Delta r}{2} \right)^2 \right) \tag{2-4}
\]

where \(Q_i\) is the flow rate through the \(i^{th}\) annulus with flow velocity \(v_i\) and a radius \(r_i\). \(\Delta r\) is the difference in radius of two consecutive annuluses. An average arrival particle size distribution was
calculated based on the volumetric flow in each annulus represented by the corresponding streamline. The average size distribution is then used for modelling the particle deposition and sintering in the boundary layer.

The particles arriving at the boundary layer deposit on the substrate due to Brownian diffusion in the boundary layer. Unlike the flame deposition system, in the ACVD process thermophoresis will reduce the deposition flux. However, for simplicity, the effect of thermophoresis has been ignored since above the boundary layer, the axial flow velocity towards the substrate dominates. Zhang et al. [32] have shown that the effect of thermophoresis for particles smaller than 2 nm can be ignored in the boundary layer of a flame reactor. The particle flux arriving on the substrate is calculated by solving the 1-D steady state diffusion of particles (2-5) from the entrance of the boundary layer to the substrate.

\[ D \cdot \nabla^2 n = 0 \]  

(2-5)

The particle size distribution obtained from the DSM model and zero number concentration at the substrate are the boundary conditions at the boundary layer entrance and the substrate surface, respectively. The arrival particle flux obtained is given by:

\[ J(d_p) = \frac{N(d_p) \cdot D(d_p, T)}{L} \]  

(2-6)

where \( J(d_p) \) is the arrival flux (\#.m\(^{-2}\).s\(^{-1}\)), \( N(d_p) \) is the number concentration (\#.m\(^{-3}\)) of the particles with size \( d_p \) calculated from the discrete sectional simulation, \( D(d_p) \) is the diffusivity of the particle (m\(^2\).sec\(^{-1}\)) reaching the substrate, and \( L \) is the thickness of the boundary layer (m). The viscosity of the fluid, the mean free path, and the particle diffusivity are calculated using the average temperature between the substrate and the entrance of the boundary layer. Using the arrival flux, a particle arrival rate in a 200 nm diameter cross-section (the typical diameter of a single
column in the nanostructured films) is calculated for each particle diameter. As the flux in equation (2-6) is based on a number concentration that is distributed as per the total discrete sizes and sections, a simple summation yields the total deposition flux. The total arrival flux of particle is calculated according to equation (2-7):

\[ J_{tot} = \sum_{i=1}^{100} J(d_{p,i}) + \sum_{j=1}^{90} J(d_{p,j}) \]  

(2-7)

where \( i \) represents the discrete sizes with particle diameter \( d_{p,i} \) and \( j \) represents the sections with midpoint section diameter \( d_{p,j} \). A characteristic time for particle arrival (\( \tau_{arr} \)) is calculated as the inverse of the total particle arrival rate obtained from equation (2-7).

Once particles deposit on the substrate, they sinter with the already deposited particles. For this study, the sintering theory proposed by Xing and Rosner [37] is used:

\[ \tau_{sin} = \frac{k_B T r^a}{c w^b D_s \Omega \gamma_{sg}} \]  

(2-8)

Where, \( w \) is the surface or grain boundary layer width, \( \Omega \) is the molecular volume, \( \gamma_{sg} \) is the surface energy of the solid/gas interface, \( r \) is the radius of the nanoparticles, and \( a = 4, b = 1, c = 225 \) for surface diffusion. \( D_s \) is the surface diffusion coefficient defined by:

\[ D_s = D_{so} e^{-\frac{Q_s T_m}{R T}} \]  

(2-9)

\[ Q_s = \frac{E_s}{T_{mb}} \]  

(2-10)

where \( E_s \) is the activation energy for surface diffusion, \( T_{mb} \) is the melting temperature for the bulk and \( T_m \) is the melting temperature of the nanoparticle. For small TiO\(_2\) nanoparticles, the melting temperature is obtained from data reported by Lehtinen et. al [38]. From equations (2-8)-(2-10), a sintering expression similar to one proposed by Tsantilis et. al [39], is derived for TiO\(_2\):
\[ \tau_{sin}(d_p) = 3.01055 \times 10^{15} \left[ \frac{sec}{m.K} \right] d_p^4 T \exp \left( \frac{3.4216 \times 10^4}{T} \left( 1 - \frac{d_{pmin}}{d_p} \right) \right) \]  \hspace{1cm} (2-11)

\[ d_{pmin} = \left( \frac{4}{L \rho_s} \right) \left( \sigma_s - \sigma_l \left( \frac{\rho_s}{\rho_l} \right)^{\frac{2}{3}} \right) \]  \hspace{1cm} (2-12)

The correction factor associated with the particle diameter in the exponential term of equation (2-12) accounts for the significantly low melting temperatures and viscous flow activation energies for small nanoparticles. As stated by Tsantilis et al. [39], the sintering of particles smaller than 1 nm (cluster of 15 molecules for TiO$_2$) has been assumed to be instantaneous. Finally, an average sintering time, weighted by the number concentration, is calculated for the particle size distribution arriving at the substrate according to the equation (2-13).

\[ \tau_{sin} = \frac{\sum N(d_p) \tau_{sin}(d_p)}{\sum N(d_p)} \]  \hspace{1cm} (2-13)

### 2.3.4 Experimental validation:

Real time particle size distribution measurements were carried out in the ACVD reactor by a scanning mobility particle sizer comprised of an electrostatic classifier (Model 3082, TSI Inc, MN) fitted with a nano differential mobility analyzer (Nano-DMA, Model 3085, TSI INC, MN), a nano-enhancer (Model 3777, TSI Inc, MN), and a condensation particle counter (Model 3772, TSI Inc, MN) capable of measuring particle size in the range of 1 - 30 nm. A sampling probe comprised of an 1/8 inch tube with a hole drilled in the wall was placed on the substrate hot plate. A sampling flow of 0.4 lpm was taken from the reactor and diluted with filtered air, resulting in a dilution ratio of 20. The size distributions presented are corrected by the dilution ratio used. In order to confirm the model predictions of morphology, the effect of two process parameters, substrate temperature and feed inflow rate, was experimentally analyzed. Substrate temperature in the process was varied in the range of 400°C-600°C and the total flow rate was varied in the range 1.0-4.0 m$^3$/s$^{-1}$. The
morphology of the synthesized thin film was confirmed by scanning electron microscopy (SEM) (FESEM, NOVA NanoSEM 230, FEI Co).

2.4 Results and Discussion

2.4.1 CFD results for the reaction zone

The velocity and temperature profile obtained from the finite element simulations for the reference case (Table 2-1) is shown in Figure 2-4. Simulation results confirm the convective heating of the incoming gas flow as it reaches close to the substrate by the outgoing gas, which exits the reactor through the spacing between the feeder tube and the quartz glass cover at the top of the reactor. The temperature in the feeder tube and the reaction chamber is fairly uniform and increases rapidly near the substrate.

The velocity streamlines in the reactor are shown in Figure 2-4c. The streamlines highlight the complex geometry of the ACVD reactor flow impinging on the substrate, turning radially and then back again due to the geometry of the outer quartz glass chamber. This causes a recirculation region in the reactor where prediction of aerosol dynamics is further complicated. Above the substrate, the velocity streamlines turn radially creating a stagnation region where diffusion is the dominant mechanism for particle transport to the substrate.

Figure 2-4d shows the velocity and temperature profile at the axisymmetric axis (center of the substrate). The boundary layer height is defined to be 0.06 mm above the substrate, where it is seen that the axial velocity is less than 1% of the velocity magnitude. The streamlines entering the boundary later are shown in Figure 2-4c (right), along which the discrete sectional simulations are carried out. It is further observed that the temperature rises rapidly in the 0.7 mm region above the
substrate, which indicates that the reaction and aerosol dynamics in this region play a major role in governing depositing particle size.

2.4.2 Simulation results for data in literature:

The process of particle diffusion, deposition, and sintering to yield a nanostructured thin film takes place in the substrate boundary layer. These processes depend on the particle size arriving at the

Figure 2-4: (a) Temperature, (b) velocity profile, (c) velocity streamlines depicting flow pattern in the ACVD reactor, and (d) velocity and temperature profile above the center of the substrate obtained from the finite element simulation
boundary layer, the number concentration of the particles, and the temperature of the substrate. The simulated size distributions of particles arriving at the substrate boundary layer, obtained using the three sets of process parameters (Test 1, 4, 8) reported by An et al.[1], are shown in Figure 2-5a. Each of the three cases represents either a dense, columnar or granular morphology, as defined by the previous study. It is observed that the morphology is correlated to the size distribution, with a shift towards the larger size corresponding to a transition of morphology from dense to columnar to granular. Further, it was observed that the particle flux arriving at the boundary layer increases significantly from $1.28 \times 10^9$ #/s for the dense film to $4.50 \times 10^{10}$ #/s for the columnar film and $9.07 \times 10^{10}$ #/s for the granular film. Thus, the larger size distribution, along with a higher particle flux arriving at the boundary layer, leads to a significant change in morphology. The model predicted results were confirmed by the experimental measurement of particle size distribution in the ACVD reactor (Figure 2-5b). Although the experimental measurements portray a larger particle size, possibly due to particle coagulation and growth in the sampling tube, the trends in number concentration are similar to the model predicted results. Overall, a significant increase in the total number concentration was observed in the columnar and granular case as compared to the dense case.

While surface reaction of the vapor on the substrate is the dominant growth mechanism, the morphology is governed by the presence of particles in the depositing mix. In order to quantitatively correlate the particle size distribution and flux arriving at the boundary layer to the film morphology, a characteristic time ratio (CTR) is defined as the ratio of the characteristic time
Figure 2-5: (a) Simulated and (b) experimentally measured particle size distribution corresponding to the three different morphologies. Results reported are obtained from simulation and experiments performed at operating conditions described by An et. al [1].

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Geometric Mean Diameter (nm)</th>
<th>Total number concentration (#.cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dense</td>
<td>5.93</td>
<td>6.95×10⁷</td>
</tr>
<tr>
<td>Columnar</td>
<td>5.96</td>
<td>7.98×10⁸</td>
</tr>
<tr>
<td>Granular</td>
<td>7.02</td>
<td>7.97×10⁸</td>
</tr>
</tbody>
</table>
for particle arrival ($\tau_{arr}$) to the characteristic time for particle sintering ($\tau_{sin}$). The $\tau_{sin}$ is an average sintering time for the different particle sizes weighted by the number concentration of the corresponding particle size. The CTR takes into account all factors governing the morphology of the thin film including, the particle size distribution, the particle arrival flux, and the sintering rate of the particles. A similar approach has been used previously by Lehtinen et al. to describe the onset of dendrite formation in TiO$_2$ particles as a result of coalescence and sintering in the gas phase [38]. The values for the dense, columnar, and granular film were calculated to be $6.1 \times 10^{25}$, $4.8 \times 10^{1}$, and $1.06 \times 10^{-2}$ respectively. This agrees with the previous understanding that the dense morphology is a result of predominantly vapor deposition, extremely long particle deposition time and ultrafast sintering times; the columnar morphology is a result of comparable arrival times and sintering times leading to the arrival of the particle and near complete sintering with the existing structure allowing for the formation of a single crystal structure; and the granular morphology is a result of highly incomplete sintering leading to stacking of particles with identifiable grain boundaries [1].

2.4.3 The influence of process parameters on particle size distribution and morphology

As described earlier, the process of nanostructure thin film synthesis in the ACVD system can be divided into two stages. The first stage is particle formation and growth in the gas phase, followed by the second stage where particle deposition and film formation take place in the substrate boundary layer. The size distribution of the particles arriving at the substrate boundary layer, the final result of particle evolution in the gas phase and the initial condition for film formation in the latter stage, plays a connecting role in the relationship between the process parameters and the
final film morphology. In order to achieve a controlled morphology, an understanding of the influence of process parameters on the arrival particle size distribution and the CTR is needed.

The arrival particle size distribution obtained from the coupled finite element – discrete sectional simulation is a result of the particle evolution process that is dictated by the complex combination of various aerosol dynamics occurring in the reaction chamber. In order to assess and explain the influence of the ACVD process parameters on the final particle size, two governing factors are extracted from the CFD simulation results: the time averaged temperature ($T_{avg}$) and the residence time ($t_{res}$) of the aerosol. The residence time indicates the time for which aerosol dynamics have been ongoing in the reactor and thus determines the final particle size. In the present case, particle formation and growth predominantly takes place after the precursor gas exits the feeder tube, which was earlier defined as the refined zone in Figure 2a. Hence the residence time has been defined as the time it takes for the precursor gas to flow from the tube exit to the boundary layer surface ($t_{res} = \sum t_i$). The time averaged temperature can be used to evaluate the temperature history of the aerosol, which will determine the rate of aerosol dynamics. Due to the temporal nature of the aerosol dynamics, the temperature has been averaged on the time scale ($T_{avg} = \sum t_iT_i/t_{res}$). In the present case, similar to the residence time, the time averaged temperature history has been calculated for the refined zone. These two governing factors are used to explain the influence of ACVD process parameters on the particle size distribution arriving at the boundary layer.

Figure 2-6 shows the influence of substrate temperature. With an increase in the substrate temperature, the arrival particle size distribution shifts towards larger sizes and a higher number concentration. This trend is attributed to the rise of the time averaged particle temperature as the substrate temperature rises (Figure 2-6b). The residence time also appears to decrease slightly with
Figure 2-6: Effect of substrate temperature on (a) the particle size distribution (b) the time averaged temperature and (c) characteristic time ratio. The dotted lines indicate the value of the characteristic time ratio ($\tau_{arr}/\tau_{sin}$) for different morphologies observed experimentally by An et. al. [1] (d) SEM images depicting the morphology of the thin films synthesized at various temperatures.
an increase in substrate temperature. Trends of these two factors have opposing effects on the particle size distribution; however, the change in time averaged temperature dominates, leading to the aforementioned trend in the particle size distribution. In addition, we also note that the change in size distribution is more rapid as the substrate temperature rises. It reflects that the time averaged temperature has a nonlinear effect on the particle size distribution, which likely originates from the exponential dependence of the rate of precursor decomposition on the temperature. The change in particle size distribution affects both the $\tau_{arr}$ and $\tau_{sin}$ since both these characteristic times are a function of the particle size. The change in substrate temperature also influences the $\tau_{sin}$ directly because sintering rate depends on the temperature of the substrate in addition to the particle size as shown in eq. (2-11). In addition, a continuous decrease in the CTR is observed with an increase in temperature (Figure 2-6c), which can be attributed to the increasing particle flux (decreasing $\tau_{arr}$) accompanied by an increasing $\tau_{sin}$ seen for larger particles. The effect of substrate temperature was experimentally verified, as shown in Figure 2-6d, by synthesizing nanostructured thin films keeping all of the process parameters for columnar conditions but varying the substrate temperatures from 400°C-600°C. In all cases, a columnar morphology was observed by SEM, but the gradual transition from granular to columnar may not be visible through this characterization technique. Model predictions at 600°C are closer to the granular CTR while the morphology observed experimentally is columnar. This deviation is likely due to the effect of thermophoresis at higher temperatures on the depositing particle size distribution which have not been accounted for in the present work. Branching of a few tall nanostructures was observed for the 400°C substrate temperature. This phenomenon of branching has been previously studied in detail and is a function of the thermal conductivity of the TiO$_2$ columns, which results in lower temperature at
the tip of the column and hence lowers the sintering rate, resulting in the formation of branches [40].

The results of the effect of feeder-substrate distance are shown in Figure 2-7, which indicates that the arrival particle size distribution is only slightly affected by the feeder substrate distance. The lack of any significant effect of this parameter occurs due to the strong opposition between the increase in time averaged particle temperature and the corresponding decrease in the residence time (Figure 2-7b). This also corresponds to a decrease in the $\tau_{arr}/\tau_{sin}$ (Figure 2-7c), however.

![Figure 2-7](image_url)

Figure 2-7: Effect of feeder-substrate distance on (a) the particle size distribution (b) the time averaged temperature and (c) characteristic time ratio.
this decrease is not thought to be significant enough to cause an observable change in the morphology.

The other three process parameters, $Q_0$, $T_0$ and $c_0$, are properties of the precursor flow, which is controlled by the precursor feed system. Figure 2-8a shows the influence of total flow rate on the arrival particle size distribution. In all cases, the precursor concentration was maintained constant at the reference value. Increase in the flow rate results in a decrease in the arrival particle size and

Figure 2-8: Effect of total inflow flow rate on (a) the particle size distribution, (b) the time averaged temperature, and (c) the characteristic time ratio with the SEM images for the corresponding experimental measurements.
the number concentration resulting in a left shift in the arrival particle size distribution (Figure 2-8a). This shift is a result of the decrease in both the time averaged temperature and residence time (Figure 2-8b). These two factors decelerate precursor decomposition and particle growth, and therefore the particle size and concentration drops sharply. This sharp drop is also reflected in a rapid decrease in the CTR, which allows the morphology to be changed just by changing the feed flow rate (Figure 2-8c). The effect of the total flow rate on the morphology of the synthesized nanostructure was also verified experimentally. Decreasing the total flow rate to 1.0 m$^3$.s$^{-1}$ causes the morphology to change from columnar to completely granular, which is in agreement with the simulation. Increasing the feed flow rate to 4.0 m$^3$.s$^{-1}$ causes the morphology to change to an irregular dense morphology, again in agreement with the simulation prediction.

Figure 2-9a presents the influence of initial precursor concentration on the arrival particle size distribution. Due to the low precursor concentration in the feed flow, the concentration of the precursor does not change the fluid flow and energy balance, and hence the time averaged temperature and residence time do not change with the initial precursor concentration. However,
the initial precursor concentration indeed has influence on the particle size distribution, which implies that initial precursor concentration also serves as an essential factor that governs particle evolution. Since the precursor decomposition reaction rate is first order with respect to the precursor, higher precursor concentration leads to a higher generation of TiO$_2$ monomers, and hence results in a higher number concentration and larger particle size, as shown by the simulation results. This effect is translated to the decrease in the CTR with increasing precursor concentration, which can be used to control the morphology of the thin film (Figure 2-9b).

Figure 2-10a shows the influence of feed inlet temperature on the arrival particle size distribution. The increase of feed inlet temperature leads to an increase of both the time averaged temperature and residence time (Figure 2-10b). However, the change in time averaged temperature is again dominant in comparison to the residence time, so the influence of feed temperature is similar with that of the substrate temperature. However, the effect of the feed inlet temperature on the CTR is different than the effect of substrate temperature. Unlike in the case of substrate temperature, the CTR follows the same trend as the particle size distribution in this case and is substantially affected by the feed inlet temperature (Figure 2-10c).

In summary, the time averaged particle temperature, residence time and the initial precursor concentration are three essential factors that govern particle evolution, which could be used to explain and predict the influence of process parameters. Among the five process parameters, the increase of substrate temperature, initial precursor concentration, and feeding flow temperature promotes aerosol generation and growth, resulting in an increase in the arrival particle size and the total number concentration. Alternatively, increasing the feed flow rate has the opposite effect. All process parameters influence the morphology consistent with their influence on the arrival particle
size distribution. Interestingly, the feeder substrate distance has no significant effect on the arrival particle size distribution and hence the morphology of the thin film.

2.5 Conclusions:

A finite element based computational fluid dynamics model was used to simulate the temperature and velocity profile in the ACVD reaction, which was then coupled to a discrete sectional model to obtain the particle size distribution evolution. A characteristic time ratio (CTR), $\tau_{arr}/\tau_{sin}$ was then calculated to predict the morphology of the nanostructured thin film. The effect
of process parameters on the morphology was predicted and an understanding of these effects was
developed based on the particle size distribution, the time averaged temperature, and the residence
time in the reactor. The prediction of morphology obtained by the model was experimentally
verified for two process parameters. The model provides key insights into the role of fluid and
aerosol dynamics, and the ability to predict nanostructure morphology in the ACVD process. This
could be used to provide a better control over the morphology of the synthesized films and help
devise strategies to improve the throughput of the process for scaled-up production. Further, this
modelling approach can be extended to other gas phases deposition processes such as the flame
aerosol deposition process and the electrospray deposition process.

2.6 Acknowledgments:

This work is based upon work supported by the Solar Energy Research Institute for India and the
U.S. (SERIIUS) funded jointly by the U.S. Department of Energy subcontract DE AC36-08G028308 (Office of Science, Office of Basic Energy Sciences, and Energy Efficiency and
Renewable Energy, Solar Energy Technology Program, with support from the Office of
International Affairs) and the Government of India subcontract IUSSTF/JCERDC-SERIIUS/2012
dated 22nd Nov. 2012. Electron microscopy was performed at the Nano Research Facility (NRF)
at Washington University in St. Louis, a member of the National Nanotechnology Infrastructure
Network (NNIN), supported by the National Science Foundation under Grant No. ECS-0335765.
The work of MMY and SQL was supported by the National Natural Science Funds of China (Nos.
51390491 and 51428602), and by the National Key Basic Research and Development Program
(2013CB228506).
2.7 References


Chapter 3

Gold Nanocage Coupled Single Crystal TiO$_2$ Nanostructures for Near-Infrared Water Photolysis

3.1 Abstract:

Gold (Au) nanocages were deposited on single crystal TiO$_2$ columnar thin films and their effect on the photoelectrochemical performance for water oxidation was studied. The performance was compared to spherical Au nanoparticles of similar size (30 nm) deposited on the columns to investigate the shape effect. The performance of spherical Au nanoparticles with a 5 nm diameter was also measured as an indicator of the size effect. All Au-TiO$_2$ thin films exhibited enhanced photocurrents compared to the pristine TiO$_2$ thin film under visible and near-infrared light irradiation. In particular, the nanocage Au deposited TiO$_2$ thin film exhibited the maximum photocurrent, approximately 8 times higher than that by the pristine TiO$_2$ film. Photocurrent action spectra of the thin films confirmed the role of surface plasmon resonance (SPR) in the performance enhancement caused by hot electron injection into the TiO$_2$ conduction band. Light absorption was controlled in the 520 – 810 nm region by change of size and shape of the Au nanoparticles (Figure 3-1). The absorption range of the nanocages in the NIR region with high photocurrent makes them promising candidates for solar water-splitting.

Figure 3-1: Graphical abstract of the work presented in Chapter 3
3.2 Introduction

Titanium dioxide (TiO$_2$) has been widely investigated for its photocatalytic properties since it was first reported by Fujishima and Honda [1] as a candidate for photoelectrochemical splitting of water. Various researchers [2-5] have focused on TiO$_2$ due to its excellent chemical inertness and the strong oxidation potential of photogenerated holes. However, two major issues with TiO$_2$ that remain persistent are high electron hole pair recombination rate within the semiconductor and the large band gap of TiO$_2$ (3.2 eV for anatase) which limits the light absorption to the ultraviolet region (approx. 4% of the solar spectrum) [6].

Attempts have been made at reducing the electron hole pair recombination within the semiconductor by using nanostructured TiO$_2$ films [7, 8], or by coupling with other semiconductors or metal nanoparticles to achieve better charge separation [9, 10]. Recent studies have suggested that one-dimensional structures of TiO$_2$ show better photoelectrochemical performance than other dense films due to higher surface area and a shorter length to be travelled by the hole to reach the surface [11]. The performance of the one dimensional structures is also better than granular films due to the absence of grain boundaries that act as recombination centers [7]. The photoelectrochemical performance of these films depends on the thickness of the films since at very low thickness the performance is light absorption limited while at higher thickness, the performance is limited by the electron-hole pair recombination [11].

Even with a low recombination rate, the use of TiO$_2$ as a photocatalyst is not attractive due to its large band gap. Various attempts have been made to extend the absorption of light by TiO$_2$ in the visible region by doping of the semiconductor with transition metal ions such as copper [12], vanadium [13], niobium [14] or doping with elements such as nitrogen [5], carbon [15], sulfur
[16], or by sensitizing the TiO$_2$ with organic dyes [4] and natural antenna complexes [17]. Another promising approach has been the deposition of nanoparticles of noble metals, such as Au [18, 19], and Ag [20] on the semiconductor. These nanoparticles exhibit a unique phenomenon by which they can absorb visible and near-infrared (NIR) light due to the excitation of the conduction band electrons induced by the oscillating electrical field of the incident light. This phenomenon known as surface plasmon resonance (SPR), creates an electric field near the surface of the nanoparticle which depends strongly on the shape, size and the surrounding medium of the nanoparticles [21, 22]. When such a metal nanoparticle is placed in contact with a semiconductor, and is excited by the incident light at its SPR wavelength, the plasmon created can undergo three possible pathways. These include, scattering which results in re-radiation as a photon, plasmon resonance energy transfer (PRET) to a semiconductor in contact with overlapping absorption band, or absorption by the metal nanoparticle leading to the production of hot electrons which may be thermalized by interaction with phonons or can be injected into the semiconductor in contact [23]. The plasmonic absorption of photon by metal nanoparticles and the subsequent injection of hot electrons into the semiconductor has been exploited to extend the absorption range of wide band gap semiconductors such as TiO$_2$ into the visible range [24]. Also, as described earlier, metal nanoparticles also aid in reducing the electron hole pair recombination. Gold nanocages have in the past been explored for biomedical applications due their remarkable SPR properties [25-27]. They provide the advantage of controlling the SPR in a broad spectral range of 400 – 1200 nm by variation of their size and frame thickness [28]. This broad control over SPR provides the opportunity of using these nanocages for plasmon enhanced water-splitting applications which has not been explored yet.

In this study, the photoelectrochemical performance of gold nanocages coupled single crystal columnar TiO$_2$ films has been examined for water oxidation. This performance has been compared
to spherical gold nanoparticles of different sizes deposited on the single crystal TiO$_2$ films. Further, this paper reports the performance of the Au-TiO$_2$ nanocomposite films under different irradiation spectra. The incident photon to current conversion efficiency (IPCE) was also measured and the effect of size and shape of the nanoparticles on the performance has been discussed.

3.3 Experimental Methods:

The aerosol chemical vapor deposition (ACVD) process is a one-step method to synthesize nanostructured thin films of metal oxides [11]. TiO$_2$ thin films were synthesized using the (ACVD) process on conductive indium tin oxide (ITO) coated glass substrates (Delta Technologies, Stillwater, MN). Titanium tetraisopropoxide (TTIP) (Sigma-Aldrich) was used as the precursor with a feed rate of $1.15 \times 10^{-6}$ mol min$^{-1}$ by bubbling 0.45 L min$^{-1}$ of nitrogen in an indigenous bubbler maintained at a constant temperature of 21$^\circ$C. A dilution flow of nitrogen (0.45 L min$^{-1}$) was used and the residence time of particles within the reactor was 20 ms. The particles were deposited onto an ITO coated glass substrate held at 550$^\circ$C for 65 mins. The morphology of the synthesized thin films was characterized using scanning electron microscopy (SEM) (FESEM, NOVA NanoSEM 230, FEI Co.) and the crystal structure of the thin film was characterized by X-ray diffraction (XRD) (Rigaku D-MAX/A Diffractometer, Cu-K$\alpha$ radiation).

Gold nanoparticles (Au NPs) of different shapes and sizes were synthesized using wet-chemical methods [29-31]. Small spherical Au NPs (SS Au) were synthesized by the citrate reduction method [29]. Large Spherical Au NPs (LS Au) were synthesized by a two-step seed mediated growth method [30]. Au nanocages (NC Au) were synthesized from Ag nanocubes by the galvanic replacement method wherein the Ag nanocubes serve as sacrificial templates for the synthesis of Au nanocages [31]. The shape and size of the synthesized particles was characterized using
transmission electron microscopy (TEM) (Technai™ Spirit, FEI Co.). The mass concentration of the gold nanoparticles in solution was measured using inductively coupled plasma mass spectrometry (ICP-MS) (ELAN DRCII, PerkinElmer) and the absorption spectra was measured using a UV-Vis-NIR spectrometer (Varian CARY 100) equipped with a diffuse reflectance accessory. From the mass measurements and from the size and shape observed from TEM, the number concentration of the gold nanoparticles was calculated. The Au NP suspensions were spin coated onto the TiO₂ thin film. Each thin film was spin coated by 100 μL of the gold NP suspension at 700 rpm for one minute. This process was repeated 50 cycles. Post spin coating, the thin films were characterized by UV-Vis-NIR absorption spectra and TEM.

The photoelectrochemical performance of the films was measured using a three electrode system. 0.05 M NaOH (Sigma Aldrich) (pH = 12.7) was used as the electrolyte and Ag/AgCl (saturated NaCl) (BASi) was used as the reference electrode. A potentiostat (Versastat 300, Princeton Applied Research) was used for testing the performance of the films. A xenon lamp (450 W) (Oriel, Newport Corporation) was used as the light source. To investigate the performance of the films under visible light illumination, a 400 nm cut off filter was placed in front of the light source. IPCE measurements were carried out in the same photoelectrochemical system at an applied bias of 0 V vs Ag/AgCl electrode. A monochromator (Model 275, Acton Research Corporation) with a resolution of ±20 nm was used in front of the xenon light source to fix the incident wavelength on the sample. The IPCE measurement was measured at wavelengths ranging from 400 – 950 nm at an interval of 50 nm. The IPCE was calculated according to the following equation [32]:
\[ IPCE \, (\%) = \frac{[1240 \times J_{sc} \left( \frac{A}{cm^2} \right)]}{[\Sigma \lambda (nm) \times I_{inc}(\lambda) \left( \frac{W}{cm^2} \right)]} \times 100 \]  

(3-1)

where \( J_{sc} \) is the current measured at an applied potential and \( I_{inc} \) is the incident intensity for a particular wavelength \( \lambda \) nm.

### 3.4 Results and Discussion

For the present study, single crystal columnar TiO\(_2\) thin films with a column height of 1.6 \( \mu \)m were synthesized since previous studies have shown that this is the optimal morphology and height for photoelectrochemical performance of TiO\(_2\) films [11]. Figure 3-2a shows the SEM images of the columnar TiO\(_2\) thin films with an average column height of 1.6 \( \mu \)m. XRD spectra of the films confirm a single crystal structure of anatase TiO\(_2\) with a high (112) plane orientation and a minimal of the (004) plane orientation (Figure 3-2b). The high orientation along the (112) plane indicates the absence of grain boundaries and thus makes the columns efficient for electron transport.

![Figure 3-2: (a) Cross section SEM image and (b) XRD spectra of the columnar TiO\(_2\) thin films synthesized by the ACVD process.](image)
The TEM images of the gold nanoparticles (Figure 3-3 inset) show SS Au NPs with a mean diameter of 5 nm; LS Au NPs with a mean diameter of 30 nm; and NC Au NPs with a mean edge length of 30 nm and a frame thickness of 3.5 nm. The SPR peak of the nanoparticles in suspension measured by the UV-Vis-NIR spectroscopy (Figure 3-4) were found to be at 512 nm, 540 nm and 780 nm for the SS Au, LS Au and NC Au nanoparticles respectively. Since the shape and size of the gold nanoparticles were different, mass or number normalization on the TiO$_2$ films would result in a bias towards smaller or larger nanoparticles respectively. Hence, absorption intensity, which is an indication of plasmon intensity generation by the Au NPs, was chosen as the constant metric for comparison of the photoelectrochemical performance of the Au-TiO$_2$ nanocomposite thin
films. The number concentration of gold nanoparticles in the suspension was fixed at $2.09 \times 10^9$ #/mL for the LS Au NPs and for the NC Au NPs. However, for the SS Au NPs, a higher number concentration ($3.52 \times 10^{11}$ #/mL) was used so as to obtain similar absorption intensities of the Au-TiO$_2$ nanocomposite films.

Figure 3-5 shows the UV-Vis-NIR spectra of the pristine TiO$_2$ films and the Au:TiO$_2$ composite films. From the spectra of the pristine TiO$_2$, the indirect bandgap of TiO$_2$ was computed using a Tauc plot (Figure 3-5a inset) and was found to be 3.27 eV. The absorption spectra of the Au:TiO$_2$ films measured post spin coating confirmed that Au NPs exhibited SPR in all the Au-TiO$_2$ nanocomposites. The absorption spectra establishes the visible and near IR absorption by the composite films. A slight shift in the SPR peak of the Au-TiO$_2$ nanocomposite films as compared to the Au colloidal solutions was observed (Table 3-1). This was due to the change in inter-particle distance and the surrounding medium of the Au nanoparticles [21]. TEM images (Figure 3-3) confirmed the attachment of the Au nanoparticles on the TiO$_2$ columns. Additionally,
by comparing the TEM images of Au NPs in solution and after spin coating on the TiO$_2$ columns, no change in Au particle size or shape was observed after attachment on the TiO$_2$ columns.

Figure 3-6a shows the photoelectrochemical performance of the films under broad wavelength illumination ($\lambda > 250$ nm) by a Xenon lamp. A significant increase (200 $\mu$A/cm$^2$) was observed in the saturated photocurrent for the SS Au-TiO$_2$ sample as compared to the pristine TiO$_2$ sample. Additionally, a slight negative shift was observed in the onset potential of the SS Au-TiO$_2$ sample compared to the pristine TiO$_2$ sample. However, no significant change was observed in either the saturated photocurrent or the onset potential for the other Au-TiO$_2$ samples (Table 3-1). Dark current measurements were also carried out and the currents were almost zero in all cases. To probe the difference in photoelectrochemical performance, the potential dependence of the squared photocurrent density was investigated. Provided that the absorption coefficient is not very high, for a crystalline semiconductor, the squared photocurrent ($i_{ph}^2$) obeys the following relation [33, 34]:

\[
i_{ph}^2 = \left( \frac{2\varepsilon\varepsilon_0I^2\alpha}{N} \right) (V - V_{fb})
\]

\[ (3-2) \]
where \( \alpha \) is the absorption coefficient, \( V \) is the applied potential, and \( V_{fb} \) is the flat-band potential. Figure 3-6b shows the squared photocurrent density as a function of the applied voltage. The linear part of the curve was fitted to equation (3-2) to calculate \( V_{fb} \). A negative shift in \( V_{fb} \) of 23 mV was observed for the SS Au-TiO\(_2\) films as compared to the pristine TiO\(_2\) film. This shift in the flat band potential closer to the conduction band of TiO\(_2\) due to the attached SS Au particles enables better charge separation and represents higher reducing nature of the Au-TiO\(_2\) nanocomposite system; hence the saturated photocurrent increase was observed in Figure 3-6a. Gold nanoparticles placed in contact with a semiconductor can store electrons in a quantized manner, shifting the

![Figure 3-6: (a) Photocurrent density versus voltage and (b) corresponding squared photocurrent density versus voltage curves of the Au-TiO\(_2\) nanocomposite films under broad wavelength illumination (\( \lambda > 250 \text{ nm} \)) (c) Photocurrent density versus voltage of the Au-TiO\(_2\) nanocomposite films under visible light illumination (\( \lambda > 400 \text{ nm} \)).](image-url)
Fermi level of the gold nanoparticles to more negative potentials [35, 36]. This shift causes the Fermi level of the Au-semiconductor composite system to shift to more negative potentials as a result of charge equilibration. This negative shift in the Fermi level due to the attachment of gold nanoparticles on a semiconductor surface has been previously referred to as the Fermi level equilibration effect [32]. However, no significant shift (<5mV) in the flat band potential was observed for the larger size of Au nanoparticles since Fermi level shift strongly depends on the size of the Au nanoparticle and would be insignificant for Au particle size greater than 15 nm [37].

Figure 3-6c shows the photoelectrochemical performance of the films under visible and NIR light illumination (\(\lambda > 400\) nm). Ideally, the photocurrent of the pristine TiO\(_2\) should be zero since the energy of incident light (<3.1 eV) is less than the band gap of TiO\(_2\) (\(\approx 3.27\) eV). However, a small photocurrent was observed for the pristine TiO\(_2\) films which was probably due to a bulk excitation process associated with the defect states in TiO\(_2\) [38]. A substantial increase was observed in the saturated photocurrent for all the Au-TiO\(_2\) samples as compared to the pristine TiO\(_2\) samples. The maximum increase was observed for the NC Au-TiO\(_2\) films (7.8×) followed by SS Au-TiO\(_2\) (6.0×) and LS Au-TiO\(_2\) (3.9×) as compared to the pristine TiO\(_2\) films (Table 3-1). The performance under visible and NIR light reflects the sub band gap excitation of the Au-TiO\(_2\) nanocomposites and hence the saturated photocurrent values were less than 1% of the saturated photocurrent observed under UV-Vis-NIR irradiation. This enhancement in photocurrent was not associated with any change in the onset potential of the nanocomposites and thus was not caused by any change in the flat band potential of the semiconductor.

To get a better understanding of the visible light activity of the films, the IPCE of the films was measured. Figure 3-7 shows the IPCE data plotted as a function of the incident wavelength. Unlike pristine TiO\(_2\) films, for the Au-TiO\(_2\) composites, we observed that the IPCE curve follows the same
The IPCE peaks for the SS Au-TiO$_2$, the LS Au-TiO$_2$, and the NC Au-TiO$_2$ were observed at 522 nm, 554 nm and 803 nm respectively. The occurrence of these peaks at the SPR of Au nanoparticles confirms that the increased performance of the Au-TiO$_2$ films under visible light illumination is due to the SPR property of the Au nanoparticles. Hot electrons generated above the Fermi level due to the plasmonic absorption either thermalize, via electron-electron coupling or via electron-phonon coupling, or by collective oscillations may gain enough energy to overcome the Schottky barrier and be subsequently injected into the conduction band of TiO$_2$ [39] followed by efficient transport through the single crystal TiO$_2$ column (Figure 3-8a). The time of electron transfer from spherical Au nanoparticles to TiO$_2$ nanoparticles has been reported to be less than 50 fs [40], much lesser than the thermalization time of the plasmon which has been reported to be greater than 2 ps [41].

Figure 3-7: Photocurrent action spectra (IPCE) of the Au-TiO$_2$ nanocomposite films.
thus making the transfer feasible. Back electron transfer time from spherical TiO$_2$ to Au nanoparticles has been estimated to be of the order of a few nanoseconds with a strong dependence on the TiO$_2$ particle diameter and the sample preparation method [39]. A higher back electron transfer time is expected for the transfer from columnar TiO$_2$ to the Au nanoparticles since the columns are single crystal structures with a well-defined space charge layer thus impeding the back electron transfer process [18].

Comparing the effect of size of the particles on the IPCE performance of the films, we observe that increasing the size of the spherical Au nanoparticles from 5 nm to 30 nm, resulted in a slight red shift in the IPCE peak concurrent with the UV-Vis-NIR absorption spectra. However, although the absorption peak intensities of the spherical Au-TiO$_2$ films were similar, indicating similar photon absorption leading to plasmon generation (hot electrons) at the excited peak, the IPCE peak of the LS Au-TiO$_2$ was much lower than that of the SS Au-TiO$_2$. The relaxation time of the hot electrons is not a function of the particle shape and size and is similar to bulk gold [42]. However,
the total interfacial contact area of TiO$_2$ structures with the SS Au particles is much higher than
with the LS Au particles. This suggests that the smaller spheres are more efficient in transferring
the generated hot electrons to TiO$_2$ as compared to the larger spheres due to the enhanced
interfacial surface area (Figure 3-8b). Additionally, the SS Au-TiO$_2$ films also show an enhanced
IPCE (≈10.5%) at 400 nm compared to the other films (≈6%). At 400 nm the IPCE is still likely
to be from the band gap excitation of TiO$_2$ owing to the resolution of the monochromator. Thus
the enhancement for the SS Au-TiO$_2$ composite films may be attributed to the Fermi level
equilibration effect described earlier in the discussion.

Comparing the effect of shape for particles of similar size, the LS Au-TiO$_2$ and the NC Au-TiO$_2$
have the same number concentration of gold nanoparticles spin coated on it. However, the intensity
of the IPCE peak of the NC Au-TiO$_2$ at 803 nm was significantly higher (1.85×) than that of the
LS Au-TiO$_2$ at 554 nm. Hollow nanostructures such as nanocages exhibit coupling of the surface
plasmon field on the interior and the exterior walls leading to a stronger surface plasmon resonance
field [43]. Also, nanocages have a thin frame and sharp edges leading to a focused SPR compared
to a large spherical particle where the SPR is more diffuse [44]. It should also be noted that due to
the geometry of the nanocages, the surface plasmon wave is nearer to the TiO$_2$ surface which
results in a smaller average diffusion length for the hot electrons to reach the Au-TiO$_2$ interface
(Figure 3-8b). Hence, there exists a much higher probability of hot electron transfer into the TiO$_2$
conduction band than thermalization. This strong focused surface plasmon field coupled with the
geometry leads to a more efficient hot electron transfer and thus a much higher IPCE of the NC
Au-TiO$_2$. In addition, the IPCE of the NC Au-TiO$_2$ was higher than the LS Au-TiO$_2$ sample in
most of the visible range due to a wide range of photon absorption, since the SPR for nanocages
is very sensitive to the dimensions of the cage. A 2 nm change in wall thickness leads to a 110 nm shift in the SPR peak [28].

### 3.5 Conclusions

This study shows that Au-TiO$_2$ nanocomposites can be used to perform photoelectrochemical oxidation of water in the visible and NIR region by hot electron injection from the Au nanoparticle into the TiO$_2$ conduction band. In the UV region, the small spherical gold nanoparticles enhance the photoelectrochemical performance of pristine TiO$_2$ by shifting the flat band potential closer to the conduction band. In the visible and NIR region, nanocages exhibit higher performance efficiency than spherical nanoparticles of the same size. Additionally, the absorption intensity of the nanocages in the NIR region makes them more suitable candidates than small spherical gold nanoparticles which absorb in the visible range. Also, it has been demonstrated that control over shape and size can be used to achieve possible tuning of the absorption range over broad wavelengths and thus address the issue of the high band gap of TiO$_2$.

### 3.6 Acknowledgements

This work is supported in part under the US-India Partnership to Advance Clean Energy-Research (PACE-R) for the Solar Energy Research Institute for India and the United States (SERIIUS), funded jointly by the U.S. Department of Energy (Office of Science, Office of Basic Energy Sciences, and Energy Efficiency and Renewable Energy, Solar Energy Technology Program, under Subcontract DE-AC36-08GO28308 to the National Renewable Energy Laboratory, Golden, Colorado) and the Government of India, through the Department of Science and Technology under Subcontract IUSSTF/JCERDC-SERIIUS/2012. Electron microscopy was performed at the Nano Research Facility (NRF) at Washington University in St. Louis, a member of the National
Nanotechnology Infrastructure Network (NNIN), supported by the National Science Foundation under Grant No. ECS-0335765.

3.7 References


Chapter 4

One-Step Aerosol Route Synthesis of Oriented One-Dimensional Additive-Free Single Crystal TiO$_2$ Nanostructured Anodes for High Rate Lithium Ion Batteries

The results presented in this chapter were published in – Chadha, Tandeep S., Alok M. Tripathi, Sagar Mitra, and Pratim Biswas. "One-dimensional, additive-free, single-crystal TiO$_2$ nanostructured anodes synthesized by a single-step aerosol process for high-rate lithium-ion batteries." Energy Technology 2(11) (2014): 906-911. Reproduced with permission from John Wiley and Sons, copyright 2014.
4.1 Abstract

Highly oriented, single crystal dendritic TiO$_2$ nano-columns were fabricated using a single step aerosol chemical vapor deposition (ACVD) process on stainless steel current collectors for use as high rate lithium-ion battery anodes (Figure 4-1). The synthesized nanostructures exhibited the highest specific capacity (183.5 mA.h g$^{-1}$ after 100 cycles at 1 C rate) ever reported for anatase TiO$_2$ without the use of any conductive additive or binding agents. Exceptional cycling performance and rate capability was also demonstrated making them an ideal electrode for high rate applications with no change in nanostructure morphology even after 100 cycles. At a current density of 16.75 A.g$^{-1}$ (50 C rate), the specific charge capacity of the columnar nanostructures was 278% higher than that of the granular nanostructures synthesized by the same technique. This facile, low cost synthesis of high performance anodes thus provides a single step scalable alternative to the conventional fabrication of anode materials.

Figure 4-1: Graphical abstract for the work presented in Chapter 4
4.2 Introduction

The increasing cost of fossil fuel resources and the concerns over greenhouse gas emissions from these sources has led to an increased demand in electric vehicles (EVs) and hybrid electric vehicles (HEVs), a critical component of which is the lithium ion battery (LIB) [1]. Efforts are underway on improving the energy density, power capability, durability and safety of the LIB while decreasing the cost [2]. Titanium dioxide has emerged as an attractive anode material for LIBs in such applications due to its advantages of minimal volume expansion (4% for anatase) upon lithium intercalation and an operating voltage of 1.0 to 3.0 V thus promising superior safety and performance over the conventional graphite anode [3, 4]. Moreover, the oxide contains earth abundant elements and hence the cost of fabrication is relatively low. However, these advantages are contrasted by several shortcomings which include poor electrical conductivity (1.9 × 10⁻¹² S m⁻¹) [5] owing to the semiconductor nature of the material and low mobility of the Li⁺ ions (10⁻¹¹ to 10⁻¹³ cm s⁻¹) [6, 7] in the crystal structure, both of which lead to a poor rate capability. Further, the theoretical bulk capacity is limited to 167.5 mA.h g⁻¹ based on 0.5 Li⁺ ion uptake per formula unit [8]. The poor electrical conductivity has often been addressed by the addition of carbon based conductive additives [9, 10] or more recently by the addition of graphene [11-13], while the other two shortcomings have been addressed by structuring the electrode in the form of nanoparticles [14], nanorods [15], nanotubes [16], nanosheets [17], and nanodisks [18] which provides a reduced path for Li⁺ diffusion and a higher surface area at the electrolyte/electrode interface resulting in surface storage of the Li⁺ ions [19]. The advantages of nanostructuring are however very limited in current systems due to the conventional electrode fabrication process. This fabrication process is a two-step process involving the synthesis of active material followed by doctor-blading the active material along with the carbon additive and an electrically insulating binding agent onto the
current collector. This limits the ability to make electrodes with oriented structures and leads to aggregation of the nanostructures during electrode preparation or cycling. Further, the presence of the non-active binder and conducting additive decreases the specific capacity of the battery [20]. Although, a few studies have attempted the fabrication of TiO$_2$ nanostructures directly onto the current collector, the performance of these anodes at high rates degraded significantly [9, 21].

In this work, we have resolved the above drawbacks using a novel approach (Figure 4-2a) with several benefits which have allowed us to achieve the highest specific capacity (183.5 mA.h g$^{-1}$ after 100 cycles at 1 C rate) ever reported for anatase TiO$_2$. First, TiO$_2$ nanostructures have been grown directly on the current collector making it a single step process for the fabrication of battery anodes without the use of any binding agents or conductive carbon additives. This technique overcomes the limitations of the oriented attachment of the nanostructures to the current collector, decreases the contact resistance at the metal-semiconductor interface [9], and makes these nanostructures exceptionally stable to Li$^+$ intercalation and de-intercalation during cycling. Second, the synthesized nanostructures are one-dimensional single crystal anatase structures, imparting excellent electrical conductivity and high Li$^+$ mobility due to the absence of grain boundaries [22]. The excellent electrical conductivity obviates the need of adding any conductive additive to the electrode since each of these single crystal columns is electrically connected to the current collector, thus contributing to the capacity [23]. Third, these are highly oriented nanostructures with crystal plane orientations engineered to provide a directed Li$^+$ diffusion into and out of the structure and fourth, the nanostructures have a dendritic form with an exceptionally high surface area [24], thus leading to a high electrode/electrolyte interfacial area.

The unique TiO$_2$ nanostructures were synthesized using the aerosol chemical vapor deposition (ACVD) process,[25] The process involves the formation of metal oxide monomers, by thermal
decomposition of an organometallic precursor at elevated temperatures, which then nucleate and grow to form particles. These particles deposit onto a heated substrate where they sinter to form thin films. By controlling the arrival particle size and the sintering rate of these particles, the morphology of the thin film can be controlled. The ACVD process has previously been used for the synthesis of nanostructured TiO$_2$ and NiO for photo water splitting[25], dye-sensitized solar cells,[22] and CO$_2$ photoreduction[24] applications. Since this process is facile, continuous and scalable, the cost of fabrication of nanostructured thin films is extremely low.

4.3 Experimental Methods:

4.3.1 Thin film synthesis and electrode preparation

Stainless Steel (SS316, ESPI Metals, OR, USA) with a thickness of 25μm and punched into 15 mm diameter discs were used as the current collector. Nanostructured thin films of TiO$_2$ with different morphologies were synthesized using the ACVD process on the current collector sheets. Titanium tetraisopropoxide (TTIP) (97%, Sigma-Aldrich, MO, USA) in an indigenous bubbler was used as the precursor for TiO$_2$. Nitrogen was used as the carrier gas for the precursor and as the dilution gas in the reactor. The particles were deposited on the stainless steel discs, maintained at varying temperature for 30 mins. The morphology of the thin films was controlled by varying the process parameters in the system (Table 4-1).

Table 4-1: Process parameters for the synthesis of columnar and granular nanostructures by the ACVD process

<table>
<thead>
<tr>
<th>Film Morphology</th>
<th>Deposition Time (mins)</th>
<th>Total flow (slm)</th>
<th>Precursor concentration (mol.m$^{-3}$)</th>
<th>Residence time (ms)</th>
<th>Substrate Temperature (°C)</th>
<th>Film Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Columnar</td>
<td>30</td>
<td>0.90</td>
<td>1.28×10$^{-3}$</td>
<td>20</td>
<td>450</td>
<td>0.8-1.0</td>
</tr>
<tr>
<td>Granular</td>
<td>30</td>
<td>0.50</td>
<td>1.81×10$^{-2}$</td>
<td>36</td>
<td>550</td>
<td>0.9-1.0</td>
</tr>
</tbody>
</table>
Post deposition, the discs were dipped in 1.2 M HCl solution for 20 mins followed by rinsing with deionized water and acetone to remove any impurity from the surface. The samples were dried in an oven maintained at 85°C for 12 hours.

4.3.2 Structure and morphology characterization

The morphology of the synthesized nanostructures was characterized using scanning electron microscopy (SEM) (FESEM, NOVA NanoSEM 230, FEI Co.). The crystal structure of the prepared sample was characterized using X-Ray diffraction (XRD) (Rigaku D-MAX/A Diffractometer, Japan) with a CuKα radiation (wavelength = 1.5406 Å) at 35 kV and 35 mA. The scattering angle (2θ) used in the measurement was from 20° to 60° with a step size of 0.02° and a dwell time of 2 sec. The detail crystal orientation, selected area electron diffraction (SAED) and morphology study before and after cycling was done with high resolution transmission electron microscopy (HR-TEM) (FEG-TEM, JEOL J2100F) operated at 200kV.

4.3.3 Electrochemical measurements

Coin cells (CR2032) with the TiO2 deposited stainless steel discs as the working electrode and lithium metal foil as the counter electrode were assembled in an Ar-filled glovebox (Unilab, MBraun Inc.) with O2 and H2O concentrations maintained at <0.1ppm levels. The electrodes were separated by a Whatman GF/D filter saturated with 1M LiPF6 electrolyte solution in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) with EC:DMC:DEC::1:1:1 volume ratio (MTI corporation, CA, USA). The assembled cells were aged for 36 hours before testing. The electrochemical characterization was carried out using a multichannel potentiostat/galvanostat (Bio-logic USA) in a potential range of 1.0 V to 3.0 V at a constant temperature of 22°C. The cycling rates were calculated on the basis of 1 Li+ exchanged
per formula unit of TiO$_2$ in 1 h (denoted 1 C) corresponding to a theoretical capacity of 335 mAh g$^{-1}$. The mass of the deposited TiO$_2$ was calculated by weighing the stainless steel discs before and after deposition of TiO$_2$.

4.4 Results and Discussion

One dimensional TiO$_2$ nanostructured thin films (columnar TiO$_2$) with a column height of 800-1000 nm (Figure 4-2b) were synthesized on stainless steel current collector foils using the ACVD process. The columns tapered at both the edges with a diameter of 150-200 nm in the thickest region. The strong diffraction peak in XRD spectra (Figure 4-2c) for the columnar TiO$_2$ structures with a Lotgering factor [26] of 1.0 indicates single crystal structures perfectly oriented along the anatase [112] direction. High resolution transmission electron microscopy (HR-TEM) (Figure 4-2e) of a single 800 nm tall column with a maximum column width of 200 nm and a tip width of 30 nm further shows the dendritic structure and confirms a d-spacing of 0.23 nm on the tip surface corresponding to a preferential growth in the [112] direction of anatase TiO$_2$ nanostructure. The selected area diffraction (SAED) (Figure 4-2f) at the tip of the column shows line patterning in the diffraction spot clearly indicating the presence of a highly ordered and crystalline phase of the TiO$_2$ nanostructure. The SAED spots near the central area correspond to the (020) plane and the (200) planes which are at an angle of 90° and the zonal axis of the SAED pattern is along the [001] direction. To investigate the role of the single crystal dendrites and preferred orientation, granular TiO$_2$ nanostructures with a similar height were synthesized by the same process with a change in operating conditions (Table 4-1). XRD pattern of the granular nanostructures shows a higher presence of (101) anatase crystal plane, compared to the columnar nanostructures, indicating the presence of grain boundaries and leading to a Lotgering factor of 0.89.
Figure 4-2: (a) Overview of the nanostructure fabrication by the ACVD process. TiO$_2$ nanostructures are synthesized directly on the stainless steel current collector and are assembled as anodes in a lithium ion battery. SEM images of the (b) columnar and (d) granular nanostructures. (c) XRD spectra of the different TiO$_2$ nanostructures synthesized by the ACVD process. Anatase standard diffraction data is from JCPDS No. 071-1166. (d) HR-TEM image of the columnar structure. Inset shows the crystal lattice at the tip of the column. (e) SAED pattern at the tip of the column.
To validate the structural merits of the nanostructures, electrochemical characterization was carried out in a half-cell configuration with the nanostructured TiO\(_2\) thin film as the anode. We first investigated the redox couple of the intercalation and de-intercalation of Li\(^+\) in the TiO\(_2\) crystal lattice by performing cyclic voltammetry of the cell (Figure 4-3a). At a scan rate of 1.0 mV/s, distinct, sharp, single anodic and cathodic current peaks were observed at 1.65 V and 2.22 V for columnar TiO\(_2\) implying the presence of phase pure anatase TiO\(_2\) [27]. The peak current scaled with the square root of the scan rate as expected for diffusion controlled irreversible kinetics (Figure 4-3a inset) (Figure S 4-1) [28]. Similar peaks were observed for the granular structure at 1.62 V and 2.23 V (Figure S 4-2). No peak shift was observed after the 1\(^{st}\) cycle in both the nanostructures indicating excellent reversibility of the lithium intercalation/de-intercalation reactions [10]. The reversible charge transfer was 97.16\% and 92.5\% for the columnar and granular structures respectively, substantiating the superior activity of the columnar structure over the granular structure for charge storage.

The galvanostatic charge discharge measurement performed for the columnar TiO\(_2\) nanostructures (Figure 4-3b) at 1 C rate (=335 mA g\(^{-1}\)) depicts an initial discharge capacity of 240.06 mA.h g\(^{-1}\), 83.76\% higher (130.64 mA.h g\(^{-1}\) for granular TiO\(_2\)) than that of the granular TiO\(_2\) nanostructure (Figure 4-3d). The initial charge capacity of the columnar TiO\(_2\) nanostructure was 207.80 mA.h g\(^{-1}\) yielding a columbic efficiency of 86.56\%. Subsequent columbic efficiencies were 92.40 \% and 95.03\% for the second and the third cycle respectively (Figure S 4-3). The increasing columbic efficiency with the increasing number of cycles indicates a decreased loss of Li\(^+\) ion in the crystal lattice of the anatase structure due to various secondary irreversible reactions. Upon analysis of galvanostatic cycling at higher current densities upto 3.35A.g\(^{-1}\) (10 C rate) (Figure 4-3c), we observe certain characteristic attributes. First, the electrode shows reversible behavior in the entire
current density range with high cumbic efficiencies (>95%). Second, two distinct plateaus at
~1.6-1.8 V and at ~1.9-2.2 V were observed in all cases, coherent with the anodic and cathodic
current peak positions in the cyclic voltammetry study. The discharge (anodic) plateau (denoted
as region II in Figure 2b) is representative of the Li⁺ insertion into the octahedral sites of anatase
TiO₂ leading to a biphasic formation of the Li-poor (Li₀.₀₅TiO₂) and the Li-rich (LiₓTiO₂; x≤₀.₅)
phase [29]. The capacity contribution from the following decline in voltage from 1.7 V to 1.0 V
(region III) corresponds to the surface storage of Li$^+$ ions after all the interstitial octahedral sites inside the crystal lattice are filled, which is a purely capacitive behavior known for TiO$_2$ [30]. Region II was the highest contributor to the loss of capacity with increasing current density evident of sluggish diffusion at higher current densities complimenting the earlier finding from cyclic voltammetry that the lithium intercalation kinetics is diffusion limited. Interestingly, the same region is accountable for the decreased capacity of the granular structures compared to the columnar structures of similar height signifying higher Li mobility in the columnar nanostructures. At a fixed current density, the potential difference between the two plateaus is lower for the columnar nanostructures than the granular nanostructures signifying lower charge transfer resistance in the columnar structures [31]. This higher Li mobility and the lower charge transfer resistance is attributed to the absence of grain boundaries in the single crystal columnar nanostructures [32]. Additionally, as mentioned earlier, the granular structures have a higher orientation along the (101) plane in comparison to the columnar structures which are perfectly oriented along the (112) plane. The surface energy of the (112) plane is $\approx$0.97 J m$^{-2}$ [33], higher than that of the (101) plane ($\approx$0.65 J m$^{-2}$), enabling higher lithium intercalation [34]. This validates our hypothesis that the columnar TiO$_2$ nanostructures exhibit improved performance due to their unique oriented single crystal dendritic structure.

Remarkable cycling performance was observed for the columnar TiO$_2$ nanostructures with 86.24% (183.49 mA.h g$^{-1}$) capacity retention (against 3$^{\text{rd}}$ cycle discharge capacity) after 100 cycles at 1 C rate (Figure 4-4a). To the best of our knowledge, this is the highest specific capacity after 100 cycles ever reported for anatase TiO$_2$ at a current density of 335 mA.g$^{-1}$ (Table S 4-1). In comparison, the granular structures demonstrated only 79.28% capacity retention under the same conditions. Even at higher cycling rates, the columnar nanostructures exhibited excellent capacity
retention of 87.28% (150.79 mA.h g\(^{-1}\)) , 88.59% (121.18 mA.h g\(^{-1}\)), and 86.80% (89.56 mA.h g\(^{-1}\)) for 2 C, 5 C and 10 C rate respectively after 100 cycles. This establishes the incredible structural stability of the columnar TiO\(_2\) nanostructures to lithium intercalation/de-intercalation which was further confirmed by ex-situ TEM analysis of the cycled anode (100 cycles at 1 C rate) (Figure 4-4c).

![Figure 4-4: (a) Cycle performance of the columnar nanostructures at varying cycling rates (1 C-10 C rate) and granular nanostructures at 1 C rate for 100 cycles. TEM image of the columnar nanostructure (b) before cycling and (c) after 100 cycles. Inset shows the amorphous SEI layer formed on the TiO\(_2\) nanostructure after cycling. (d) Rate capability of the columnar and the granular nanostructures. The charge rate was varied from 1 C to 50 C while the discharge rate was kept constant at 1 C. (e) Structural uniqueness of the dendritic columnar structure over the granular structure and its benefits to battery operation.](image-url)
Except for the formation of a ~10 nm thick amorphous layer, no structural change was observed in the columns or its dendritic branches. The amorphous layer is attributed to the formation of a solid electrolyte interface (SEI) layer which was confirmed by the presence of extra peaks for phosphorus and fluorine in the EDAX analysis of the cycled electrode (Figure S 4-4).

Rate capability analysis of the nanostructures further highlights the superiority of the columnar structures over the granular structures (Figure 4-4d). The specific charge capacity ratio between the columnar and the granular structure widens with increasing charging rates (115% at 1 C to 278% at 50 C) making the performance of the granular structures more susceptible to higher cycling rates due to the presence of grain boundaries. For the columnar structures, a charge capacity retention of 72.04% and 46.26% even at high charging rates of 20 C (=6.70 A g\textsuperscript{-1}) and 50 C (=16.75 A g\textsuperscript{-1}), respectively, makes them suitable for use as high rate anodes without the use of any conductive additives. Upon reducing the charging rate back to 1 C, the capacity retention was 96.5% for the columnar nanostructures and 91.70% capacity for the granular nanostructures.

4.5 Conclusions:

In summary, we have demonstrated that the use of single crystal, highly oriented dendritic TiO\textsubscript{2} nanostructures can lead to excellent electrochemical performance without the use of any binding agents or conductive additives. With these columnar nanostructures we have been able to achieve the highest specific capacity ever reported for anatase TiO\textsubscript{2} and remarkable cycling behavior even at high cycling rates of 10 C (3.35 A g\textsuperscript{-1}). The nanostructures exhibit excellent rate capabilities, which in conjunction with the safety associated with phase pure anatase TiO\textsubscript{2}, makes them suitable for high rate applications in EVs and HEVs. This exceptional performance has been attributed to four key factors (Figure 4-4e): (1) The single crystal nature which provides higher electronic
conductivity and higher Li$^+$ mobility through the structure, (2) perfect orientation along the high surface energy (112) plane which enables higher lithium intercalation (3) the direct fabrication of the 1D nanostructure on the current collector which provides enhanced structural stability and (4) the dendritic structure that provides a high surface area at the electrode-electrolyte interface. Furthermore, the facile single step synthesis route makes the fabrication of these nanostructured anodes scalable at low cost. A similar approach for the synthesis of single crystalline, oriented nanostructures directly on the current collector could be used for other materials associated with lithium ion batteries, thereby enhancing their performance.

### 4.6 Acknowledgements

This work is based upon work supported under the US-India Partnership to Advance Clean Energy-Research (PACE-R) for the Solar Energy Research Institute for India and the United States (SERIIUS), funded jointly by the U.S. Department of Energy (Office of Science, Office of Basic Energy Sciences, and Energy Efficiency and Renewable Energy, Solar Energy Technology Program, under Subcontract DE-AC36-08GO28308 to the National Renewable Energy Laboratory, Golden, Colorado) and the Government of India, through the Department of Science and Technology under Subcontract IUSSTF/JCERDC-SERIIUS/2012 dated 22nd Nov. 2012. Alok M. Tripathi acknowledges the support by the McDonnell Academy Global Energy and Environment Partnership (MAGEEP) for a visiting fellowship at Washington University in St. Louis.
4.7 References:


4.8 Supplementary Information

Figure S4-1: Cyclic voltammograms of the columnar nanostructures at a scan rate of (a) 0.5 mV/s (b) 0.25 mV/s (c) 0.1 mV/s (d) 2.0 mV/s
Figure S 4-2: Cyclic voltammograms of the granular nanostructures at a scan rate of 1.0 mV/s

Figure S 4-3: Columbic efficiency for different cycles for the (a) columnar (b) granular nanostructured anodes
Table S 4-1: Electrode capacity for different anatase TiO₂ structures reported in literature. The specific capacity is given for the 100<sup>th</sup> cycle unless specified otherwise.

<table>
<thead>
<tr>
<th>Electrode Structure</th>
<th>Specific capacity [mA.h g&lt;sup&gt;-1&lt;/sup&gt;]</th>
<th>Charge Rate [1C = 335 mA.g&lt;sup&gt;-1&lt;/sup&gt;]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>183.5</td>
<td>1C</td>
<td><em>Adv. Mater.</em>, 2014, 26, 13.</td>
</tr>
<tr>
<td>TiO₂ quantum dot – graphene composites</td>
<td>190</td>
<td>0.5C</td>
<td><em>J. Phys. Chem. C</em>, 2014, Article ASAP.</td>
</tr>
<tr>
<td>Carbon free nanorods</td>
<td>150†</td>
<td>1C</td>
<td><em>Energy Environ Sci.</em>, 2013, 6, 2932.</td>
</tr>
<tr>
<td>2D ice electrode</td>
<td>150††</td>
<td>1C</td>
<td><em>Nano Lett.</em>, 2013, 13, 5289.</td>
</tr>
<tr>
<td>Electrospun Nanofibers&lt;sup&gt;*&lt;/sup&gt;</td>
<td>160†††</td>
<td>0.5C</td>
<td><em>Adv. Mater.</em>, 2012, 24, 4124.</td>
</tr>
<tr>
<td>Anatase nanocage</td>
<td>110</td>
<td>0.5C</td>
<td><em>J. Mater. Chem.</em>, 2012, 22(40), 21513.</td>
</tr>
<tr>
<td>Anatase nanosheets</td>
<td>150</td>
<td>1C</td>
<td><em>J. Mater. Chem.</em>, 2012, 22(41), 22135.</td>
</tr>
</tbody>
</table>

†50<sup>th</sup> cycle capacity; ††1<sup>st</sup> cycle capacity; †††15<sup>th</sup> cycle capacity; *No binder or carbon
Figure S 4-4: SEM image (top) and EDAX spectra (bottom) of the columnar nanostructures (a,c) before and (b,d) after cycling.
Chapter 5

Model based analysis of one-dimensional oriented lithium ion battery electrodes

Submitted to Journal of Power Sources, July 2016
5.1 Abstract

Oriented one-dimensional nanostructures have been of substantial interest as electrodes for lithium ion batteries due to the better performance both in terms of initial capacity and lower capacity fade compared to powder pressed electrodes. This paper focuses on a model driven approach to understanding the relationship between the morphology of these oriented nanostructures to the performance of the battery. TiO$_2$ columnar nanostructures of varying heights were synthesized using the aerosol chemical vapor deposition (ACVD) and their performance as electrodes in a lithium-ion battery was measured. An electrochemical transport model was formulated (Figure 5-1) and validated with the experimental data. This model was used to understand the role of transport parameters, including the diffusivity of lithium in the TiO$_2$ and the electronic conductivity of the TiO$_2$ columns, and structural parameters, including the height of the columns and the porosity of the electrode, on the areal capacity of a lithium ion battery at different rates of discharge. The model enables for the prediction of optimized structural parameters of one-dimensional electrodes tailored to the desired application of lithium and sodium-ion batteries.

Figure 5-1: Graphical Abstract for the work presented in Chapter 5
5.2 Introduction

Lithium-ion batteries (LIBs) have emerged as the dominant power source for most electronic applications today, as well as the most suitable candidates for electric vehicles and hybrid electric vehicles. The diverse range applications for which LIBs are used demand both high energy densities and high power densities, although they are inversely related [1]. Several research approaches have been adopted for increasing both the energy density and the power density of lithium ion batteries, and controlling the nanostructure of the electrode material has been one such widely adopted approach [2].

One-dimensional (1D) nanostructures in particular have received considerable attention for both cathode and anode materials [3-5] due to the several advantages provided by the 1D nanostructures, which can enhance both the energy and the power density of the battery. These advantages include (1) the efficient electron transport pathway provided by the nanostructure [6], (2) shorter ion diffusion path owing to the less tortuous path and the larger surface to volume ratio [7], and (3) better strain relaxation due to the accommodation space in between the nanostructures [8]. Recent research has focused on the direct growth of the 1D nanostructures on the current collector to obtain oriented nanostructures which further provide improved performance due to the direct attachment of each 1D nanostructure to the current collector ensuring their participation in the electrochemical reaction and obviating the need for any binding agent [4, 8]. Such nanostructures have been demonstrated to outperform powder pressed electrodes or randomly oriented nanostructures for silicon [4], cobalt oxide [9], germanium [8], tin oxide [10], iron oxide [11], and titanium dioxide [12].
Different applications of LIBs demand the optimization of their energy density and power density. While nanostructuring aims to maximize both the densities, further tuning of the nanostructure can be performed to achieve the optimum balance of the energy density and the power density of the battery. Use of electrochemical engineering based models for LiB has been demonstrated in design optimization of LiBs with porous electrodes. First use of these modeling approaches in choosing porosity and thicknesses for a LiB was demonstrated by Newman using reaction zone model [13] and pseudo two dimensional model [14]. Ramadesigan et. al. [15] have incorporated ohmic drop in porous electrode to derive optimal porosity distribution. Use of electrochemical models incorporating capacity fade mechanisms has also been used to provide insights into the effect of porosity distribution and tortuosity on Ragone plots for LiBs [16]. Recently, Dai and Srinivasan [17] suggested an approach for improving energy density of a LiB by graded porosity design tool. However, a fundamental study to understand the effects of the structural parameters of oriented nanostructures on the performance of a battery is lacking. While the abovementioned studies have been focused on the porous electrode made out of smaller particles, the present work focuses on macro-homogeneous modeling approach to quantify the performance of an electrode made out of one-dimensional oriented nanostructures. The objectives of this paper are (1) to study the effect of 1D nanostructure height on the performance of the lithium ion battery electrode performance, (2) to develop a mathematical model to aid in the understanding of the influence of 1D oriented nanostructure properties on the performance of the LIB and (3) to predict an optimized structure to achieve the best performance LIB for a specific application depending on the desired energy density and the desired rate of charge and discharge. We propose the use of a modified porous P2D model to simulate the role of nanostructure on the high rate electrochemical performance of the TiO$_2$ anode. This macro-homogeneous model can provide a system level understanding of the
coin cell, such as how various resistances (e.g. kinetic resistances, transport resistances etc.) affect the overall battery voltage and battery performance. The model is validated with experimental results obtained for 1D single crystal oriented TiO$_2$ anode synthesized directly on stainless steel current collector foils using the aerosol chemical vapor deposition (ACVD) process.

5.3 Model description

A P2D (Newman type) model [18] is used to quantify the effects of various transport processes in a porous anode, cathode, and separator. In the present work, the Newman type model (i.e. a macro homogeneous model with concentrated solution theory) is used to describe the dynamics of TiO$_2$
cylindrical rods as cathode (vs. lithium foil) (Figure 5-2). There are four variables of interest: electrolyte concentration $c$, solid phase potential $\Phi_1$, electrolyte potential $\Phi_2$, and solid phase lithium concentration in cathode $c_p^s$. Figure 5-2 shows the equations used to describe the transport and reaction processes. The input parameters needed for the model are listed in Table 1.

Table 5-1: Values of parameters used for the modeling study

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Positive Electrode</th>
<th>Separator</th>
<th>Anode (Li foil)</th>
<th>Units</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brugg</td>
<td>Bruggeman coefficient</td>
<td>1.0 (straight columns)</td>
<td></td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_p$</td>
<td>Surface area per volume of electrode</td>
<td>3.429×10^{-8}</td>
<td></td>
<td></td>
<td>m²/m³</td>
<td>Calculated</td>
</tr>
<tr>
<td>$c_0$</td>
<td>Initial electrolyte concentration</td>
<td>1000</td>
<td>1000</td>
<td></td>
<td>mol/m³</td>
<td>Measured</td>
</tr>
<tr>
<td>$c_0^s$</td>
<td>Initial solid phase concentration</td>
<td>469 (1% of $c_{max}^s$)</td>
<td></td>
<td></td>
<td>mol/m³</td>
<td>Assumed</td>
</tr>
<tr>
<td>$c_{max}^s$</td>
<td>Maximum solid phase concentration</td>
<td>46,889</td>
<td></td>
<td></td>
<td>mol/m³</td>
<td>Calculated</td>
</tr>
<tr>
<td>$D$</td>
<td>Electrolyte phase diffusion coefficient</td>
<td>7.5×10^{-10}</td>
<td>7.5×10^{-10}</td>
<td></td>
<td>m²/s</td>
<td>[19]</td>
</tr>
<tr>
<td>$D^s$</td>
<td>Solid phase diffusion coefficient</td>
<td>1.76×10^{-15}</td>
<td></td>
<td></td>
<td>m²/s</td>
<td>[20, 21]</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant</td>
<td>96487</td>
<td></td>
<td></td>
<td>C/mol</td>
<td></td>
</tr>
<tr>
<td>$i_0$</td>
<td>Exchange current density</td>
<td></td>
<td>12.6</td>
<td></td>
<td>A/m²</td>
<td>[22]</td>
</tr>
<tr>
<td>$k$</td>
<td>Reaction rate constant</td>
<td>2×10^{-11}</td>
<td></td>
<td></td>
<td>m/s</td>
<td>[20]</td>
</tr>
<tr>
<td>$l_i$</td>
<td>Region thickness</td>
<td>5</td>
<td>25</td>
<td></td>
<td>µm</td>
<td>Measured</td>
</tr>
<tr>
<td>$R_c$</td>
<td>Column radius</td>
<td>87.5</td>
<td></td>
<td></td>
<td>nm</td>
<td>Measured</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
<td>8.314</td>
<td></td>
<td></td>
<td>J/mol/K</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>298.15</td>
<td></td>
<td></td>
<td>K</td>
<td>Measured</td>
</tr>
<tr>
<td>$t_+$</td>
<td>Transference number</td>
<td></td>
<td></td>
<td></td>
<td>0.364</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Porosity</td>
<td>0.34</td>
<td>0.55</td>
<td></td>
<td></td>
<td>Measured</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Electrolyte phase ionic conductivity</td>
<td>0.1809</td>
<td>0.1809</td>
<td></td>
<td>S/m</td>
<td>[23]</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Solid phase electronic conductivity</td>
<td>2.35×10^{-6}</td>
<td></td>
<td></td>
<td>S/m</td>
<td>Measured</td>
</tr>
</tbody>
</table>
Second order finite difference formulation is used to discretize the equations. Compared to a porous electrode battery, where the porous structure assumed to be made up of small spherical particles of anode and cathode materials, here the cathode is composed of continuous cylinders oriented along the $x$ axis (Figure 5-2). The formulation presented here is general enough to account for the axial and radial direction diffusion in solid rods. The solid phase diffusion equation for cylindrical coordinates is used with appropriate boundary conditions. Intercalation reaction at the cathode-separator interface is ignored due to the large aspect ratio of length to diameter, hence no-flux boundary condition is used for the solid cylinder at the cathode-separator interface. Note that this model uses Fick’s law of diffusion in the solid phase, although the actual intercalation mechanism may be different (e.g. core-shell phase change processes). The model described here only gives a system level understanding of how different transport processes affect the overall battery performance of a battery.

The electrolyte phase voltage at the anode-separator interface is determined by Butler-Volmer kinetics with the exchange-current density of lithium-foil. Continuity relations for concentration and flux are used for lithium ions in the electrolyte phase at the anode-separator interface. Transport in electrolyte phase is considered only in the $x$ direction. Only the solid cylinder is modelled in two directions: axial and radial. Since the cylindrical rods are straight, the tortuosity is assumed to be unity in the cathode. The formulation of P2D model is general enough to take care of any tortuosity in the separator.

The equations used in the model are as follows:

Cathode/Current collector boundary conditions

No mass flux of Li ions in electrolyte at cathode/collector interface: $$\frac{\partial c}{\partial x} \bigg|_{x=0} = 0$$  \hspace{1cm} (5-1)
No mass flux of Li in solid phase at cathode/collector interface:  \( \frac{\partial c^s_p}{\partial x} \bigg|_{x=0} = 0 \)  \( (5-2) \)

Current is carried by the solid:  \( \frac{\partial \Phi_1}{\partial x} \bigg|_{x=0} = \frac{-I}{\sigma_{\text{eff},n}} \)  \( (5-3) \)

Zero electrolyte current at the current collector:  \( \frac{\partial \Phi_2}{\partial x} \bigg|_{x=0} = 0 \)  \( (5-4) \)

**Cathode/electrolyte and axisymmetric boundary conditions**

Symmetry boundary condition at column axis:  \( \frac{\partial c^s_p}{\partial r} \bigg|_{r=0} = 0 \)  \( (5-5) \)

Mass flux at column surface:  \( \frac{\partial c^s_p}{\partial r} \bigg|_{r=R} = -\frac{j_p}{D^s_{p,r}} \)  \( (5-6) \)

**Cathode**

Liquid phase diffusion:  \( \epsilon_p \frac{\partial c}{\partial t} = \left( \frac{\partial}{\partial x} \left[ D_{\text{eff},p} \frac{\partial c}{\partial x} \right] + a_p \left( 1 - t_+ \right) j_p \right) \)  \( (5-7) \)

Solid phase diffusion:  \( \frac{\partial c^s_p}{\partial t} = \left( \frac{1}{r} \frac{\partial}{\partial r} \left[ rD^s_{p,r} \frac{\partial c^s_p}{\partial r} \right] + \frac{\partial}{\partial x} \left[ D^s_{p,x} \frac{\partial c^s_p}{\partial x} \right] \right) \)  \( (5-8) \)

Solid phase potential flux:  \( \frac{\partial}{\partial x} \left[ \sigma_{\text{eff},p} \frac{\partial \Phi_1}{\partial x} \right] = a_p F j_p \)  \( (5-9) \)

Charge balance:  \( I = \left( -\sigma_{\text{eff},p} \frac{\partial \Phi_1}{\partial x} - \kappa_{\text{eff},p} \frac{\partial \Phi_2}{\partial x} + \frac{2\kappa_{\text{eff},p} RT (1-t_+) \partial \ln c}{F} \right) \)  \( (5-10) \)

**Cathode/Separator boundary conditions**

Mass continuity:  \( c \bigg|_{x=l_p^-} = c \bigg|_{x=l_p^+} \)  \( (5-11) \)

Mass flux continuity:  \( -D_{\text{eff},p} \frac{\partial c}{\partial x} \bigg|_{x=l_p^-} = -D_{\text{eff},s} \frac{\partial c}{\partial x} \bigg|_{x=l_p^+} \)  \( (5-12) \)
No mass flux into top of columns (ASSUMED): \[
\frac{\partial c_p}{\partial x} \bigg|_{x=l_p} = 0 \quad (5-13)
\]

No solid potential flux at top of column: \[
\frac{\partial \Phi_1}{\partial x} \bigg|_{x=l_p} = 0 \quad (5-14)
\]

Flux continuity: \[
-K_{eff,p} \frac{\partial \Phi_2}{\partial x} \bigg|_{x=l_p} = -K_{eff,s} \frac{\partial \Phi_2}{\partial x} \bigg|_{x=l_p} \quad (5-15)
\]

Electrolyte potential continuity: \[
\Phi_2 \bigg|_{x=l_p} = \Phi_2 \bigg|_{x=l_p} \quad (5-16)
\]

Separator

Electrolyte phase diffusion: \[
\varepsilon_s \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D_{eff,s} \frac{\partial c}{\partial x} \right] \quad (5-17)
\]

Charge balance: \[
I = -K_{eff,s} \frac{\partial \Phi_2}{\partial x} + \frac{2K_{eff,s}RT}{Fc} \left( 1 - t^* \right) \frac{\partial c}{\partial x} \quad (5-18)
\]

Separator/Anode boundary conditions

Ion dissociation from Li foil: \[
\frac{\partial c}{\partial x} = I \frac{1-t^*}{D_{eff,s} F} \quad (5-19)
\]

Reference potential: \[
\Phi_2 = 0 \quad (5-20)
\]

The output of the battery model is the charge/discharge curve for any rate. From these charge/discharge curves, specific capacity (mA.h.g\(^{-1}\)) and areal capacity (mA.h.cm\(^{-2}\)) are computed for different structural parameters which can aid in deciding the optimal parameters for a given power application.
5.4 Experimental Methods:

5.4.1 1D Nanostructure synthesis, and cell fabrication

1D nanostructures were synthesized directly on the current collector by the ACVD process [24, 25] as described previously [21]. Briefly, titanium tetraisopropoxide (TTIP) (97%, Sigma-Aldrich, MO, USA) was fed into a reaction chamber towards a heated substrate (current collector). Gas phase reaction and nucleation leads to the formation of TiO$_2$ particles which deposit onto the heated substrate wherein they sinter to form the 1D nanostructures (columns). The height of the columns was controlled by the varying the deposition time. Stainless Steel (SS316, ESPI Metals, OR, USA) with a thickness of 25μm and punched into 15 mm diameter discs were used as the current collector. Post deposition, the discs were cleaned to remove any impurity followed by drying in an oven at 85°C for 12 hours. Coin cells (CR2032) were assembled in an Ar-filled glovebox (Unilab, MBraun Inc, USA) with O$_2$ and H$_2$O concentrations maintained at <0.1ppm levels. The columnar TiO$_2$ deposited stainless steel discs were used as the working electrode (cathode) and the lithium foil as the counter electrode (anode) in a half-cell configuration.

5.4.2 Electrochemical Testing

Electrochemical characterization of the coin cells was carried out using a multichannel potentiostat/galvanostat (Bio-logic USA, TN, USA) in a potential range of 1.0 V to 3.0 V at a constant temperature of 22°C. The cycling rates were calculated on the basis of 1 Li$^+$ exchanged per formula unit of TiO$_2$ in 1 h (denoted 1 C) corresponding to a theoretical capacity of 335 mAh g$^{-1}$. The mass of the deposited TiO$_2$ was calculated by weighing the stainless steel discs before and after deposition of TiO$_2$. 

122
5.4.3 Structural Characterization

The morphology of the synthesized nanostructures was characterized using scanning electron microscopy (SEM) (FESEM, NOVA NanoSEM 230, FEI Co.). The crystal structure of the prepared sample was characterized using X-Ray diffraction (XRD) (Bruker D8 Advance) with a CuKα radiation (wavelength = 1.5406 Å) at 35 kV and 35 mA. The scattering angle (2θ) used in the measurement was from 20° to 60° with a step size of 0.02° and a dwell time of 2 sec.

5.5 Results and Discussion:

5.5.1 Experimental Results

The synthesized 1D nanostructures, observed to be of columnar morphology, for three different deposition time of 30 mins, 60 mins and 75 mins had column heights of 0.8 µm, 1.6 µm and 2.0 µm respectively as measured by SEM analysis (Figure 5-3). XRD spectra confirmed the preferred orientation of these columnar structures along the (112) direction (Figure 5-3d). In our previous study, we have characterized the single crystal nature of these columnar structures [21]. With increasing column height, an increase in the (101) peak intensity is observed in the XRD spectra, indicative of branching in the columnar structures. The branching of columnar nanostructures has previously been studied by our group in detail and has been attributed to the decrease in the tip
surface temperature of the TiO$_2$ nanostructure due to thermal conduction effects as the column height increases [26]. This decrease in surface temperature results in a decrease in the sintering rates, thus leading to the formation of a branched structure. The branching of the nanostructures becomes observable by SEM for taller columns with height greater than 5 µm. For the purpose of this study, the branching of the TiO$_2$ nanostructures has been ignored since the growth of branches was minimal up to the 75 mins deposition time used in the experimental work.

The columns of different heights were cycled at a 1C (335 mA.h.g$^{-1}$) rate, and the 3$^{rd}$ cycle charge discharge curve is shown in Figure 5-4a. A significant decrease in the specific capacity was observed with increasing column height. This is expected due to the low electron conductivity of the columns, which would result in electron transport limitation with increase in column height. Similar transport limitations were observed previously for the granular structures compared to the columnar structures [21]. It should be noted that even the tallest column (3 – 7 µm) used in the study exhibited better specific capacities than the 0.8 – 1.0 µm granular structures studied in the previous study, highlighting the better transport characteristics of the columnar nanostructures, which allow much higher mass loading. Long term cycling of the columns revealed an initial capacity decrease of 8 – 10% in the first 10 cycles but stable performance (<10% total decrease) afterwards up to 100 cycles at 1C rate for all the column heights (Figure 5-4b). The initial capacity decrease is attributed to the buildup of the SEI layer on the surface of the columns in the initial few cycles resulting in coulombic efficiencies in the range of 90 – 95% which increases to >99% in the following cycles.
The results above indicate that shorter columns have higher specific capacities and hence more suitable for practical applications; however, areal capacity is also an important factor which governs the size of the battery. Figure 5-4c shows the areal capacity of the various height electrodes for the 100 cycles. It was observed that the areal capacity increases with increasing column height. While the increase seen in the above data appears to be linear with the height of the columns, there are very few data points to establish a relationship of height with the areal capacity. Hence, we see an inverse effect of column height on the specific capacity and the areal capacity of the battery.
This prompts the use of a modelling based optimization to predict the optimum column height for practical applications.

5.5.2 Model input and validation:

The parameters and properties of the one dimensional TiO$_2$ nanostructures were either measured or obtained from the literature. Table 1 list the parameters used for this study and the source of the parameter. The diffusion coefficient of the 1 D nanostructures was estimated to be $1.76 \times 10^{-15} \text{ m}^2 \cdot \text{s}^{-1}$ based on data from the cyclic voltammetry reported in our previous study [21] and also agreed with previously reported values in the literature [20]. The electronic conductivity of the TiO$_2$ columnar nanostructures was measured by four probe measurements and was found to be $2.35 \times 10^{-6} \text{ S/m}$, consistent with the values found in literature for TiO$_2$ [27]. Since these nanostructures are directly synthesized on the current collector and no carbon additive is use, the electronic conductivity of the TiO$_2$ is directly used.

For the input and validation of the model, data from our previous study was used [21]. The electrochemical performance of the 0.8 µm at 0.1C rate (33.5 mA.h.g$^{-1}$) served as open circuit potential of the battery. The voltage time curve was fitted to a parametrized equation [16] as shown below:

$$U(\theta) = 0.14334 \times 10^{-2} + 0.25952 \exp(-0.71758\theta) + .66825 \tanh(0.28724\theta - 0.14795)$$
$$-3.68355 \tanh(6.27217\theta - 5.34464) - 3.16496 \tanh(15.11589\theta + 0.85263)$$
$$-1.16891 \tanh(217.33899\theta - 149.81706)$$

where $\theta = c^e / c_{\text{max}}^e$. Using the above discharge curve at 0.1C rate, the performance of the 0.8 µm at higher discharge rates (up to 10C) was simulated. Figure 5-5a shows the experimental and modelled discharge curves of the TiO$_2$ column at different discharge rates. It can be seen that the model performs well in simulating the kinetics of the lithium insertion into the TiO$_2$ nanostructure. However, at very high discharge rate of 10C, the model deviates from the experimental
performance, predicting lower voltage plateau compared to experimental observations. This is possibly due to the simplistic assumption in the model which ignores biphasic (Li$_{0.05}$TiO$_2$ and Li$_x$TiO$_2$) formation and the change in the electronic conductivity and the lithium diffusivity as a result of this biphasic transformation. However, the model still predicts the specific capacity of the electrode at all rates of charge and discharge considerably well with a less than 5% deviation in the predicted capacity vs. the experimental values. These results validate the ability of the model to predict the performance of the electrodes at varying rates of discharge.

The model was then validated against the experimental results obtained for varying column heights reported above. It should be noted that for varying heights, the input to the model is only the OCP relationship obtained from 0.1C performance of the 0.8 µm columns. Using the same physical parameters of the columns, the mass of the electrode was estimated for taller columns and used in the model. It is seen that the model performs well in predicting the performance of the columnar nanostructures of varying heights (Figure 5-5b). Again, the difference between the predicted specific capacity and the experimental result is less than 5%. The lowering of the plateau potential
is also predicted well by the model, with the predicted plateau potential lowering from 1.81V to 1.68V for column height increasing from 0.8 to 1.6 µm. Experimentally, plateau potentials range from 1.75V to 1.70V for the same increase in column heights.

5.5.3 Understanding the role of transport parameters

The successful validation of the model allows us to understand the role of transport parameters on the performance of the oriented nanostructured electrodes. Figure 5-6 shows the effect of diffusivity of lithium in the nanostructure and the electronic conductivity of the columnar nanostructures on the areal capacity of the 0.8 µm height columnar TiO$_2$ battery electrodes at 1C and 5C rates of discharge. The experimentally measured values of diffusivity and conductivity are indicated by the dashed line on the plot. An increase in either conductivity or diffusivity results in better performance of the electrodes, with a saturation point attained at higher values of conductivity and diffusivity. At a 1C rate of discharge, the electronic conductivity and diffusivity in the 0.8 µm columnar nanostructure is near the saturation performance. However, at a 5C rate, the performance is not at saturation, and it is seen that the dominating factor limiting the performance is the diffusivity of the lithium in the TiO$_2$ nanostructures rather than the electronic conductivity.

Figure 5-6: Predicted effect of (a) diffusivity of the lithium in the TiO$_2$ column and (b) electronic conductivity of the TiO$_2$ column on the performance of 0.8 µm tall columnar nanostructures. The dashed line indicates the experimentally measured values of the parameters.
conductivity of the TiO$_2$ nanostructures. These results also support the previous conclusion about poorer performance of granular TiO$_2$ nanostructures compared to columnar nanostructures being attributed to the lower electronic conductivity and the lithium diffusivity in the granular nanostructures due to the presence of grain boundaries impeding the diffusion rate.

5.5.4 Prediction of optimal electrode structures

In addition to understanding the role of the kinetic parameters, the model’s capability in successfully predicting the charge discharge profiles at varying rates as well as varying nanostructure heights, the model was utilized to predict optimal electrode design strategies. Results above have shown that increase in electrode thickness results in a decrease in specific capacity but an increase in the areal capacity. Using the model, the effect of column height (0.8 – 10µm) on the areal capacity was mapped at different rates of discharge (0.1 – 5C) (Figure 5-7). At low rate of discharge (0.1C), increasing the column height results in an increase in the areal capacity. This increase is evident because at 0.1C rate, the current density is low (33.5 mA.g$^{-1}$) and near

![Figure 5-7: Predicted areal capacity for columnar structures of varying heights at varying rates of discharge.](attachment:figure57.png)
equilibrium condition exist. Thus taller columns provide more active material for the lithium to intercalate and, without any transport limitation, results in increased areal capacities with increasing column heights. However, as the rate of discharge is increased, the effect of transport limitation becomes evident on the areal capacities. At 1C rate of discharge, the areal capacities increase up to 3 µm column height, above which the areal capacity is observed to decrease rapidly. The decrease in the areal capacity is mainly due to the lower electronic conductivity of the cathode (nano rods). Simulation results for 3 µm column height at 5C rate of discharge shows that solid phase conductivity remains the bottleneck. An almost 1 V potential drop occurs between top and bottom of the solid cylinders (Figure 5-8a) for the conductivity values used for TiO₂. Due to straight pores, the lithium ion concentration in the electrolyte phase remains almost uniform offering little transport limitation. Such maxima or inflection points in the areal capacity vs the electrode thickness have also been reported previously in slurry coated electrodes for lithium ion battery cathodes [28]. Similar to the present study, the inflexion point was observed to shift to lower C rates with increasing electrode thickness.

Figure 5-8: Simulated voltage-time profile at different axial locations in the TiO₂ column for 3µm tall columns with electronic conductivity of (a) 2.35×10⁻⁶ S/m (as prepared) and (b) 59 S/m (hypothetical carbon coated electrodes). The different curves are equally spaced on the column in the axial direction.
The P2D model allows us to evaluate performance of battery modified with other materials. For example, addition of conductive carbon to the TiO$_2$ cylinders can improve the electronic conductivity of the solid phase of cathode. Figure 5-8b shows the voltage profile for the 3 µm column height at 5C rate of discharge with an increased conductivity value of graphite (59 S/m) which essentially eliminates the potential drop across the solid phase of cathode. Using the increased conductivity value, significant performance gain in terms of areal capacity can be achieved for the TiO$_2$ columns as shown in Figure 5-9a. The inflexion points shift significantly to the right with higher areal capacities. The carbon addition is one way to improve the conductivity of these columnar nanostructures but other ways can also be employed to do similar enhancement in conductivity, such as by doping the nanostructures [29]. On the other hand, similar analysis of performance gain can also be performed by improving the transport limitations during intercalation.

![Figure 5-9: Predicted areal capacity for hypothetical carbon coated columnar structures of (a) varying heights at varying rates of discharge and (b) 10 µm carbon coated columnar structures with varying column spacing (porosity)](image)}
Another morphology factor that can be optimized to obtain high areal capacities is the column–column distance, represented as the porosity of the electrode in the model. Figure 5-9b shows the shows the effect of the porosity on the areal capacity of an electrode with 10 µm columns with increased conductivity. For the 0.1C and 1C rate, the areal capacity is observed to increase with decreasing porosity due to the increasing packing and thus increasing total active material on the electrode. However, for 2C rate, a maxima is seen for the areal capacity, below which the capacity rapidly decreases. This maxima occurs due to narrowing electrolyte channels between the columns causing transport limitations in the electrolyte phase depending on the rate of discharge. Thus an optimal porosity value for a column of certain height can be obtained depending on the desired rate of discharge. Work done by Suthar et al. [16] on dual porous electrode lithium-ion battery also suggests similar results, where the less porous electrode provides higher transport resistance in the electrolyte phase leading to reduced specific energy at higher rates of discharge. Although, in that work, porosity also affects tortuosity of electrode whereas in this case, as the tortuosity takes as unity, porosity only affects the overall lithium ion intake.

5.6 Conclusions

One dimensional oriented TiO$_2$ columnar nanostructures were synthesized and the effect of the column height on the electrochemical performance was studied. An electrochemical P2D model was formulated to predict the performance of 1D nanostructured electrodes in lithium ion battery systems and was successfully validated by the experimental results. The model was utilized to understand the role of kinetic and structural parameters on the electrochemical performance of the TiO$_2$ columnar nanostructures. Optimal column lengths and column spacing were observed depending on the rate of discharge. Further improvements in the model can be made by considering phase transformation in the solid electrode and radial diffusion in the electrolyte phase. The model
can serve as a powerful tool to optimize 1D electrode design for different lithium–ion battery applications depending on the required energy density and the power density and can also be extended to other intercalation based battery applications such as sodium-ion batteries.

5.7 List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brugg</td>
<td>Bruggeman coefficient</td>
</tr>
<tr>
<td>(a_p)</td>
<td>Surface area per volume of electrode</td>
</tr>
<tr>
<td>(c)</td>
<td>Electrolyte concentration</td>
</tr>
<tr>
<td>(c^e)</td>
<td>Solid phase concentration</td>
</tr>
<tr>
<td>(c_{\text{max}}^e)</td>
<td>Maximum solid phase concentration</td>
</tr>
<tr>
<td>(D)</td>
<td>Electrolyte phase diffusion coefficient</td>
</tr>
<tr>
<td>(D^e)</td>
<td>Solid phase diffusion coefficient</td>
</tr>
<tr>
<td>(F)</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>(I)</td>
<td>Applied current</td>
</tr>
<tr>
<td>(j_p)</td>
<td>Current density gradient flux in electrolyte phase of positive electrode</td>
</tr>
<tr>
<td>(k)</td>
<td>Reaction rate constant</td>
</tr>
<tr>
<td>(l_i)</td>
<td>Region thickness</td>
</tr>
<tr>
<td>(R_c)</td>
<td>Column radius</td>
</tr>
<tr>
<td>(R)</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>(r)</td>
<td>Radial coordinate</td>
</tr>
<tr>
<td>(T)</td>
<td>Temperature</td>
</tr>
<tr>
<td>(t^+)</td>
<td>Transference number</td>
</tr>
<tr>
<td>(U)</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>Porosity</td>
</tr>
<tr>
<td>(\Phi_1)</td>
<td>Solid phase potential</td>
</tr>
<tr>
<td>(\Phi_2)</td>
<td>Electrolyte phase potential</td>
</tr>
<tr>
<td>(\kappa)</td>
<td>Electrolyte phase ionic conductivity</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Solid phase electronic conductivity</td>
</tr>
</tbody>
</table>

**Subscripts**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)</td>
<td>Related to the negative electrode—the anode</td>
</tr>
<tr>
<td>(p)</td>
<td>Related to the positive electrode—the cathode</td>
</tr>
<tr>
<td>(s)</td>
<td>Related to the separator</td>
</tr>
</tbody>
</table>

**Superscripts**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>(s)</td>
<td>Related to solid phase</td>
</tr>
</tbody>
</table>
5.8 Acknowledgments

This paper is based upon work supported under the US-India Partnership to Advance Clean Energy-Research (PACE-R) for the Solar Energy Research Institute for India and the United States (SERIIUS), funded jointly by the U.S. Department of Energy (Office of Science, Office of Basic Energy Sciences, and Energy Efficiency and Renewable Energy, Solar Energy Technology Program, under Subcontract DE-AC36-08GO28308 to the National Renewable Energy Laboratory, Golden, Colorado) and the Government of India, through the Department of Science and Technology under Subcontract IUSSTF/JCERDC-SERIIUS/2012 dated 22nd Nov. 2012. Electron microscopy was performed at the Nano Research Facility (NRF) at Washington University in St. Louis, a member of the National Nanotechnology Infrastructure Network (NNIN), supported by the National Science Foundation under Grant No. ECS-0335765.

5.9 References


Chapter 6

Additive-free Anatase Dendrites as Ultra-stable Anodes for Sodium-ion Batteries

To be submitted to Journal of American Chemical Society, June 2016
6.1 Abstract

Despite the fact that sodium is an environmentally friendly and highly abundant element in the earth’s crust (unlike Li), many challenges currently impede the development of sodium-ion battery technology. Finding suitable electrode and electrolyte materials remain the most tangible challenges. In this work, we demonstrate one-step synthesis of monolithic anatase TiO$_2$, a carbon and binder-free electrode, used as the anode in conjunction with a sodium metal as the counter electrode and an organic-based electrolyte (e.g., PC-NaClO$_4$). The cell exhibits high energy efficiency ($\sim$99.5%), a 1000 cycle lifetime, and improved rate capability. The one-dimensional orientation of the single-crystalline TiO$_2$ columns allows the electrolyte to interact with the entire material surface, providing a higher electrolyte-electrode contact area. As a result, the nanostructured anode exhibits a high specific capacity of 180 mAh g$^{-1}$ at 100 mA g$^{-1}$. The results, supported by state-of-the-art electrochemical and analytical techniques such as in-situ electrochemical and ex-situ structural studies, enable an understanding of the true energy storage mechanism of these carbon-free and binder-free nanostructures (Figure 6-1).

![Figure 6-1: Graphical abstract of the work presented in Chapter 6](image-url)
6.2 Introduction

Rapidly increasing demand for Li-ion batteries augmented by concerns of its limited availability has prompted recent interest into Na-ion batteries [1]. While the principle of operation of the two metal-ion batteries is very similar, the different physical and chemical characteristics of the transporting ion present new challenges for electrode material selection and design. Graphite, the most popular negative electrode material for Li-ion batteries, is incapable of serving as an insertion host for Na ions due to the incompatibility of the size of the Na-ion with the spacing between the 2D carbon planes [2]. Although other forms of carbon, such as hard carbon (non-graphitic carbon), have been used as negative electrodes for Na-ion batteries, they suffer from severe drawbacks of poor durability and high material cost [2]. Metal oxide anodes, such as TiO$_2$ [3, 4], and V$_2$O$_5$ [5], are currently being explored as possible negative electrodes for Na-ion batteries.

In the past, TiO$_2$ has been widely investigated as an anode material for Li-ion batteries due to its specific capacity, which is comparable to that of graphite, exceptional structural stability, high rate capability and safer intercalation voltage (~1.5V vs. Li/Li$^+$) [6-9]. These characteristics make TiO$_2$ a possible candidate anode material for Na-ion batteries, but the larger ionic radius of the Na-ions (1.02 Å) compared to that of the Li-ions (0.76 Å) necessitates a larger distortion of the metal oxide lattice to accommodate the Na-ion [10]. Nanostructuring the electrode provides an effective means of improving the performance of the electrode, with 1D oriented nanostructures considered to be the most effective due to the high electrode-electrolyte interfacial area, facile strain relaxation, and 1D electron transport [11]. A few studies have investigated the applications of TiO$_2$ to Na-ion battery systems [3, 4, 12], all of which utilized the conventional electrode fabrication technique which includes the use of carbon and binding agents along with the active material. This technique severely restricts the control of the nanostructure on the electrode, leading to stacking of the
nanomaterial, thus limiting performance. Kim et. al. [12] used TiO$_2$ nanorods as anode materials for rechargeable Na-ion batteries. However, the nanorods stacked randomly during the roller pressing process leading to significant capacity fade. Further, such studies are unable to isolate the true performance of the bare nanostructured material without the contribution of the added carbon. The advantages of using carbon- and binder-free approaches to synthesizing TiO$_2$ based electrodes has been demonstrated in Li-ion system recently by our group and others [6, 13].

The current work reports the use of single crystal one-dimensionally oriented TiO$_2$ dendritic nanostructures synthesized by the aerosol chemical vapor deposition (ACVD) process directly on the current collector, thus creating carbon- and binder-free anodes for use in a Na-ion battery. The electrochemical performance and the long-term electrochemical stability of these nanostructures are studied. Detailed structural investigations to see the effect of the sodiation and de-sodiation process on the TiO$_2$ nanostructures are also presented. The absence of any binder or carbon allows us to study the true electrochemical performance of anatase TiO$_2$, and the oriented arrangement of the dendritic columns on the current collector provides insight into the reaction and sodiation process, even with ex-situ studies. The outstanding electrochemical performance of single crystal TiO$_2$ in a carbon-free and binder-free sodium-ion battery anode is the first report in the literature.

6.3 Experimental Section

6.3.1 Nanostructured TiO$_2$ thin films synthesis:

TiO$_2$ nanostructures were synthesized using the single-step ACVD process [14, 15]. Vapors of titanium tetraisopropoxide at a concentration of $1.29 \times 10^{-3}$ mol.m$^{-3}$ were introduced into the reactor where they thermally decomposed to form TiO$_2$ molecules which nucleated and grew to form particles. These particles were deposited onto a 1 cm diameter stainless steel substrate (25
µm thickness) maintained at 500° C, on which the particles sintered to form 1D columnar nanostructures. The deposition was carried out for 30 min.

6.3.2 Material Characterization:

The morphology of the nanostructures was analyzed using field emission gun scanning electron microscopy (FEGSEM, NOVA NanoSEM 230, FEI Co.), and the crystal structure was characterized using X-ray diffraction (XRD) (Bruker D8 Advance) with CuKα radiation (wavelength = 1.5406 Å) at 35 kV and 35 mA. The scattering angle (2θ) was from 20° to 60°, with a step size of 0.02° and a dwell time of 2 sec. Rietveld refinement to obtain the lattice parameters from the XRD spectra was carried out using Topas 5 software (Bruker). Before and after cycling, detailed studies of crystal orientation, selected area electron diffraction (SAED) and morphology studies were done with high-resolution transmission electron microscopy (HR-TEM, JEOL J2100F) operated at 200 kV.

6.3.3 Electrochemical Cell Fabrication and Measurements:

Anatase TiO₂, deposited on a stainless steel substrate with a diameter of 1 cm, was used as a working electrode (WE) to study the electrochemical behavior of TiO₂ as an electrode for Na-ion batteries. Galvanostatic charge-discharge tests were carried out using a lab scale Swagelok type stainless steel setup, having a cell configuration of Na|electrolyte|TiO₂. All electrochemical cells were assembled in an argon-filled glovebox (Lab Star, MBraun, Germany) under controlled moisture and oxygen concentrations below 1 ppm. Na foil (Alfa Aesar, 99.8%) was used as the counter electrode as well as the reference electrode (CE/RE). Electrolyte preparation for this study was done inside the glove box. A solution (EC:PC) of ethylene carbonate (EC) (Sigma, 99%) and propylene carbonate (PC) (Sigma, 99%), in a 1:1 volume ratio was prepared. NaClO₄ salt (Sigma,
99%), which was vacuum dried for two days and inserted into the glove box, was dissolved into the EC:PC solution to achieve a 1 M concentration. This solution was used as the electrolyte. The separator was a porous borosilicate glass microfiber filter (Whatman), soaked with a few drops of the electrolyte.

Electrochemical charge-discharge experiments were performed to evaluate the durability of the prepared cells, using an Arbin battery testing instrument (BT2000, USA) at various constant current rates. Potentiostatic electrochemical impedance spectroscopy (PEIS) was carried out for the first discharge cycle at four different potentials during the charge-discharge process, using a Bio-Logic VMP-3 electrochemistry workstation. During the entire PEIS process, the cell was not disconnected from the circuit, thus the technique is termed as in-situ impedance spectroscopy. The technique was performed within a frequency range of 1 MHz to 1 Hz and with a voltage amplitude of $\Delta V = 5$ mV. For in-situ experiments, charge-discharge was carried out at a constant current density of 50 mA.g$^{-1}$ and a constant temperature of 20$^\circ$ C. Further, the galvanostatic intermittent titration technique (GITT) was used to study the kinetics of Na-ion diffusion into the TiO$_2$ matrix.

**6.3.4 Ex-situ analysis**

Cells were disassembled at four points in the first two cycles (sodiated and de-sodiated conditions) to investigate the changes in physical properties due to Na-ion storage. Ex-situ analysis of the cycled electrodes was carried out using XRD, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), HR-TEM, SAED, and scanning transmission electron microscopy – energy dispersive X-ray spectroscopy (STEM-EDX) to examine the structural changes in the nanocolumns upon Na-ion insertion and de-insertion. Raman spectroscopy (using a Renishaw InVia Raman Spectrometer) confirmed the composition of the electrode, using a 514 nm laser source with a spot size of 1 $\mu$m$^2$ and a numerical aperture of 0.75. STEM-EDX analysis was carried
out in the HR-TEM instrument at the operating parameters mentioned previously. Line scan EDX analysis was conducted along the length and the width of the column. XPS measurements were carried out using a PHI 5000 VersaProbe II equipped with monochromatic Al Kα (1486.6 eV) X-ray source. Fine scans were done for Na, Ti, C, and O. XPS peak analysis was done using Multipak (v9.6, ULVAC-PHI), and peaks were fitted to a Gaussian-Lorentzian mixed function via the iterated Shirley method. The peaks were calibrated using the peak for adventitious surface carbon at 284.80 eV, corresponding to C 1s photoemission.

6.4 Results and Discussion

The TiO$_2$ nanostructure investigated in the presented study is expected to provide key structural benefits including enhanced electrode-electrolyte interfacial area due to the dendritic columnar structure. These benefits provide enhanced electrochemical performance and long-term stability. Moreover, the single crystalline nature would allow investigation of even minor changes to the crystallinity of the material upon intercalation, and the one-dimensional orientation of the columns on the electrode surface would allow uniform sodium intercalation along the surface of the column, which can be investigated via ex-situ characterization.

6.4.1 Structural Characterization:

FEG-SEM image (Figure 6-2d) confirms the dendritic columnar morphology of the nanostructure, with a column height of 800-1000 nm and a diameter of 150-200 nm, oriented approximately perpendicular to the stainless steel current collector substrate. An XRD spectrum of the columnar nanostructures (Figure 6-5c) depicts a pure anatase structure with a preferred orientation of the columns along the (112) plane. Previously, we have studied and reported the single crystal nature of these columns using HR-TEM measurements [6]. The oriented dendritic columnar
nanostructures on the current collector provide a high surface area for reaction and ion intercalation, and the electrolyte can reach deep in between the columns near the current collector.
6.4.2 Electrochemical Performance:

In the absence of carbon or binders, the electrochemistry of dendritic TiO$_2$ shows the true reaction with Na-ion as it diffuses through the solid TiO$_2$ matrix. The power cycle performance, shown in Figure 6-2a, illustrates discharge capacities at increasing current rates of 20 mA g$^{-1}$, 50 mA g$^{-1}$, 100 mA g$^{-1}$, 200 mA g$^{-1}$, 500 mA g$^{-1}$, and 1000 mA g$^{-1}$ for the first 30 cycles. Following the power cycles, the current rate was held constant at 100 mA g$^{-1}$ up to 1000 cycles to examine the durability of the TiO$_2$ nanostructures experiencing repeated intercalation and de-intercalation in the same electrochemical environment. The as-prepared electro-active material exhibits 357 mAh g$^{-1}$ (2$^{nd}$ cycle), 223 mAh g$^{-1}$ (6$^{th}$ cycle), 180 mAh g$^{-1}$ (11$^{th}$ cycle), 151 mAh g$^{-1}$ (16$^{th}$ cycle), 115 mAh g$^{-1}$ (21$^{st}$ cycle), and 89 mAh g$^{-1}$ (26$^{th}$ cycle) discharge capacities at constant current rates of 20 mA g$^{-1}$, 50 mA g$^{-1}$, 100 mA g$^{-1}$, 200 mA g$^{-1}$, 500 mA g$^{-1}$, and 1000 mA g$^{-1}$, respectively, at 20$^\circ$ C within the potential range of 3.0 to 0.05 V vs. Na/Na$^+$. After 1000 cycles, the TiO$_2$ columns exhibited a 120 mAh g$^{-1}$ discharge capacity, thus retaining 85.1% capacity with respect to the 31$^{st}$ cycle (141 mAh g$^{-1}$). Figure 6-2b shows galvanostatic charge-discharge profiles, carried out at variable current densities within the same potential range. During the first cycle, a drastic irreversible specific capacity loss occurs due to the formation of a solid-electrolyte interface (SEI) layer and other irreversible side reactions, because of the high surface to volume ratio of the deposited TiO$_2$. The Coulombic efficiencies at different cycles are tabulated in Table S 6-1 in the ESI. The material reaches a high reversibility of 99% after 250 cycles. Ex-situ HR-TEM studies and SAED patterns (Figure 6-2c) on the electrodes after 1000 cycles show that the columnar morphology of the TiO$_2$ nanostructure has been retained but the columns have turned polycrystalline. A slight expansion of the lattice was also observed after the 500$^{th}$ (Figure S 6-2) as well as the 1000$^{th}$ cycle. These findings highlight the exceptional structural stability of the columnar nanostructures during cyclic
insertion and extraction of large Na-ions (ionic radius = 1.04 Å), never observed before with bare anatase TiO$_2$ anodes for such long cycling.

To evaluate the reactions at different voltages with respect to Na/Na$^+$, the dQ/dV [d(capacity)/d(voltage)] for different cycles at varying current rates was plotted (Figure 6-3a). The illustration shows reduction and oxidation of TiO$_2$ as a function of applied potential for different cycles. Two prominent reduction peaks were observed during the reduction process in all cycles. The peak near 0.74 V vs. Na/Na$^+$ can be attributed to Na-ion insertion into the TiO$_2$ host matrix. Vice versa, de-insertion of Na-ions from the TiO$_2$ was observed in the oxidation cycles near 0.78 V vs. Na/Na$^+$. As the rate increases, the sodiation and de-sodiation become more difficult due to electronic and ionic transport limitations, therefore the difference between redox reactions increases. Another prominent peak was observed near 0.1-0.2 V, which was due to storage of Na-ions on the TiO$_2$ surface [16]; this storage is confirmed further in the PEIS study in this report.

![Figure 6-3: dQ/dV plots](image)

Figure 6-3: dQ/dV plots (a) at different current rates during the power cycles and (b) at 100 mA g$^{-1}$ during the long term cycling. (c) Charge discharge curves for selected cycles during the long term cycling at 100 mA g$^{-1}$. (d) GITT at 2$^{nd}$ cycle at a current rate of 50 mA g$^{-1}$. 
This peak was very prominently observed until the 50th cycle (Figure 6-3b). The as-prepared material exhibited an extraordinary reversibility of 99.55% at the 1000th cycle, with a 41 mV redox difference (Figure 6-3c) which shows Na-ion insertion peak at 0.738 V and Na-ion de-insertion peak at 0.779 V, which is exceptional in the field of Na-ion batteries [17].

The diffusion of Na-ions into the TiO_2 matrix was quantified by GITT measurement (Figure 6-3d) during the 2nd cycle, with 20 min of discharge and 30 min rest at a discharge rate of 50 mA g\(^{-1}\) until 0.5 V. GITT was performed on the second cycle since the first Na-ion insertion is associated with other irreversible reactions. The illustration shows that Na-ions are inserted into the host matrix at a particular voltage only. The diffusion co-efficient was calculated to be \(8.54 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}\). Details of the calculations are included in the supplementary information.

### 6.4.3 In-situ Potentiostatic Electrochemical Impedance Spectroscopy:

To develop a detailed understanding of the interfacial properties and the associated surface additions upon the first sodiation, we performed in-situ potentiostatic electrochemical impedance spectroscopy (in-situ PEIS) (Figure 6-4a) during the 1st discharge cycle. In this typical experiment, we measured the impedance from high frequency to low frequency at four different states-of-charges (WE vs. RE/CE potential), as depicted in Figure 6-4d. At the last voltage point (0.05 V), the cell was disassembled, and FEG-SEM image was taken by tilting the columnar film. Wu et al. [18] reported that Na oxides had formed flower-like features after cycling. Here, we observed no such changes in the surface morphology of the TiO_2 columns after the first discharge (Figure 6-4e), which might well explain the outstanding 1000 cycle electrochemical performance of these nanostructures.
Figure 6-4c shows the equivalent circuit, where $R_e$ is indicative of the electrolyte resistance and associated uncompensated resistance arising from the instrumental components (corresponding to the high frequency region), $R_{SF}$ is the resistance due to surface film formation, $R_{ct}$ is the charge transfer resistance ($R_{SF}$ and $R_{ct}$ are for medium-frequency region), and $W$ (the Warburg impedance low-frequency region) represents the diffusion of Na-ions into the solid TiO$_2$ matrix [19]. In this typical case, curve fittings have been performed for the semi-circular regions (Table 6-2). At OCV (without any current pulse), the small semi-circle is observed due to the formation of a surface film, which is quite common [7]. At 0.8 V, there are two semi-circles, one much larger than the other. The smaller semi-circle is attributed to the formation of the SEI layer due to minimal decomposition of carbonates on the surface of the active material [20].
Table 6-2: Non-linear least square fit to the experimental EIS spectra and fitted parameters for four different voltage points

<table>
<thead>
<tr>
<th>Voltage (vs. Na/Na⁺)</th>
<th>Rₑ (ohm)</th>
<th>Rₛₚ (ohm)</th>
<th>Rₖ (ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCV</td>
<td>6.77</td>
<td>67.65</td>
<td>NA</td>
</tr>
<tr>
<td>0.8 V</td>
<td>13.35</td>
<td>18.89</td>
<td>191.40</td>
</tr>
<tr>
<td>0.45 V</td>
<td>13.36</td>
<td>NA</td>
<td>344.50</td>
</tr>
<tr>
<td>0.05 V</td>
<td>13.34</td>
<td>NA</td>
<td>525.70</td>
</tr>
</tbody>
</table>

The $Rₑ$ shifted from 6.77 ohms to 13.35 ohms (avg.) and became constant at that value, indicating that an additional and stable uncompensated resistance was offered by the electrolyte as well as the SEI layer throughout the cycling. This stable resistance contributed to the exceptional durability of the TiO₂ host. The larger semi-circular region was due to the charge transfer impedance (transfer of Na ions from the electrolyte to the surface), suggesting the initiation of reversible Na storage. But there was no observable change in the diffusive component as the low-frequency part shows high angle (with real Z axis).

From 0.45 V on, the $Rₑ$ contribution is not distinguishable, because the $Rₖ$ overlaps with it. At 0.45 V, the charge transfer resistance increases, which suggests that the transfer of Na-ions from the electrolyte to the surface encounters resistance, because Na-ions are already present on the surface. At the last investigation voltage point, a sudden change in the low-frequency range depicts the storage of Na-ions on the surface of the TiO₂ [16, 19, 21], which also confirms that the peaks near 0.1-0.2 V were due to surface storage of Na (Figure 6-3a). Hence, this PEIS study confirms that the electrolyte used was able to create a stable SEI, enabling an easy transfer of Na ions into the host TiO₂.
The exceptional electrochemical performance of Na-ion storage in the dendritic TiO\(_2\) nanostructures and the stability of these nanostructures, coupled with the insights on SEI formation offered by the PEIS study, prompted further investigation of structural and surface changes in the nanostructure upon sodiation and de-sodiation. The oriented dendrites offer the unique ability to characterize sodium storage and its structural effects spatially via \textit{ex-situ} techniques, which allow us to gain a better understanding of the sodium storage mechanism.

\textbf{6.4.4 \textit{Ex-situ} analyses:}

\textit{Ex-situ} analyses of the cycled electrodes were performed at four voltage points (Figure 6-5a): after the 1\textsuperscript{st} and 2\textsuperscript{nd} discharges (0.05 V), and after the 1\textsuperscript{st} and 2\textsuperscript{nd} charges (3.00 V). \textit{Ex-situ} Raman spectra (Figure 6-5b) of the pristine and cycled TiO\(_2\) samples exhibited strong characteristic peaks of TiO\(_2\) at 142.88 cm\(^{-1}\), 195.69 cm\(^{-1}\), 393.54 cm\(^{-1}\), 516.28 cm\(^{-1}\), and 635.66 cm\(^{-1}\). These respectively correspond to the E\(_g\), E\(_g\), B\(_{1g}\), A\(_{1g}\), and the E\(_g\) lattice modes of anatase TiO\(_2\) [22, 23]. Interestingly, no weakening in the anatase peaks was observed in the cycled TiO\(_2\) as compared to the pristine TiO\(_2\), suggesting extraordinary stability of the crystal structure to repeated sodium intercalation and de-intercalation. This is in contrast to the previous report of Raman studies which indicates that the reduction of the anatase peaks is due to destruction of the crystal structure [4, 18]. However, a broad peak at 446.60 cm\(^{-1}\) was observed for the de-sodiated samples (after the 1\textsuperscript{st} and 2\textsuperscript{nd} charges), and new peaks were observed at 952 cm\(^{-1}\) for all the samples. The first peak is possibly from the appearance of rutile TiO\(_2\) in the charged state, which also exhibits an E\(_g\) peak at 446.60 cm\(^{-1}\) [24]. The second peak at 952 cm\(^{-1}\) corresponds to NaClO\(_4\), and is a result of any remaining electrolyte on the surface of the electrode [25]. \textit{Ex-situ XRD} analysis (Figure 6-5c) of the cycled nanostructures and comparison with the pristine TiO\(_2\) nanostructure confirms that the crystal structure of anatase was preserved throughout the sodiation and de-sodiation process. The
pristine TiO\textsubscript{2} sample was predominantly oriented along the (112) plane. However, upon cycling, the preferred orientation along the (112) plane was lost. Further, new diffraction lines were observed for the cycled samples, corresponding to the (103), (004), (200), (105), (213), and the (214) anatase planes. This loss of orientation and the new diffraction lines suggest the formation of grain boundaries as a result of sodiation in the single crystal column. A slight increase in lattice constants was also observed for all the cycled TiO\textsubscript{2} samples, as compared to the pristine TiO\textsubscript{2} samples (Figure 6-5d). Going from pristine to the first sodiation, both unit cell parameters, \(a\) and \(c\), increase from 3.7845 Å to 3.7868 Å and from 9.4957 Å to 9.5027 Å, respectively. This increase is due to the large Na-ion intercalation into the anatase crystal structure, which expands to accommodate the Na-ion, thus retaining its stability. This expansion is consistent with previously reported detailed \textit{in-situ} and \textit{ex-situ} XRD analyses for Li and Na-ion intercalation into anatase.
However, after the first discharge, a trend in the unit cell parameters begins, with the lattice parameter $a$ decreasing, and $c$ increasing upon sodiation. This trend suggests that sodium intercalation maybe along the direction perpendicular to the (100) plane. Further, one of the substrate’s peak intensity ($2\theta=27.44^\circ$) increases and a new peak occurs at $2\theta=39.33^\circ$. These two observations are likely due to the formation of small amounts of rutile TiO$_2$ in the columns as a result of the sodiation reaction. The rutile and stainless steel substrate peaks at 27.44° overlap, and hence are easily confused. However, the 39.33° peak is exclusively the rutile (200) plane. Interestingly, the peak intensity of the rutile phase decreases in the discharged samples and increases in the charged samples. Our earlier ex-situ Raman spectroscopy also exhibited similar behavior for the $E_g$ band rutile peak. Usui et.al. [27] similarly observed a peak intensity decrease with sodiation and recovery with de-sodiation in rutile TiO$_2$. Ex-situ XPS analysis revealed the oxidation state of Ti in the cycled columns. The Ti 2p spectrum shows two peaks in the region of 456-460 eV and the 462-466 eV range, corresponding to the Ti $2p_{3/2}$ and the Ti$2p_{1/2}$ binding energies respectively (Figure 6-6). The $2p_{3/2}$ peaks for discharged samples (after the 1$^{st}$ and 2$^{nd}$ discharges) are shifted towards higher binding energies. Deconvolution of the Ti $2p_{3/2}$ peak reveals two peaks centered at 457.64 eV and 458.53 eV for the 1$^{st}$ and 2$^{nd}$ discharged samples, while the Ti $2p_{3/2}$ peak for charged samples (after the 1$^{st}$ and 2$^{nd}$ charges) revealed only a single peak centered at 458.39 eV for the 1$^{st}$ and 2$^{nd}$ discharged samples. Previous reports noted that the peak at 457.64 eV corresponds to the Ti$^{3+}$ binding energy, while the 458.53 eV corresponds to the Ti$^{4+}$ binding energy [28]. This correspondence suggests that Na-ion intercalation into TiO$_2$ follows a similar mechanism as Li$^+$ intercalation by a reversible Ti$^{4+/3+}$ redox reaction pathway, in agreement with the previous study by Kim et. al. [12]. Wu et. al. [18], however, have reported an irreversible partial transformation to metallic Ti$^0$ along with a transition to amorphous TiO$_2$. No such Ti$^0$ was
observed in our electrodes, and moreover, the XRD pattern and Raman spectra confirm the retention of the anatase structure, highlighting the exceptional structural stability of our nanostructured TiO$_2$ electrodes.

To further investigate the interaction of sodium with the nanostructure, and to gain insight into the sodium storage in the nanostructure, *ex-situ* STEM-EDX mapping, and elemental line scans were performed (Figure 6-7). A unique advantage of having oriented columnar structures on the current collector is that *ex-situ* imaging and elemental measurement can provide insights into the distribution of sodium in the TiO$_2$ electrode between the current collector and the separator. The STEM-EDX mapping of the sodiated sample shows a very uniform distribution of Na in the column from the base to the tip. This uniformity validates our previous claim that the dendritic columnar structures provide uniform electrolyte-electrode interaction, reaction, and ion...
intercalation along the entire length of the column. As expected, the mapping of the de-sodiated sample shows a very sparse signal for the presence of Na. The presence of Na can also be quantitatively observed in the line scan along the width of the column. For the sodiated sample, the signal intensity for the Na and O are comparable at the edges, but the oxygen peak intensity is higher in the center. This distribution implies that the amount of Na in the TiO$_2$ column is higher.
near the surface and decreases towards the center, which is anticipated since Na-ion diffuses from the surface to the interior of the column. In the de-sodiated sample, the signal intensity of Na is negligible compared to the O signal, suggesting almost complete removal of the sodium from inside the columns. The above STEM-EDX results were obtained by dispersing the cycled TiO₂ columns in water, following by dropping and drying them on the TEM grid. Dispersion of the columns in water removes the irreversible Na absorbed on the surface of the columns as a result of SEI formation and other low voltage reactions. Hence, the above results originate from the Na-ion intercalated into the TiO₂ crystal structure. We also tried dispersing the cycled TiO₂ columns in isopropyl alcohol (IPA) and performing the STEM-EDX mapping (Figure S 6-4). IPA does not react with Na as vigorously as water, and hence surface Na is likely to be preserved and can be analyzed. IPA-based results show a good amount of Na even in the de-sodiated sample, confirming the irreversible surface Na storage that we observed in the first cycle. Hence, the sodiated and de-sodiated samples were designated as NaₓTiO₂ and NaᵧTiO₂, respectively, where x>>y.

Insights into the changes to the crystal structure were provided by SAED measurements, which show a slight rotation in the (101) plane for the sodiated sample, while no rotation was observed for the de-sodiated sample. The stored sodium was likely the reason for the distortion, suggesting that the storage may be at sites in or near the (101) plane. While the rotation in the plane appears to be largely reversible, it is also likely the reason for the slight anatase to rutile transformation due to the strain induced in the crystal structure. HR-TEM images further support the argument of nanostructure stability and reversible lattice rotation. Rotational Moirè fringe patterns observed on the column surface for the sodiated samples (Figure S 6-5) suggest the presence of two overlaying lattices on the surface, which reconfirms the rotational distortion of the anatase structure to accommodate the Na-ion in the structure. This continuous distortion of the lattice is hypothesized
to cause a slight transformation of the anatase to rutile, which we reported previously with *ex-situ* XRD and Raman studies. Over the course of 1000 charge-discharge cycles, while the anatase phase still dominates, the rutile phase, represented by the peak at 445.20 cm\(^{-1}\), becomes more observable by *ex-situ* Raman studies (Figure 6-8) [24]. Electrolyte (NaClO\(_4\)) peak at 945 cm\(^{-1}\) was observed in all of the cycled samples, with a high intensity in the SEI lumps on the surface. As expected, on the surface, the rutile phase was more prominent because the surface was exposed to Na-ion insertion and de-insertion. In the bulk, the rutile phase appeared to be lower than at the surface, due to less interaction with Na-ions. While crystal phase transition as a result of metal-ion intercalation has been reported previously for other materials [29, 30], this is the first such observance in TiO\(_2\).

As highlighted in the study, this single crystal, dendritic, oriented one-dimensional morphology not only delivers exceptional performance in Na-ion systems, but also provides information regarding the Na-ion storage in anatase TiO\(_2\) nanostructures. From the extensive results obtained
in this study, we show that the dendritic tree-like structure delivers a high initial discharge capacity of 965 mAh g\(^{-1}\) at a current rate of 20 mA g\(^{-1}\). STEM-EDX analysis after the 1\(^{st}\) charge allowed us to visually confirm irreversible storage on the column surface. Along with the surface storage, at 0.75 V the sodium starts to intercalate into the TiO\(_2\) crystal structure via diffusive transport. The diffusion coefficient of Na-ion in the anatase TiO\(_2\) structure is estimated to be approximately 8.54×10\(^{-18}\) cm\(^2\) s\(^{-1}\), which is much lower than the value of 1.76×10\(^{-11}\) cm\(^2\) s\(^{-1}\) estimated for Li-ions in the same columnar TiO\(_2\) structures, due to the larger size of the Na-ion than the Li-ion. This diffusion into the crystal structure is hypothesized to be parallel to the (001) plane, causing a slight expansion in the unit cell lattice parameter ‘c’ and a one-time expansion in lattice parameter ‘a’, in order to accommodate the Na ion into the lattice. For the first time, via Moirè fringes in the HR-TEM images and the SAED pattern, we have observed rotational distortion in the (101) plane due to Na-ion insertion, which subsequently leads to a slight transformation of the metastable anatase to the thermodynamically stable rutile phase. Sample processing in water to remove the surface-stored Na, followed by STEM-EDX analysis, allowed us to view solely the Na-ion intercalated into the TiO\(_2\) structure. The distribution of Na was uniform throughout the entire column (from top to bottom) as a result of the well-spaced and oriented one-dimensional geometry. The columns exhibited exceptional reversible Na-ion storage capacities and good rate capability. In spite of the large size of the Na-ion, the columnar TiO\(_2\) nanostructures, due to their hierarchical structure, are extremely stable during cycling in Na-ion systems, with the morphology and crystallinity being preserved even after 1000 cycles, during which they were subjected to current rates as high as 1000 mA g\(^{-1}\).

The morphological and structural stability are reflected in the electrochemical performance of the columns, showing 85.1% capacity retention after 1000 cycles (compared with the 31\(^{st}\) cycle) at a
current density of 100 mA g\(^{-1}\), and a 99.55% Coulombic efficiency at the 1000\(^{th}\) cycle, the highest reported for anatase TiO\(_2\). This exceptional performance and high stability are attributed to the distinctive nanostructure, in which the dendritic branches provide the high surface area needed for Na-ion insertion, while the column core provides structural stability.

6.5 Conclusions

In this work, we report the successful growth of one-dimensionally oriented single crystal dendritic TiO\(_2\) nanostructures on stainless steel foil via a facile single-step ACVD process. These structures allowed us to study the true electrochemical behavior of anatase TiO\(_2\) as binder- and carbon-free electrode structure. A high reversible capacity of 180 mAh g\(^{-1}\) was achieved at a 100 mA g\(^{-1}\) current rate, which is exceptionally stable, with a discharge capacity of 120 mAh g\(^{-1}\) even after 1000 cycles at the same rate. The material exhibits a high reversibility of 99.55% and a redox difference of 41 mV at the 1000\(^{th}\) cycle. Extensive structural characterization of the highly durable material was carried out using \textit{ex-situ} SEM, XPS, Raman spectroscopy, HR-TEM, SAED, and STEM-EDX analysis during the first two cycles, providing valuable insights into the sodium insertion and storage in the TiO\(_2\) crystal structure. We confirmed that the morphology and the crystal structure are retained even after 1000 cycles, a finding that demonstrates the robustness of the material in the Na-ion electrochemical environment. Our proprietary methods to make binder- and carbon-free battery electrodes are presently under development at both Washington University in St. Louis and the Indian Institute of Technology. The carbon-free electrode architecture holds promise for achieving a high rate capability and high energy density in a sodium-ion battery, and the current process of making the electrode facilitates Na-ion movement in the TiO\(_2\) lattice much more freely even in an organic electrolyte. Currently, we are in process of making pre-commercial grade full cell comprising of a TiO2 anode and a suitable high potential cathode.
6.6 Acknowledgments

This work is based upon work supported under the US-India Partnership to Advance Clean Energy-Research (PACE-R) for the Solar Energy Research Institute for India and the United States (SERIIUS), funded jointly by the U.S. Department of Energy (Office of Science, Office of Basic Energy Sciences, and Energy Efficiency and Renewable Energy, Solar Energy Technology Program, under Subcontract DE-AC36-08GO28308 to the National Renewable Energy Laboratory, Golden, Colorado) and the Government of India, through the Department of Science and Technology under Subcontract IUSSTF/JCERDC-SERIIUS/2012 dated 22nd Nov. 2012. The authors acknowledge Dr. Huafang Li at the Institute of Material Science and Engineering (IMSE), Washington University in St. Louis for help with STEM measurements and analysis.

6.7 References


6.8 Supplementary Information

6.8.1 Material Characterization:

Top view of the titled electrode showing the deposited columnar dendritic TiO$_2$ nanostructures (Figure S 6-1) used in Figure 6-2a.

Figure S 6-1: Cross sectional SEM image of the columnar TiO$_2$ nanostructures on stainless steel substrate

6.8.2 Electrochemical Performance and HR-TEM analysis:

The power performance of the TiO$_2$ nanostructured anodes for different electrolytes is depicted in Figure S 6-2. This study was performed to evaluate the long term cycling performance of: 1 M NaClO$_4$ in PC solvent, and 1 M NaClO$_4$ in EC:PC solvent mixture (v/v). The electrolyte in EC:PC solvent performed better, hence was used for the further studies to evaluate the performance as well as the mechanism of Na-ion storage in the TiO$_2$ host.
6.8.3 1000 Cycles Extended Performance:

The Coulombic efficiency at different cycles for the cycling depicted in Fig. 1a in the main manuscript is tabulated in Table S 6-1. Coulombic efficiency was calculated as (charge capacity/discharge capacity) × 100, i.e., Na leaving/Na insertion. The result shows that the efficiency continuously improves with cycling and becomes more than 99% after 250 cycles.

<table>
<thead>
<tr>
<th>Cycle No</th>
<th>Coulombic Efficiency (%)</th>
<th>Current Rate</th>
<th>Cycle No</th>
<th>Coulombic Efficiency (%)</th>
<th>Current Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>50.26</td>
<td>20 mA g⁻¹</td>
<td>50</td>
<td>95.31</td>
<td>100 mA g⁻¹</td>
</tr>
<tr>
<td>6</td>
<td>79.22</td>
<td>50 mA g⁻¹</td>
<td>100</td>
<td>97.62</td>
<td>100 mA g⁻¹</td>
</tr>
<tr>
<td>11</td>
<td>86.59</td>
<td>100 mA g⁻¹</td>
<td>250</td>
<td>99.08</td>
<td>100 mA g⁻¹</td>
</tr>
<tr>
<td>16</td>
<td>90.14</td>
<td>200 mA g⁻¹</td>
<td>500</td>
<td>99.58</td>
<td>100 mA g⁻¹</td>
</tr>
<tr>
<td>21</td>
<td>91.28</td>
<td>500 mA g⁻¹</td>
<td>750</td>
<td>99.47</td>
<td>100 mA g⁻¹</td>
</tr>
<tr>
<td>26</td>
<td>92.65</td>
<td>1000 mA g⁻¹</td>
<td>1000</td>
<td>99.55</td>
<td>100 mA g⁻¹</td>
</tr>
</tbody>
</table>

Figure S 6-2: (a) Galvanostatic cycling at different current rates followed by long term cycling at 100 mA g⁻¹ for PC and EC:PC electrolytes up to 500 cycles, along with the (b) TEM and (c) HR-TEM analysis after 500 cycles for EC:PC.
6.8.4 FEG-SEM Analysis (with EDS Line Scan on 1000\textsuperscript{th} Cycle):

Figure S 6-4 show comparative cross sectional views of the initial morphology and the morphology after 1000 cycles. The results show that the dendritic columnar morphology is retained even after 1000 cycles. The columns remain in good contact with the SS substrate, which also proves the particular advantage of the synthesis process. At four different zones, elemental line scans were performed through SEM-EDS measurement. After 1000 cycles, Na is distributed throughout the column, and the Na atomic % is slightly higher at the tip of the column.

![Image](image_url)

Figure S 6-3: Cross-sectional view of TiO\textsubscript{2} (a) before and (b) after 1000 cycles, along with elemental line scan data at different zones. The green line corresponds to Na, and red lines are for O, measured by the SEM-EDS line scan.

6.8.5 Diffusion Co-efficient Calculation:

The diffusion co-efficient was calculated using the following equation:\textsuperscript{1, 2}

$$D = \frac{4}{\pi \tau} \left( n_m V_m \right) \frac{(n_m V_m)^2 \Delta E_s^2}{S^2 \Delta E_i^2}$$

where D is the diffusion co-efficient; \( \tau \) is the duration of the current pulse (s); \( n_m \) is the number of moles (mol); \( V_m \) is the molar volume of the electrode (cm\(^3\) mol\(^{-1}\)); S is the electrode/electrolyte
contact area (cm$^2$); $\Delta E_s$ is the steady-state voltage change, due to the current pulse; and $\Delta E_t$ is the voltage change during the constant current pulse, eliminating the iR drop.

In the case of the 2nd cycle (Fig. 2b), the calculation was done in the following manner:

$\tau = 1200$ sec

$S = 11.14 \text{ cm}^2$ (calculated from the observed geometry and measured mass, assuming cylindrical columns)

$n_mV_m = 4.87 \times 10^{-5} \text{ cm}^3$

$\Delta E_s = 0.00345 \text{ V}$

$\Delta E_t = 0.16818 \text{ V}$

Hence, $D = 8.53937 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$.

**6.8.6 Elemental Analysis (STEM-EDS):**

Two different solvents were used to evaluate surface-stored Na and Na diffused inside the TiO$_2$ host. Cells were disassembled inside a glove box after cycling. The cycled electrode consisted of (i) diffused Na stored inside the solid TiO$_2$ medium, (ii) SEI and other trapped Na (possibly in some unknown form, such as metallic or semi-metallic clustered), and (iii) sticky electrolytes. The electrode was washed with PC (the solvent used for making the electrolyte), which helped to dissolve the salt NaClO$_4$ (as an electrolytic component) present onto the surface. This process made sure that no residual electrolyte was present on the surface. In the next step, the SEI and trapped Na were removed by washing the electrode with water, since water reacts vigorously with Na. In this report, TiO$_2$ columns were dispersed in water and used for STEM-EDS analysis.
Following another path, after washing the TiO₂ electrode with PC, we dispersed it into IPA (isopropyl alcohol). Typically, IPA did not remove SEI and associated trapped Na onto the surface. Hence, we were able to clearly differentiate Na stored on the surface from solid state Na in TiO₂ (Figure S 6-4).

![Comparative ex-situ STEM-EDX images of desodiated TiO₂ columns washed with (a) IPA, (b) water and (c) sodiated TiO₂ columns washed with water.](image)

**6.8.7 Ex-situ HR-TEM analysis**

The HR-TEM images of the sodiated and desodiated sample during the first charge discharge cycles are shown in Figure S 6-5.
6.8.8 Supplementary References:


Chapter 7

Single Step Synthesis of Nb doped TiO$_2$

nanostructured electrodes as high capacity
anodes for sodium ion batteries

To be submitted for publication, August 2016
7.1 Abstract

A promising approach to improving the performance of TiO$_2$ as anode for sodium ion batteries is to improve the diffusivity of sodium in the TiO$_2$ nanostructure and to improve the electronic conductivity of the TiO$_2$ nanocolumns. This chapter focuses on the synthesis of niobium doped titanium dioxide nanostructures using a multi component aerosol chemical vapor deposition process. The doping rate of niobium was controlled up to 15% in the TiO$_2$ nanostructures and material characterization was performed to characterize the effect of doping on the crystal structure. The synthesized nanostructures were used as binder and carbon free anodes for sodium ion batteries and the performance was studied (Figure 7-1). Electrochemical performance results demonstrate significant capacity and rate capability improvements for the electrodes doped with up to 10% niobium, beyond which the capacity decreases.

Figure 7-1: Graphical abstract of the work presented in Chapter 7
7.2 Introduction

Annual lithium consumption in 2015 was estimated at 650,000 tons, with lithium-ion batteries accounting for over 30% of the consumption. For more than two decades, lithium ion batteries have been the prominent form of secondary energy storage. As their demand grows exponentially with increasing demand for electronics, HEVs and EVs, there is growing concern about the limited availability of lithium leading to increasing prices. Sodium-ion batteries are a viable alternative, sodium being the second most abundant material in the earth’s crust [1]. There has been growing research interest in possible electrode materials for sodium-ion batteries. Since sodium is similar to lithium in many aspects, research has focused on applying electrodes used for lithium ion batteries to sodium ion batteries [2]. However, graphitic carbon does not perform well as an anode for sodium ion batteries and hence other materials are being explored [3]. Recent studies [3-6] and the work presented in the previous chapter were focused on utilizing TiO$_2$ as an anode material for sodium ion batteries. Detailed studies on the intercalation of sodium into TiO$_2$ and the effect of crystal phase and morphology were carried out. Although sodium is similar to lithium in many aspects, it does present a problem due to its larger size. TiO$_2$ suffers from the disadvantage of low diffusion coefficient for lithium intercalation ($10^{-11} - 10^{-13}$ cm.s$^{-1}$) and low electronic conductivity ($1.9\times10^{-12}$ S.m$^{-1}$). The larger ionic radius of sodium further impedes intercalation into the crystal structure impacting stability of the host material thus lowering the performance [7].

A possible solution to both the limiting transport parameters is the doping of the TiO$_2$ crystal structure. Nb doped anatase TiO$_2$ has been widely researched for application as a transparent conducting oxide, owing to the substantial enhancement in electrical conductivity caused by the introduction of the Nb$^{5+}$ [8]. Nb$^{5+}$ is an n-type dopant that modifies the band structure of TiO$_2$ generating additional carriers in the conduction band [9]. This metallic conductivity is
accompanied by an expansion of the TiO$_2$ crystal lattice due to the large size of the Nb$^{5+}$ cation (ionic radius = 0.64 Å) that substitutes the smaller Ti$^{4+}$ cation (ionic radius = 0.605 Å) [10]. Nb doped anatase TiO$_2$ has been explored previously for lithium ion batteries and has exhibited better performance at higher rates due to the above mentioned advantages [10-12]. While, a previous study has already been conducted investigating the application of Nb doped anatase as anode materials in sodium-ion batteries, they used nanoparticles of the doped material along with carbon and binder materials. We have previously demonstrated the different behavior of carbon and binder free oriented TiO$_2$ nanocolumnar structures in lithium-ion batteries leading to enhanced performance [13].

In this study, we synthesize one dimensional oriented single crystal Nb doped TiO$_2$ nanostructures using a single step aerosol chemical vapor deposition process [14] directly on stainless steel current collectors for use as anodes in sodium ion batteries [13]. Structural characterization of the doped thin films was performed and the effect of doping of the nanostructures on the performance as anodes in sodium-ion chemistry is studied.

7.3 Experimental Methods:

7.3.1 Synthesis of Nb doped TiO$_2$ using the ACVD process

Stainless Steel (SS316, ESPI Metals, OR, USA) with a thickness of 25μm and punched into 15 mm diameter discs were used as the current collector. Nanostructured thin films of Nb doped TiO$_2$ were synthesized using the ACVD process on stainless steel substrates (SS316, ESPI Metals, OR, USA) with a thickness of 25μm and punched into 10 mm diameter discs. Titanium tetraisopropoxide (TTIP) (97%, Sigma-Aldrich, MO, USA) and Niobium ethoxide (99.5%, Sigma-Aldrich, USA) placed in indigenous bubblers, maintained at 25 °C and 100 °C respectively were
used as the precursors. Nitrogen was used as the carrier gas for both the precursors and as dilution gas in the reactor. 5% hydrogen was added to the total flow to provide a reducing environment. Feeding lines for the titanium and niobium precursors were heated to 35 °C and 125 °C to prevent condensation of the precursor in the tubing. The two precursor vapor streams were mixed upstream of the feeder tube and the mixture was introduced in the reaction chamber. Doping ratios were controlled by controlling the flow of carrier nitrogen through the niobium precursor and the dilution nitrogen as shown in Table 7-1. The particles were deposited on the stainless steel discs, maintained at a temperature of 550°C, for 30 mins. Post deposition, the discs were dipped in 1.2 M HCl solution for 20 mins followed by rinsing with deionized water and acetone to remove any impurity from the surface. The samples were dried in an oven maintained at 85°C for 12 hours.

Table 7-1: Feed flow rates of carrier nitrogen bubbled the niobium and titanium precursor in the ACVD process. The calculated molar feed percentage of Nb and the doping percentage of Nb in the TiO₂ as measured by SEM-EDX and XPS.

<table>
<thead>
<tr>
<th>Carrier Nitrogen Flow Rate (sccm)</th>
<th>Calculated feed % of Nb</th>
<th>Measured Nb doping %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nb-ethoxide</strong></td>
<td><strong>Ti-tetraisopropoxide</strong></td>
<td><strong>Dilution flow</strong></td>
</tr>
<tr>
<td>0 &amp; 450</td>
<td>450</td>
<td>0%</td>
</tr>
<tr>
<td>250 &amp; 450</td>
<td>200</td>
<td>15%</td>
</tr>
<tr>
<td>350 &amp; 450</td>
<td>150</td>
<td>19%</td>
</tr>
<tr>
<td>450 &amp; 450</td>
<td>0</td>
<td>24%</td>
</tr>
</tbody>
</table>

### 7.3.2 Nanostructure characterization

The morphology of the nanostructures was analyzed using scanning electron microscopy equipped with an energy dispersive x-ray (SEM-EDX) spectrometer (FESEM, NOVA NanoSEM 230, FEI Co.) and the crystal structure was characterized using X-ray diffraction (XRD) (Bruker D8
Advance) with a CuKα radiation (wavelength = 1.5406 Å) at 35 kV and 35 mA. The scattering angle (2θ) used in the measurement was from 20° to 60° with a step size of 0.02° and a dwell time of 0.5 sec. Rietveld refinement of the anatase crystal structure (PDF no. 01-071-1166) was carried out in Topas 5 (Bruker) using the measured XRD spectra.

XPS measurements were carried out using PHI 5000 VersaProbe II equipped with monochromatic Al Kα (1486.6 eV) X-ray source. Fine scans were done for the Ti, Nb, C and O elements at a step size of . The XPS peaks fitting was performed using Multipak (v9.6, ULVAC-PHI) to a Gaussian-Lorentzian mixed function via an iterated Shirley method.

7.3.3 Electrochemical measurements

The current collector with the deposited Nb doped TiO₂ nanostructures was used as working electrode (WE) in a swagelok type stainless steel setup, with a cell configuration of Na|Electrolyte|TiO₂. Cells were assembled in an argon-filled glovebox (Lab Star, Mbraun, Germany) under controlled moisture and oxygen concentration below 1 ppm. A proprietary solution composition was used as the electrolyte. Metallic Na foil (Alfa Acear, 98%) was used as a counter electrode as well as reference electrode (CE/RE). Porous borosilicate glass microfiber filter (Whatman GF/D) was used as a separator into which few drops electrolyte was soaked. Electrochemical charge-discharge experiments were performed using Arbin Instrument (BT2000, USA) at various constant current rates.

7.4 Results and Discussion:

The co-feeding of niobium and titanium precursor in the ACVD reactor generates clusters of niobium and titanium based oxides [15]. These cluster grow as a result of collisional growth to form doped nanoparticles which deposit onto the substrate and sinter yielding a nanostructured
thin film (Figure 1). The percentage doping of niobium in the TiO$_2$ depends on the temperature of the two precursors and the flow rate of the nitrogen through them. Table 7-1 lists a comparison of the estimated doping % obtained via calculations and observed by SEM-EDX measurements and XPS measurements. Experimentally measured doping rates by SEM-EDX (Figure 7-3c) and XPS were very similar (within ±1%), but did not agree well with theoretically calculated Nb loading %. This deviation from theoretical estimates is likely due to the different kinetics of thermal decomposition of TTIP and niobium ethoxide. The synthesized thin films of niobium doped TiO$_2$ were visibly different from the undoped TiO$_2$ thin films with a bluish tinge increasing with increasing feed flow of niobium. The morphology of the thin films was observed to be one-dimensional columnar oriented vertically on the substrate with an average column height of 750

![Figure 7-2: Schematic of the multicomponent ACVD process for the synthesis of doped nanostructured thin films.](image)
nm and an average column diameter of 250 nm (Figure 7-3). No identifiable differences were in morphology were observed between the undoped and the doped samples. XRD spectra (Figure 7-4a) shows a shift in orientation from the (112) direction for the undoped samples to the (101) and (211) direction for the niobium doped thin films. A left shift in the (101) peak (Figure 7-4b) was observed for the samples with increasing doping concentration and no peaks corresponding to any niobium based oxides were seen in the spectra. This confirms the substitutional of Ti$^{4+}$ with Nb$^{5+}$ which leads to an expansion of the TiO$_2$ lattice due to the larger size of the Nb$^{5+}$ ion. Using Rietveld refinement, the lattice parameters for the tetragonal structure were calculated and, as expected, were found to increase linearly with the increasing doping concentration of Nb (Figure 7-4c). This linear increase is in accordance with Vegard’s law confirming that upto 15% Nb ions are soluble in the anatase TiO$_2$ structure [8]. This increase in the lattice parameters was accompanied by an expansion of the unit cell volume with a 0.96% volume expansion for the 15% Nb doped TiO$_2$ thin film (Figure 7-4d).
Figure 7-3: (a) Cross-section view and (b) Top view SEM image of the one-dimensional Nb doped TiO$_2$ thin film with 15.3\% Nb doping. (c) SEM-EDX spectra of the doped and undoped thin films.
Figure 7-4: (a) XRD spectra of the Nb doped TiO2 thin films with the (b) 25–26° two theta range zoomed in. Change in (c) unit cell lattice parameters and (d) the cell volume of the tetragonal crystal structure (I41/amd) obtained via Rietveld refinement of the measured XRD spectra.
Figure 7-5 shows the XPS spectra of the undoped and the doped TiO$_2$ thin films. The peaks are calibrated using the peak for adventitious surface carbon at 284.80 eV corresponding to the C 1s photoemission. Two characteristic peaks corresponding to $2p_{3/2}$ and $2p_{1/2}$ of Ti$^{4+}$ are observed in the region between 457 eV and 467 eV for all samples (Figure 7-5a). A small shift towards higher binding energies is observed in both the peaks for the doped samples compared to the undoped sample with the shift increasing with the Nb% doping. The shift in the peak is attributed to the substitution of the Ti$^{4+}$ with the Nb$^{5+}$ in the lattice leading to the possible formation of Nb–O–Ti bonds [16]. Characteristic Nb 3d peaks are observed between the 205 eV and 212 eV region for

![XPS spectra of the Nb doped TiO$_2$ thin films showing the (a) Ti (b) Nb and (c) O peaks. Curve fitting of the spectra peaks was used to deconvolution the peaks and observe the peak shifts.](image-url)

181
the Nb doped samples (Figure 7-5b). The O1s region exhibits two peaks in the region between 527 eV and 535 eV for all samples (Figure 7-5c). An increase in the binding energy for the peak centered at 529.84 eV (for undoped TiO\textsubscript{2}) is observed while a decrease in the binding energy of the peak centered at 531.52 eV (for undoped TiO\textsubscript{2}) is observed with introduction of the Nb doping. The former peak corresponds to the O\textsuperscript{2-} in the TiO\textsubscript{2} lattice (Ti–O–Ti) and an increase in the peak is attributed to the introduction of Nb\textsuperscript{5+} in the lattice leading to the formation of Nb–O–Ti bonds as was observed for the Ti 2p peaks [16]. The later peak is attributed to the surface hydroxyl groups (Ti–OH).

Figure 7-6 shows the galvanostatic charge discharge curves for the undoped and doped TiO\textsubscript{2} nanostructured electrodes at 20 mA.g\textsuperscript{-1}. The voltage profile is similar to that of the pristine nanostructured TiO\textsubscript{2} electrodes studied in Chapter 6 indicating similar intercalation mechanism in
the doped structures. However, it is clear that the performance of the Nb doped nanostructures depends on the doping % in the TiO$_2$ nanostructures. Figure 7-7 shows the rate capability and the cycling performance for the doped nanostructured electrodes. All samples exhibit an initial drop in discharge capacity attributed to the formation of the SEI layer followed by a relatively stable capacity profile. In order to get a clear idea of the impact of doping on the performance of these nanostructures, the 5$^{th}$ cycle discharge capacity is plotted against the %Nb in the nanostructure (Figure 7-7 inset). It is evident that the capacity increases drastically upon doping the TiO$_2$ with Nb upto 8% doping following which the capacity drops with further increase in doping. The

![Figure 7-7: Rate Capability of the Nb doped TiO$_2$ anodes in a sodium-ion system. Inset shows the 5$^{th}$ cycle discharge capacity as a function of the Nb doping %.]
performance of the 13% doped electrode was worse than the undoped TiO$_2$. The initial improvement in performance followed by a decrease has been reported previously for Nb doped TiO$_2$ thin films in lithium ion systems. Shin et. al. [17] carried out measurements of ionic diffusivity in Nb doped TiO$_2$ nanoparticles and observed a similar trend with lithium diffusivity reaching a peak at 10% Nb doping. The trend in diffusivity was attributed to the electronic-ionic (defects) association. The shift in the point at which the maxima is attained between the work by Shin et. al. and the current study is hypothesized to be due to the different material characteristics of the host material and the different intercalating ion (Li$^+$ vs Na$^+$).

Rate capability measurements, however show that the 8% Nb doped TiO$_2$ deteriorates in capacity to a higher extent than the 10% Nb doped TiO$_2$, both eventually exhibiting almost equal capacities (~200 mAh.g$^{-1}$) at current densities of 1000 mA.g$^{-1}$. It should be noted that the capacity of the 8% and 10% Nb doped structures at a 1C rate is approximately 300 mAh.g$^{-1}$, which is higher than any reported study for TiO$_2$ or doped TiO$_2$ in sodium-ion systems and is comparable to current graphite systems in lithium-ion batteries. This establishes the feasibility of using these nanostructures as an anode material in sodium-ion batteries. When the current density is decreased back to 100 mA.g$^{-1}$, the 8% Nb doped films retain 86% of their original capacity, while the 10% doped films exhibit 92% capacity retention. This suggests that while the 8% doped electrodes are better at low rates of cycling, they have issues of stability at higher rates. Long term cycling and rate performance of the undoped and 10% Nb doped TiO$_2$ electrodes was carried out to examine the stability of the nanostructures with repeated intercalation and de-intercalation of sodium. Results show that the increased performance of the doped electrodes is sustained at higher cycling rates and for long term cycling (upto 250 cycles). Thus, the doped nanostructures (upto 10% Nb)
are shown to exhibit better performance at various current densities and also after repeated long term cycling.

7.5 Conclusions:

Single step synthesis of one dimensional nanostructures of niobium doped titanium dioxide with a control over the doping percentage was achieved using the ACVD process. Significant performance enhancement was observed for the 8% and 10% Nb doped TiO$_2$ electrodes over the undoped TiO$_2$ electrodes in sodium-ion batteries. The effect of doping on the electrochemical performance agrees well with previous studies on Nb doped TiO$_2$ with lithium-ion systems. Further, the capacities reported for the Nb doped TiO$_2$ in sodium ion battery systems are comparable to currently used graphite anodes in lithium ion systems. Thus, these nanostructured electrodes can make sodium ion batteries feasible for commercial use.

7.6 Acknowledgments

This paper is based upon work supported under the US-India Partnership to Advance Clean Energy-Research (PACE-R) for the Solar Energy Research Institute for India and the United States (SERIIUS), funded jointly by the U.S. Department of Energy (Office of Science, Office of Basic Energy Sciences, and Energy Efficiency and Renewable Energy, Solar Energy Technology Program, under Subcontract DE-AC36-08GO28308 to the National Renewable Energy Laboratory, Golden, Colorado) and the Government of India, through the Department of Science and Technology under Subcontract IUSSTF/JCERDC-SERIIUS/2012 dated 22nd Nov. 2012. Electron microscopy was performed at the Nano Research Facility (NRF) at Washington University in St. Louis, a member of the National Nanotechnology Infrastructure Network (NNIN), supported by the National Science Foundation under Grant No. ECS-0335765.
7.7 References


Chapter 8

Conclusions and Future Directions
8.1 Conclusions

The work presented in the dissertation has developed a fundamental understanding of nanostructured thin films synthesis by the ACVD process and their application in energy storage devices. It explores how process parameters govern nanostructure morphology in the ACVD process. These nanostructures have been studied as photoanodes for visible light photoelectrochemical water splitting and as anodes for lithium-ion and sodium-ion batteries. Further, this work establishes the synthesis of doped nanostructured thin films using the ACVD process. The major conclusions drawn by this work are:

i. An aerosol dynamics model coupled with fluid dynamics in the reactor along with Brownian deposition and sintering on the substrate has been developed. The model provides a detailed understanding of the role of process parameters on the aerosol size distribution in the reactor and eventually, the nanostructure thin film morphology. The study highlights the importance of the mean residence time and the time average temperature in influencing the aerosol size distribution arriving at the boundary layer above the substrate. Finally, the study predicts and experimentally validates the role of the ratio of arrival time to sintering time in governing the nanostructure morphology of TiO$_2$.

ii. 1D nanostructures of TiO$_2$ decorated with gold nanoparticles have been studied for photoelectrochemical water-splitting. Results shows that these nanocomposites can be used to perform photoelectrochemical oxidation of water in the visible and NIR region owing to hot electron injection from the Au nanoparticle into the TiO$_2$ conduction band. Further, the absorption range can be tuned by controlling the shape and size of the gold nanoparticles.

iii. Single step synthesis of nanostructured TiO$_2$ thin films directly on current collectors has been demonstrated towards carbon and binder free anodes for lithium-ion batteries. The
effect of morphology on the electrochemical performance has been studied. The columnar nanostructures perform exceptionally, due to a combination of: the single crystal nature which provides higher electronic conductivity and higher Li\textsuperscript{+} mobility through the structure; perfect orientation along the high surface energy (112) plane which enables higher lithium intercalation; the direct fabrication of the 1D nanostructure on the current collector which provides enhanced structural stability and the dendritic structure that provides a high surface area at the electrode-electrolyte interface.

iv. An electrochemical transport model was formulated to predict the performance of 1D nanostructured electrodes in lithium ion battery systems and was successfully validated by the experimental results. The model was utilized to understand the role of kinetic and structural parameters on the electrochemical performance. The model can serve as a powerful tool to optimize 1D electrode design for different lithium–ion battery applications depending on the energy and power requirements.

v. The binder free 1D nanostructures were also studied as anodes for sodium-ion batteries. Rate capability and long term cycling tests conducted highlight the stability of the nanostructures to sodiation and de-sodiation. Detailed structural characterization and electrochemical transport measurements were carried out to understand the Na-ion diffusion and storage process in anatase TiO\textsubscript{2}. This work highlighted several unique advantages of the columnar nanostructures that enables better performance and long term stability. The single crystal nature of the columns have enabled the investigation of the impact of sodium insertion on the anatase crystal structure.

vi. The ACVD process has been extended to the synthesis of doped nanostructured thin films. The synthesis of 1D nanostructured Nb-TiO\textsubscript{2} thin films was studied to achieve controlled
doping and the doped nanostructures were applied as anodes for sodium-ion batteries. Remarkable improvements in performance over undoped TiO$_2$ were observed, depending on the doping percentage in the structures. The performance reported are comparable to currently used graphite anodes in lithium-ion systems demonstrating the feasibility of sodium-ion batteries for commercial use.

8.2 Future Directions

This work has studied the growth of nanostructured metal oxide and doped metal oxide thin films by the ACVD process directly onto desired substrates. From the modeling studies of the ACVD process, it was observed that the dynamics in the boundary layer and the substrate play a vital role in governing the nanostructured film morphology. However, within the boundary layer, the current model uses 1D steady state Brownian diffusion and ignores any aerosol dynamics. Further, on the substrate only two particle sintering is considered for film growth, ignoring any precursor reaction on the substrate. Thus, future work can be carried out to develop a mesoscale model for the boundary layer, and the reaction and sintering on the substrate. Moreover, the properties of the material could be included while considering crystal formation and growth on the substrate. This would allow the extension of the model to other materials and multi-components systems which would lead to a much better understanding of the nanostructure growth.

The current synthesis using the ACVD is limited to lab-scale and the throughput is rather low. The model developed to understand the role of process parameters on the nanostructure morphology with the suggested future work can be utilized to scale-up the process for pilot scale fabrication. A promising approach for this could be to utilize a roll to roll (R2R) process with multiple feed nozzles onto a moving substrate (Figure 8-1). The multiple feed nozzles can be used to deliver a
single or multiple precursors to deposit single or mixed oxide nanostructures on heated flexible substrates such as Corning willow glass for solar and TCO applications or on stainless steel substrates for battery electrodes. Argon curtains maybe used for providing a controlled environment in the reactor or to isolate multiple deposition stages for layered composites. The impact of moving substrates, multiple nozzles and the argon curtain on the fluid and aerosol dynamics could be further studied. *In-situ* monitoring of particle size distribution, chemical speciation and film morphology could be used to achieve real-time control over the process.

The feasibility of the ACVD process for the direct growth of nanostructures on current collectors for binder free battery electrodes has been established. The multi-component capabilities of the ACVD process can be extended to the synthesis of mixed oxides as battery cathodes. Most of the battery cathode materials for lithium-ion or sodium-ion batteries are mixed oxides containing lithium and sodium respectively. The availability of suitable organometallic precursors for lithium
and sodium is a potential challenge, however, novel precursor delivery routes such as electrohydrodynamic atomization maybe explored. The synthesis of both the cathode and the anode, at scale by the ACVD process would allow full cell fabrication capabilities (Figure 8-2).

Other potential applications of these nanostructures are immense. The improved conductivity and light absorption characteristics of the synthesized Nb doped TiO$_2$ thin films enable their use as transparent conducting oxide (TCO) and as electron transport layer for perovskite solar cells. The doping rate and the morphology of the thin films will need to be optimized for these applications. The process can also be utilized for the synthesis of other metal oxides such as 1D tin oxides as anodes for batteries or gas sensors. The process holds promising potential and addressing the challenges, related to improving understanding and scale-up, by future work would help realize the potential of the process.

![Figure 8-2: Utilization of the ACVD process for direct fabrication of binder free oriented one-dimensional nanostructured electrodes directly on current collectors for lithium and sodium-ion batteries. Figure reprinted by the permission of John Wiley and Sons from Chadha et. al [1], copyright 2014.](image-url)
8.3 References

Appendix A

Design and operation of the multicomponent Aerosol Chemical Vapor Deposition (ACVD) Reactor
A.1 Process Design

The multicomponent ACVD reactor allows for the synthesis of doped and mixed oxide nanostructured thin films by co-feeding multiple precursors into the reactor system. The process consists of three parts:

i. Precursor delivery system

ii. Reactor

iii. Control system

A.1.1 The precursor delivery system

The design of the precursor delivery system is shown in Figure A-1. The system consists of multiple bubblers mounted on an indigenously built frame. Each bubbler has an upstream mass flow controller, to bubble nitrogen through the precursor, and a downstream valve to isolate the bubbler if not being used. A purge line for each bubbler allows bypassing of the bubbler to clean the tubing after every experiment. A separate mass flow controller is present for the supply of dilution nitrogen, if needed.

Figure A-1: Design of the precursor feed system for the multicomponent ACVD system
A.1.2 The Reactor

The overall reactor system is shown in Figure A-2. It consists of a substrate holder, types of covers which allow the reactor operation in closed or open setting, and a holder base which also mounts the heaters. The closed setting allow a controlled atmosphere in the reactor and has been designed for materials which may be sensitive to ambient environments. The open setting is used for ambient condition synthesis and is mostly implemented for the synthesis of metal oxides. The closed setting is enabled by the chamber which is designed to have 1) pipe threading (NPT female fitting) at the top where feeder tube will enter 2) holes for nut bolts (to provide air-tight seal between chamber, gasket, and substrate holder) to go through at the bottom. Once all the fittings are properly tightened, this design only permits gas to exit via holes present in the substrate holder. In case of the open setting,
a glass cover is used instead of the chamber and the exit holes in the substrate holder are closed. The substrate holder design is shown in Figure A-3. The holder consists of a top plate for holding the substrate (Figure A-5) and a base for mounting the cartridge heaters (Figure A-4). Four ¼” holes on the top which lead the exit gas to escape from the side of the side of the holder via four ¼” NPT threaded holes. These holes are placed 90 degrees apart from each other right next to the 1x1 inch substrate pocket. The substrate holder pocket is 0.7 mm deep. The substrate holder also consists of a 1/8” port drilled into the plate housing the thermocouple for monitoring the temperature of the substrate.

Figure A-3: Design of the substrate holder

Figure A-4: Design of the substrate holder base which mounts the heater cartridges
A.1.3 The Control System

The entire process is monitored and controlled via a data acquisition system (cDAQ 9174, National Instruments) and a LABVIEW® program. The control system monitors and controls all the mass flow rates (via analog I/O) and temperatures (via analog input and digital output) in various parts of the process. Further, it allows for programmed deposition to yield thin films of different configurations (Figure A-6).

The LABVIEW® program consists of a main module (vi) and several sub vi’s. The main features of the program include:

i. Programmed deposition and autoshut off upon completion

ii. Pulse width modulation and PID implemented temperature control

iii. Alarm features which activate if flow or temperature readings indicate operational faults.
iv. Safety auto shutdown if alarms remain active for more than 15 secs continuously. System informs the operator automatically via text message.

Since the main vi block diagram is large, it has been shown in sections (Figure A-7 Section 1-7). This is followed by the sub vi’s. Only one subvi of each type has been shown – Mass flow controller sub vi and heater PID subvi.
Figure A-7: Overview of the Labview main vi.
Section 7
Figure A-8: Block diagram of a mass flow controller sub vi.
Figure A-9: Block diagram of heater control sub vi implemented via pulse-width modulation and PID control
Figure A-10: Front Panel of the Labview program for the ACVD system
A.2 Standard Operating Procedure

Version 3.0 – Updated on 02/02/2016 by Tandeep S. Chadha

A.2.1 Scope and Applicability

This standard operating procedure applies to the operation of the multicomponent Aerosol Chemical Vapor Deposition (ACVD) reactor in Room 3035. The ACVD reactor is used to synthesize thin films of single component and mixed metal oxides (TiO$_2$, Nb doped TiO$_2$, SnO$_2$) with well controlled morphologies for several applications.

A.2.2 Summary of the Method

An ACVD reactor is used to synthesize thin films of metal oxides with smooth, granular or columnar morphologies on different substrates (Stainless steel, ITO coated glass, FTO coated glass) for various applications. The process parameters in the reactor determine the morphology of the thin film formed.

A.2.3 Definitions

ACVD: Aerosol Chemical Vapor Deposition.

TTIP: Titanium(IV) Isopropoxide

TMT: Tetramethyl Tin

Nb ethoxide: Niobium (V) ethoxide

NTO: Niobium doped TiO$_2$

PPE: Personal protective equipment
A.2.4 Health and Safety Warnings

i. The ACVD operates at high temperatures (up to 600 C). Extreme care and caution should be taken to prevent injury from burns. Flame retardant PPE should be used when operating the ACVD. Make sure that non approved personnel in the lab area are fully aware of the risks during ACVD operation.

ii. The ACVD generates aerosol nanoparticles. The ACVD enclosure should always be vented in a fume hood. Extreme care should be taken to prevent any leakages of nanoparticles in the lab environment. Risks for nanoparticle inhalation should be minimized.

A.2.5 Equipment and Supplies

i. Personal Protective equipment:
   a. Safety glasses (worn at all times)
   b. Nitrile gloves (worn at all times)
   c. Flame retardant lab coat (worn at all time)
   d. Heat protective glove (worn while sample exchange)
   e. N95 particulate mask (worn while FLAR is in operation)

ii. Chemicals and gases (see appendix for MSDS)
   a. Titanium(IV) Isopropoxide
   b. Niobium Ethoxide
   c. Tetramethyl Tin
   d. Pressurized gas (Oxygen, Nitrogen, Hydrogen)
A.2.6 Apparatus and Materials

i. Enclosure hood-used to contain the generated aerosols, must be kept under negative pressure at all times

ii. ACVD deposition substrate with glass cover. The deposition substrate is maintained at high temperature. Caution must be taken while handling the substrate or the glass cover.

iii. Mass flow controllers-used to control gas flow rates in the ACVD. All gas lines supplying MFCs should be maintained below 40 psi line pressure.

iv. Precursor bubblers (X2)-used to contain the precursors for nanoparticle generation. These precursors are typically metal organic compounds and can be toxic when inhaled thus they must always be properly sealed. If the bubblers leak/break, spray water onto/near the bubblers to hydrolyze the precursors so they form inert oxides. If toxic substance, contact EHS.

v. Precursor feeder tube attached to the delivery line. This tube can get hot during operation. Heat protective gloves must be worn while handling.
Figure A-11: Photograph of the ACVD process reactor
A.2.7 Procedures

A.2.7.1 Preliminary Checklist

☐ Make sure all proper PPE is being worn

☐ Fittings are all properly tightened

☐ Gas tanks are adequately full while the regulators are at the right pressure

☐ Flow valves are operating normally and in the right position

☐ Mass flow controllers are warmed up and stable

☐ Check the flow rates of the gas in the mass flow controllers using the Gilibrator (if necessary)

☐ No leakages are detected

☐ The precursor bubblers are properly filled

☐ Precursor delivery lines are properly wrapped

A.2.7.2 System Startup

1. Ensure that the water/oil level in the isothermal water/oil bath around the precursors is full.
   Fill additional water/oil if required.

2. Turn on all power switches attached to the system.

3. Turn on the MFC power box.

4. Turn on the PC and RUN the labview program.

5. In the program front panel, switch on the needed heaters and set the desired substrate temperature, delivery tube temperatures and precursor temperatures. Allow temperature to stabilize. This will take usually 1 hour.

6. Clean the feeder tube and the glass cover and place in the oven to dry.
A.2.7.3 System Stabilization

7. Place the glass cover on the substrate holder.

8. Attach the precursor tubing to the system. Use 2 wrenches to tighten and ensure that precursor feed lines are not disturbed.

9. Raise the level plate upto the standard plate level. Check height using level indicator.


11. Place the glass slide onto the substrate using tweezers.

12. Open the central nitrogen supply valve (on the fume hood).

13. In the program, select which precursors will be used and set the desired precursor and dilution flow rates in the labview program.

14. Set the deposition time to 180 mins and turn on the deposition switch on the program.

15. After 180 mins the deposition switch will automatically turn off.

16. Lift the glass cover and take out the slide

A.2.7.4 Depositing on desired substrates

17. Lower the level plates.

18. Remove the precursor feeding nozzle. Use two wrenches.

19. With heat resistant gloves on, clean the nozzle with tissue and ethanol. Then blow air into the nozzle to ensure complete drying.

20. Tighten to the setup again as described in step 8.

21. Keep the substrate on the substrate holder using tweezers. Ensure that the substrate covers the entire substrate pocket on the holder. If not, place a steel foil below the substrate.

22. If needed, place a mask on one side of the slide to ensure deposition free area for attaching the electrode.
23. In the program, select which precursors will be used and set the desired precursor and dilution flow rates in the labview program.

24. Set the desired deposition time and turn on the deposition switch on the program.

25. After the set deposition time is over, the deposition switch will automatically turn off.

26. Lift the glass cover and take out the substrate.

27. Hold the substrate using tweezers in air and shake to cool. DO NOT place directly on table if glass.

28. After the substrate has cooled down, place it on the table.

29. Repeat steps 17-28 for subsequent samples.

**A.2.7.5 Switching off the system**

30. Turn off all heaters in the program.

31. Switch the three way valves on the precursors to purge mode (bypassing the bubbler).

32. Repeat steps 17-28 with a glass sample, 15 mins deposition time with a flow rate of at least 500 ccm through all precursors.

33. Turn off the labview program by hitting the big STOP button. DO NOT switch off the program from the labview software terminated button on the top.

34. Turn off all gas supply valves in the system.

35. Lower the level plates and remove the feeder tube.

36. Remove the glass cover and place upside down (Narrow portion down) on the side.

37. Turn off mass flow controller power box and PC.

38. Switch off all power switches.
Appendix B

COMSOL model setup for simulating fluid dynamics and heat transfer in the ACVD Reactor
### B.1 Global Definitions

#### B.1.1 Parameters

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{s0}$</td>
<td>723.15</td>
<td>Substrate temperature</td>
</tr>
<tr>
<td>$Q_{in0}$</td>
<td>9.17E-6</td>
<td>Inflow rate</td>
</tr>
<tr>
<td>$E$</td>
<td>74.03e3[J/mol]</td>
<td>Activation Energy</td>
</tr>
<tr>
<td>$A$</td>
<td>1.54e6[1/s]</td>
<td>Frequency factor</td>
</tr>
<tr>
<td>$T_{in0}$</td>
<td>323.15</td>
<td>Inflow temperature</td>
</tr>
<tr>
<td>$h_0$</td>
<td>20[mm]</td>
<td>tube height from substrate</td>
</tr>
<tr>
<td>$t_s$</td>
<td>2[mm]</td>
<td>substrate thickness</td>
</tr>
<tr>
<td>$R_s$</td>
<td>37.5[mm]</td>
<td>Radius of substrate</td>
</tr>
<tr>
<td>$t_c$</td>
<td>3[mm]</td>
<td>Thickness of the cover</td>
</tr>
<tr>
<td>$h_1$</td>
<td>90[mm]</td>
<td>first height of the cover stair</td>
</tr>
<tr>
<td>$h_2$</td>
<td>110[mm]</td>
<td>total height from the substrate</td>
</tr>
<tr>
<td>$R_t$</td>
<td>4[mm]</td>
<td>tube inner radius</td>
</tr>
<tr>
<td>$t_t$</td>
<td>1[mm]</td>
<td>tube thickness</td>
</tr>
<tr>
<td>$w$</td>
<td>19[mm]</td>
<td>cover radius change</td>
</tr>
<tr>
<td>$R_{s2}$</td>
<td>10[mm]</td>
<td>Radius of the substrate 2</td>
</tr>
<tr>
<td>$t_{s2}$</td>
<td>1[mm]</td>
<td>thickness of the substrate 2</td>
</tr>
<tr>
<td>$c_0$</td>
<td>0.0060</td>
<td>Initial concentration of TTIP</td>
</tr>
</tbody>
</table>
B.2 Model 1 (mod1)

B.2.1 Geometry 1

Figure B-1: Setup of the geometry of the ACVD reactor in COMSOL.

B.2.1.1 Units

<table>
<thead>
<tr>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length unit</td>
<td>mm</td>
</tr>
<tr>
<td>Angular unit</td>
<td>deg</td>
</tr>
</tbody>
</table>

B.2.1.2 Geometry statistics

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space dimension</td>
<td>2</td>
</tr>
<tr>
<td>Number of domains</td>
<td>7</td>
</tr>
<tr>
<td>Number of boundaries</td>
<td>28</td>
</tr>
</tbody>
</table>
B.3 Materials

B.3.1 Air

Figure B-2: Setup of simulation domains in COMSOL. The domain highlighted in blue is air.

B.3.1.1 Selection

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domains 3–4, 6</td>
</tr>
</tbody>
</table>
B.3.2 Steel AISI 4340

![Diagram showing setup of simulation domains in COMSOL. The domains highlighted in blue are steel.]

Figure B-3: Setup of simulation domains in COMSOL. The domains highlighted in blue are steel.

B.3.2.1 Selection

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domains 1, 5</td>
</tr>
</tbody>
</table>
B.3.3 Silica glass

Figure B-4: Setup of simulation domains in COMSOL. The domain highlighted in blue is silica glass.

B.3.3.1 Selection

<table>
<thead>
<tr>
<th>Geometric entity level</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selection</td>
<td>Domains 2, 7</td>
</tr>
</tbody>
</table>
B.4 Heat Transfer (ht)

Figure B-5: Setup of the heat transfer module for the ACVD reactor. Domains for which the heat transfer simulation was carried out are highlighted in blue.

**Features**

<table>
<thead>
<tr>
<th>Feature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Transfer in Fluids 2</td>
</tr>
<tr>
<td>Axial Symmetry 1</td>
</tr>
<tr>
<td>Thermal Insulation 1</td>
</tr>
<tr>
<td>Initial Values 1</td>
</tr>
<tr>
<td>Heat Transfer in Solids 2</td>
</tr>
<tr>
<td>Temperature 1</td>
</tr>
<tr>
<td>Convective Cooling 1</td>
</tr>
<tr>
<td>Open Boundary 1</td>
</tr>
<tr>
<td>Outflow 1</td>
</tr>
</tbody>
</table>
B.5 Laminar Flow (spf)

Figure B-6: Setup of the heat transfer module for the ACVD reactor. Domains for which the laminar flow simulation was carried out are highlighted in blue.

Features

<table>
<thead>
<tr>
<th>Fluid Properties 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial Symmetry 1</td>
</tr>
<tr>
<td>Wall 1</td>
</tr>
<tr>
<td>Initial Values 1</td>
</tr>
<tr>
<td>Inlet 1</td>
</tr>
<tr>
<td>Wall 2</td>
</tr>
<tr>
<td>Outlet 1</td>
</tr>
</tbody>
</table>
B.6 Transport of Diluted Species (chds)

Figure B-7: Setup of the transport of diluted species module for the ACVD reactor. Domains for which the transport of diluted species simulation was carried out are highlighted in blue.

**Features**

<table>
<thead>
<tr>
<th>Feature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Convection and Diffusion</td>
</tr>
<tr>
<td>Axial Symmetry</td>
</tr>
<tr>
<td>No Flux</td>
</tr>
<tr>
<td>Initial Values</td>
</tr>
<tr>
<td>Inflow</td>
</tr>
<tr>
<td>Outflow</td>
</tr>
</tbody>
</table>
B.7 Mesh 1

Figure B-8: Mesh formulation for the ACVD reactor simulation in COMSOL

B.8 Study 1

B.8.1 Stationary

Mesh selection

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry 1 (geom1)</td>
<td>mesh1</td>
</tr>
</tbody>
</table>

Physics selection

<table>
<thead>
<tr>
<th>Physics</th>
<th>Discretization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Transfer (ht)</td>
<td>physics</td>
</tr>
<tr>
<td>Laminar Flow (spf)</td>
<td>physics</td>
</tr>
<tr>
<td>Transport of Diluted Species (chds)</td>
<td>physics</td>
</tr>
</tbody>
</table>
Curriculum Vitae

Tandeep S. Chadha
Email: chadha@wustl.edu

ACADEMIC BACKGROUND
      Advisor: Prof. Pratim Biswas
2013  M.S., Energy, Environment and Chemical Engineering., Washington University in St. Louis
2009  B.Tech., Biotechnology, SAstra University, Thanjavur, India

PROFESSIONAL EXPERIENCE
2014- present  Co-Founder, Applied Particle Technology, LLC
               Developing and commercializing a disruptive air–purification technology
               Principal Investigator for a National Science Foundation STTR Phase I grant
               “Soft X-ray Enhanced Electrostatic Precipitator for High Efficiency Air
               Purification in Indoor Environments” (Jan–Dec 2016)

RESEARCH EXPERIENCE
2010- present  Graduate research assistant, Washington University in St. Louis
               Ph.D. Thesis: “Synthesis of nanostructured thin films by chemical vapor-aerosol
deposition (CVAD) process for energy applications.”
2009-2010  Junior research fellow, IIT Bombay, Mumbai, India
               Aerosol routes for the synthesis of nanoparticles with controlled structural
               properties” Applications to biodegradable particles for drug delivery
2008  Summer research intern, Chung-Ang University, Seoul, South Korea
               2D patterning of gold nanoparticles on PS-b-PEO block copolymer thin
               films
               and crystallization of Guanosine-5’-Monophosphate to identify new
               crystal polymorphs
2007-2008  Undergraduate research, SAstra University, Thanjavur, India
               Synthesis of anti-microbial properties of silver nanoparticles for applications in
               water purification.

HONORS AND AWARDS
2015  Global Impact Award 2015, Washington University in St. Louis
2015  Breakthrough Technology of the Year Award 2015, CleanTech Open
2015  Winner, Arch Grants for the development of Applied Particle Technology
2015  Student Travel Award, Battery Division, 227th Meeting of the Electrochemical Society, Chicago, IL
2014  Student Travel Award, Battery Division, 226th Meeting of the Electrochemical Society, Cancun, Mexico
2014  Graduate Student Teaching Assistant Award, Department of Energy Environmental and Chemical Engineering, Washington University in St. Louis
2013  Best poster award, 32nd American Association for Aerosol Research Annual Conference, Portland, OR
2012  Student Travel Award, 31st American Association for Aerosol Research Annual Conference, Minneapolis, MN
2011  Best poster award, 30th American Association for Aerosol Research Annual Conference, Orlando, FL
2010-2011  Recipient of Cherryl Walzel-Frick & F. Alan Frick Endowed Scholarship

PROFESSIONAL ACTIVITIES
2010-2011  Elected Vice-President of Umang - Indian Graduate Students Association, Washington University in St. Louis

PATENTS, PUBLICATIONS AND PRESENTATIONS

Patents:

Journal Publications:


18. Vazquez-Pufleau, M., Chadha, T.S., Yablonsky, G., & Biswas, P., “Determination of activation energy of carbon elimination from Si kerf by thermogravimetric analysis and insights in its reaction mechanism” *in preparation*


**Selected Conference Presentations**


