The Pennsylvania State University

The Graduate School

Department of Electrical Engineering

EFFECT OF ARCHITECTURE AND DOPING ON THE PHOTOELECTROCHEMICAL PROPERTIES OF TITANIA NANOTUBES

A Thesis in

Electrical Engineering

by

Karthik Shankar

© 2007 Karthik Shankar

Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

May 2007

The thesis of Karthik Shankar was reviewed and approved* by the following:

Craig A.Grimes Professor of Electrical Engineering Thesis Advisor Chair of Committee

Tom Mallouk DuPont Professor of Materials Chemistry and Physics

Jerzy Ruzyllo Professor of Electrical Engineering and Materials Science and Engineering

Srinivas Tadigadapa Associate Professor of Electrical Engineering

W. Kenneth Jenkins Professor of Electrical Engineering Head of the Department of Electrical Engineering

*Signatures are on file in the Graduate School

ABSTRACT

N-type nanocrystalline titania has attracted significant attention in the scientific community for its unique properties such as size quantization effects, large specific surface area and the possibility of large-scale use in high-efficiency semiconducting photoelectrochemical cells. While the nanocrystalline titania typically used in photoelectrochemical cells is prepared from a colloidal sol of nanoparticles, the titania nanotubes in the present study are robust immobilized structures grown anodically upright to form a compact self-organized non-particulate film.

This dissertation investigates the effect of the formation parameters such as the anodization potential, the concentration of water and fluoride species in the anodization electrolyte, the nature of the cation, the anodization temperature and the nature of the solvent used on the architecture of TiO_2 nanotube arrays fabricated by anodization of a starting Ti foil in a fluoride ion containing electrolyte. By varying the nature of the anodization electrolyte, an unprecedented degree of control over the architecture of TiO_2 nanotube arrays has been achieved. Nanotube arrays ranging from 0.1 µm to 100 µm in length, wall-thickness from 6 nm to 34 nm and pore diameters ranging from 12 nm to 250 nm were fabricated. While the nanotube length in all-aqueous electrolytes is limited to less than 10 µm, nanotube lengths as great as 360 µm were obtained by employing organic solvents in conjunction with water. The fast formation of very long high-aspect ratio TiO_2 nanotubes in electrolytes containing formamide and ethylene glycol are considered in terms of a growth model. It is suggested that faster high field ionic

conduction through a thinner barrier layer is responsible for the higher growth rates observed in electrolytes containing formamide and ethylene glycol.

Also examined are the photoelectrochemical properties that result as a consequence of the nanotubular architecture of TiO₂. The magnitude of the anodic photocurrents obtained from the nanotube photoelectrodes under band-gap illumination are significantly higher than that reported for any other form of nanocrystalline titania. Open circuit voltage decay experiments revealed that the electron recombination lifetimes in titania nanotube array photoelectrodes are superior to those in nanoparticulate electrodes of similar thickness and as a consequence, the nanotubular electrodes are expected to have superior charge collection efficiencies. Under band-gap illumination, 30 µm long TiO₂ nanotube array based photoanodes performed photo-assisted water splitting at an efficiency as high as 16.25 %. Anionic doping of TiO_2 nanotube arrays has been investigated as a technique to extend the photoresponse of titania into the visible region with emphasis on the carbon and nitrogen as dopants. An electrochemical doping technique was successful in introducing a nitrogen doping level as high as 12 % with nitrogen occupying the photoelectrochemically useful substitutional sites in the TiO_2 lattice instead of the more typical interstitial sites.

The nanotube arrays have an extremely large internal surface area compared to a planar surface. TiO₂ nanotube arrays 20 μ m in length and with a pore diameter of 90 nm are found to have an internal surface area 3000 times that of a planar unstructured film. Dye sensitized solar cells using different architectures and dyes have been constructed and photoconversion efficiencies as high as 6.9 % have been demonstrated.

TABLE OF CONTENTS

LIST OF FIGURES	viii
LIST OF TABLES	xvi
ACKNOWLEDGEMENTS	xvii
Chapter 1 Introduction	1
1.1 Nanostructured metal oxide architectures	1
1.2 Low cost metal oxide solar cells	3
1.2.1 Regenerative photoelectrochemical cell :	6
1.2.2 Non-regenerative photoelectrochemical cell (water-splitting cell):	9
1.2.3 Organic heterojunction cell :	10
1.3 Nanotubular vs. Nanoparticulate Architectures	11
1.4 Scope of the thesis	13
Chapter 2 Fabrication of Titania Nanotube Arrays	15
2.1 Fabrication of TiO_2 nanotube arrays in aqueous electrolytes	15
2.1.1 Experimental details	15
2.1.2 Control of Pore-Diameter	17
2.1.3 Control of Wall-Thickness	19
2.1.4 Formation of tapered nanotubes (nanocones)	23
2.1.5 Ridging-effect on nanotube sidewalls	25
2.1.6 Control of nanotube length	27
2.1.7 Effect of Chloride ions	31
2.1.8 Insight from the effect of Oxidizing/Reducing agents	33
2.2 Fabrication of TiO ₂ nanotubes in organic electrolytes	38
2.2.1 High permittivity amphiprotic protophilic solvents	38
2.2.2 Dipolar aprotic protophilic solvents	45
2.2.2.1 DMSO	45
2.2.2.2 DMF	48
2.2.3 High viscosity amphiprotic neutral solvents	49
2.2.3.1 Glycerol	49
2.2.3.2 Ethylene Glycol (EG)	50
2.2.4 Dipolar protophobic solvents	53
Chapter 3 Effect of the Cation on the Formation of Titania Nanotubes in	
Formamide-water mixtures	54

3.1 Experimental methods	55
3.2 Effect of cation and water content on the anodic current transient	60
3.3 Effect of cation on the morphology of titania nanotubes	69
3.3.1 Morphologies obtained by anodization at 35 V and 20 V	69
3.4 Discussion	83
3.5 Summary	84
Chapter 4 Evolution of the Nanotubular Structure	86
4.1 Theory of evolution of porous structure in Alumina	86
4.2 Theories of the evolution of the nanotubular structure in Titania	92
4.3 Anodic current transients in aqueous electrolytes	96
4.4 Anodic current transients in organic electrolytes	98
4.5 Growth Models	103
Chapter 5 Electronic Transport in TiO ₂ Nanotubular films	115
5.1 Importance of Electron Transport	115
5.2 Electronic band structure in TiO ₂ nanotubes	116
5.3 Transport and recombination in TiO_2 nanotube photoelectrodes	
5.3.1 Open circuit voltage decay technique: theory and application	
5.3.2 Electrical Impedance Spectroscopy (EIS)	
5.3.3 Intensity modulated spectroscopies	
5.4 Charge collection efficiency	131
Chapter 6 Dye Sensitized Solar Cells Using Titania Nanotubes	133
6.1 Surface area of TiO_2 nanotube array photoelectrodes	133
6.2 Dye desorption measurements to determine surface area of TiO_2	
nanotube arrays	135
6.2.1 Light harvesting efficiency (LHE)	140
6.3 Liquid Junction Dye Sensitized Solar Cells using TiO ₂ Nanotubes	142
6.3.1 Cell configurations	142
6.3.2 Experimental details	144
6.3.3 Performance of TiO ₂ NT array based solar cells	146
6.4 Solid State Dye Sensitized Solar Cells using TiO ₂ Nanotube Arrays :	150
Floor of Concept	130
Chapter 7 Photo-assisted Electrolysis of Water Using TiO ₂ Nanotubes Under Bandgap Illumination	154
7.1 Band-structure at the Semiconductor/Electrolyte Interface	154
1.2 Experimental details	157

7.3 Effect of architecture on photoelectrochemical properties	158
7 3 1 Effect of nanotube array Pore-Diameter	158
7.1 Effect of non-style Well Thickness on the techomical momenties	1
7.4 Effect of nanotube wall-1 nickness on photochemical properties	
7.5 Effect of nanotube length on photochemical properties	166
7.6 Hydrogen generation rates of titania nanotubes	170
7.7 Quantum Yield of TiO_2 nanotube array photoanodes	172
Chapter 8 Anionic Doping of Titania Nanotubes	174
8.1 Introduction	174
8.2 Conceptual routes for doping TiO ₂ nanotubes	177
8.2.1 Pre-Anodization	
8.2.2 Modifying the anodization bath chemistry	178
8.2.3 Pre-annealing treatments	
8.2.4 Annealing treatments	
8.3 Carbon incorporation through Flame-Annealing	
8.3.1 Why Flame Anneal ?	
8.3.2 Flame-Annealing of titania nanotube arrays	
8.4 Nitrogen doped nanostructured TiO_2 thin films : An electrochemical	
strategy to incorporate anionic dopants	191
Chapter 9 Conclusions	
Bibliography	206

LIST OF FIGURES

Figure 1: Field Emission Scanning Electron Microscope (FESEM) image of an arra titania nanotubes	ay of
Figure 2 : Solar radiation spectrum	6
Figure 3 : Schematic of regenerative photoelectrochemical cell	8
Figure 4: Schematic of non-regenerative photoelectrochemical cell	8
Figure 5: Photograph of n-type semiconductor based water splitting cell	9
Figure 6: Anodization setup	16
Figure 7: Top-view of nanotube array anodized at 10 V	18
Figure 8: Top-view of nanotube array anodized at 20 V	18
Figure 9: FESEM images of the top view of titania nanotube arrays anodized at 10V at A) 5°C B) 25°C C) 35°C and D) 50°C	20
Figure 10: FESEM images of the topview of titania nanotube arrays anodized at A)5°C and B) 25°C	22
Figure 11: Nanocone array obtained by ramped anodization in 0.1 M NaF (7.5 V-23V)	24
Figure 12 : Nanocone array obtained by ramped anodization in 0.5 % HF (10 V-23V)	24
Figure 13 : Schematic of a ridged nanotube	25
Figure 14: Nanotubes with continuous ridges by anodization in aqueous NaF	26
Figure 15: Cross-section of 0.2 μ m nanotubes fomed at pH < 1	30
Figure 16: Cross-section of 2 μ m nanotubes fomed at pH = 2.8	30
Figure 17: Cross-section of 6.6 µm long nanotubes formed in at pH 5	31
Figure 18 : Disordered nanorods formed by anodization in an aqueous electrolyte containing 0.1 M NH ₄ F and 5 M NH ₄ Cl. (Top-right) Inset showing the top-view at a magnification of 90K	32

viii

Figure 19: Nanotubes formed at 25 V in an aqueous electrolyte at pH 4 containing 0.5 M KI A] Topview and B] Cross-section	36
Figure 20 : Nanotubes formed at 25 V in an aqueous electrolyte at pH 4 containing 0.5 M KI added fifty seconds after the start of anodization	37
Figure 21: FESEM images of TiO ₂ nanotubes formed in FA based electrolyte at 35 V showing A] Cross-section at lower magnification and B] Cross-section at high magnification	12
Figure 22: FESEM images of TiO ₂ nanotubes grown in NMF based electrolyte at 40 V showing A] Cross-section at lower magnification B] Top-view4	12
Figure 23 : Illustrative FESEM cross-sectional [A] and [B], top [C] and bottom [D] images of a nanotube array ⁴⁵	17
Figure 24: Top-views of an irregular nanoporous structure formed at 20V in 0.1 M solution of NH ₄ F in DMF [A] Low magnification (5K) and [B] High magnification (50K)	18
Figure 25: FESEM images of the bottom [A] and top [B] of a nanotube array sample grown at 60 V in an ethylene glycol electrolyte containing 0.25 wt% NH ₄ F	52
Figure 26 : Cross-sectional FESEM image of a TiO ₂ nanotube array obtained by anodization of Ti foil for 96 hours at 60 V in an electrolyte containing 0.3% wt NH ₄ F and 2 vol % H ₂ O in ethylene glycol	52
Figure 27: Molecular structure of Tetrabutylammonium Fluoride	55
Figure 28 : Molecular structure of Benzyltrimethylammonium fluoride	56
Figure 29 : Current voltage behavior of different electrolytes probed using planar platinum electrodes with a cell constant of 1.25 in the low field regime	58
Figure 30 : Current voltage behavior of different electrolytes probed using planar platinum electrodes with a cell constant of 1.25 in the high field regime	58
Figure 31 : Real time observation of anodization behavior of a Ti foil (99.8 % pure) anodized at 20 V in a formamide solution containing 5 wt % H ₂ O and identical molar concentrations (0.27M) of fluoride ion bearing compounds with four different cationic species : Hydrogen (H ⁺), Ammonium (NH ₄ ⁺), Tetrabutylammonium (Bu ₄ N ⁺) and Benzyltrimethylammonium (BnMe ₃ N ⁺)6	52

Figure 32 : Real time observation of the effect of the water concentration on the anodization behavior of a Ti foil (99.8 % pure) anodized in an electrolyte containing 0.27 M NH ₄ F in N-methylformamide	68
Figure 33 : Cross-sectional FESEM image of TiO ₂ NTs formed at 35 V in formamide electrolyte containing 5 wt % water and 0.27 M HF. Upper-inset shows topview while lower inset shows enlarged cross-section	71
Figure 34 : Cross-sectional FESEM image of TiO ₂ NTs formed at 20 V in formamide electrolyte containing 5 wt % water and 0.27 M HF. Inset shows topview.	72
Figure 35 : Cross-sectional FESEM image of TiO ₂ NTs formed at 35 V in formamide electrolyte containing 5 wt % water and 0.27 M NH ₄ F. Upper-inset shows topview while lower inset shows enlarged cross-section	73
Figure 36 : Cross-sectional FESEM image of TiO ₂ NTs formed at 20 V in formamide electrolyte containing 5 wt % water and 0.27 M NH ₄ F. Upper-inset shows topview while lower inset shows enlarged cross-section	74
Figure 37 : Cross-sectional FESEM image of TiO ₂ NTs formed at 35 V in formamide electrolyte containing 5 wt % water and 0.27 M NaF. Upper-inset shows topview while lower inset shows enlarged cross-section	75
Figure 38 : Cross-sectional FESEM image of TiO ₂ NTs formed at 35 V in formamide electrolyte containing 5 wt % water and 0.27 M Bu ₄ NF. Upper-inset shows topview while lower inset shows enlarged cross-section	76
Figure 39 : Cross-sectional FESEM image of TiO ₂ NTs formed at 20 V in formamide electrolyte containing 5 wt % water and 0.27 M Bu ₄ NF. Upper-inset shows topview while lower inset shows enlarged cross-section	77
Figure 40 : Cross-sectional FESEM image of TiO ₂ NTs formed at 20 V in formamide electrolyte containing 5 wt % water and 0.27 M BnMe ₃ NF. Upper-inset shows topview while lower inset shows enlarged cross-section8	80
Figure 41 : Cross-sectional FESEM image of TiO ₂ NTs formed at 20 V in formamide electrolyte containing 1 wt % water and 0.27 M Bu ₄ NF. Inset shows enlarged cross-section	81
Figure 42 : FESEM images of nanotubes formed in 0.5 M solution of Bu ₄ NF in formamide electrolyte containing 5% water	82

Figure 43: Histogram showing effect of anodization potential, cation specie (0.27 M concentration), and water concentration on aspect ratio of the
resulting nanotubes regime
Figure 44: Schematic describing the evolution of the porous structure during the potentiostatic anodization of aluminum
Figure 45: Schematic representation of three possible pore base situations, r_1 , r_2 and r_3 representing the radii of curvature at pore bases, b the constant barrier-layer thickness and ω the (constant) solid angle subtended from the center of curvature to the pore bases. r_2 is the steady-state radius of curvature under the prevailing anodization conditions
Figure 46: Schematic diagram of the evolution of straight nanotubes at a constant anodization voltage, as follows: (a) oxide layer formation (b) pit formation on the oxide layer (c) growth of the pit into scallop-shaped pores (d) the metallic part between the pores undergoes oxidation and field-assisted dissolution and (e) fully developed nanotubes with a corresponding top view
Figure 47: Anodic current transient of a Ti foil sample anodized at 25V in a KF based buffered electrolyte of pH 5. The inset shows the period from 10^3 - $2x10^4$ s in greater detail
 Figure 48: Real time observation of anodization behavior of a Ti foil (99.8 % pure) anodized at 25 V in A] Electrolyte containing 0.5 wt % NH₄F and FA/NMF in the ratio 8:5 B] Aqueous electrolyte containing 0.5 wt % NH₄F and C] Aqueous electrolyte containing 0.5 wt % KF. Inset : region of local maxima in anodization current for aqueous solutions
Figure 49 : Real time observation of anodization behavior of a Ti foil (99.8 % pure) anodized in an electrolyte containing 0.4 wt % NH ₄ F in FA electrolyte 101
Figure 50 : Voltage dependent current – time behavior during the first 30 minutes of anodization of Ti samples in an electrolyte comprised of 0.3 wt % NH ₄ F, and 2 vol % H ₂ O in ethylene glycol
Figure 51 : Anodic current transients in FA based electrolyte fit to Power Law (Eq. 16)
Figure 52 : Anodic current transients in EG based electrolyte fit to Power Law (Eq. 16)
Figure 53 : f(i,i') versus ln i for potentiostatic anodization of Ti in EG based electrolyte

Figure 54: Schematics of the cross-section (left) and top-view (right) of the vertical TiO ₂ nanotube/barrier layer structure	.117
Figure 55 : Band structure of a grain in the nanotube wall	.119
Figure 56 : Photovoltage decay measurement of a TiCl ₄ treated transparent nanotube array dye sensitized solar cell at 100% sun	. 128
Figure 57 : Electron lifetimes determined by open circuit photovoltage decay measurements for front and back-side illuminated TiO ₂ nanotube array DSSCs, as well as response times for TiO ₂ nanoparticle DSC replotted from Fabregat-Santiago et al ⁸⁹	. 129
Figure 58 : Idealized unit cell of TiO_2 nanotube array with inner diameter D, wall-thickness W, $a = D+W$.	. 135
Figure 59 : Calculated geometric roughness factor as a function of nanotube length	.136
Figure 60: Molecular structure of N-719 dye	.137
Figure 61: Molecular structure of Black Dye	.138
Figure 62 : UV-Vis absorption spectra of caustic solutions of N-719 and Black dye	. 140
Figure 63 : Light harvesting efficiency as a function of wavelength	.143
Figure 64: Light harvesting efficiency as a function of amount of dye adsorbed	. 144
Figure 65 : Integration of transparent nanotube array architecture into front-side illuminated dye solar cell architecture	. 145
Figure 66 : Illustration of backside illuminated nanotube-array dye solar cell architecture	. 146
Figure 67 : Current-voltage characteristics of transparent nanotube array DSCs, under 100% AM-1.5 frontside illumination ¹⁰³	.148
Figure 68 : Effect of electrode area on the current-voltage characteristics of DSCs using non-transparent porous TiO ₂ formed in fluorinated 1:1 DMF-H ₂ O, under 100% AM-1.5 backside illumination.	. 149
Figure 69: Effect of nanotube array length and geometry on DSC performance	.151
Figure 70 : Effect of nanotube array length and geometry on DSC efficiency	.151

Figure 71: Current-voltage characteristics of DSCs constructed using 19 µm long nanotube arrays sensitized with Black Dye, under 100% AM-1.5 backside illumination.	. 152
Figure 72: Current-voltage characteristics of DSCs constructed using 19 μm long nanotube arrays sensitized with N-719, under 100% AM-1.5 backside illumination.	. 152
Figure 73 : Molecular structure of hole conducting organic compound Spiro- OMeTAD	.154
Figure 74: Current-voltage characteristics of a solid state DSC using sol-gel deposited CuSCN as the hole conductor, under 100% AM-1.5 frontside illumination.	. 154
Figure 75 : Energy band diagram for photoelectrolysis of water with n-type TiO ₂ and Pt	. 157
Figure 76 : TiO ₂ nanotube photoanode under band-gap illumination	. 161
Figure 77: Photocurrent density as a function of measured potential (vs. Ag/AgCl) for 22 nm diameter nanotubes (annealed at 350 and 500°C), 76 nm diameter nanotubes (annealed at 350 and 500°C) and as-anodized amorphous samples	. 162
Figure 78 : A variation of photocurrent density as a function of measured potential [vs. Ag/AgCl] is plotted for 10V samples anodized at four temperatures [i.e. 5°C, 25°C, 35°C and 50°C]	. 164
Figure 79 : Photocurrent squared-potential curves for 10 V samples anodized at four temperatures [i.e. 5°C, 25°C, 35°C and 50°C]	. 165
 Figure 80: Effect of nanotube-length on photoresponse [A] Photocurrent Density and [B] Photoconversion efficiency as a function of potential (1M KOH electrolyte and 98mW/cm² ultra-violet illumination) 	. 170
Figure 81: [A] Photocurrent density and [B] corresponding photoconversion efficiency, of annealed nanotube array samples fabricated using a formamide electrolyte, our so-called K1 bath of 0.56 grams of Ammonium Fluoride in a solution mixture of 5 ml de-ionized water + 95 ml formamide, at indicated anodization voltages.	. 171
Figure 82: [A] Photocurrent density and [B] corresponding photoconversion efficiency of nanotube array samples fabricated in an electrolyte of 1.2 g of NH ₄ F in a solution of 5 ml de-ionized water + 95 ml formamide at 35 V. The samples were annealed at indicated temperatures for 1 hour in oxygen prior	

to measurement. The resulting nanotube array samples were 30 μ m in length, with an outer diameter of 205 nm	.172
Figure 83 : Hydrogen photoproduction in a photoelectrochemical cell consisting of a 200 nm long 22 nm diameter nanotube array annealed at 500°C with a wall-thickness of 34 nm.	. 173
Figure 84 : The rate of hydrogen generation from crystallized nanotube arrays of different lengths annealed at 500°C	.174
Figure 85 : The 337 nm and 365 nm photocurrent wavelength photocurrent generated from a 6 µm nanotube array annealed at 600° C	.175
Figure 86 : Photocurrent vs. wavelength plots for TiO ₂ photoelectrodes recorded in 1 M KOH at anodic bias of 0.8 V	.187
Figure 87 : Photocurrent action spectra for TiO ₂ photoelectrodes recorded in 1 M KOH at anodic bias of 0.8 V	.187
Figure 88 : Incident photon-to-current efficiency for TiO ₂ electrodes in the visible wavelength region	.188
Figure 89 : The optical absorption spectra (obtained by diffuse reflectance measurements) of TiO ₂ electrodes in the visible wavelength region	.189
Figure 90: Photocurrent vs. Applied potential curves for the TiO_2 electrodes recorded in 1 M KOH solution, under simulated solar AM 1.5 illumination at an intensity of 100 mW/cm ² (scan rate = 10 mV s ⁻¹)	. 190
Figure 91 : Incident photon-to-current efficiency vs. wavelength plots for the long nanotube photoelectrode as a function of anodic bias	. 192
Figure 92 : FESEM image of the top-view of 6 μm long titania nanotube arrays anodized at 25 V before flame annealing	.192
Figure 93 : FESEM image of the top-view of 6 μm long titania nanotube arrays anodized at 25 V after flame annealing	. 193
Figure 94 Real time observation of anodization behavior of a Ti foil (99.8 % pure) anodized at 25 V in an electrolyte of pH 3.5 containing 0.07 M HF and 0.4 M NH ₄ NO ₃	. 195
Figure 95 N 1s XPS spectra for samples A-C with respective nitrogen doping levels [x]	.197

xiv

Figure 96: XPS depth profile of a N-doped anodic TiO ₂ film showing nitrogen concentration as a function of depth	198
Figure 97 : FESEM images of sample removed after 4 minutes of 25 V anodization in an aqueous electrolyte containing 0.4 M NH ₄ NO ₃	199
Figure 98 : FESEM images of sample removed after 6 hours of 25 V anodization in an aqueous electrolyte containing 0.4 M NH ₄ NO ₃	199
Figure 99 : FESEM images of A] Sample anodized for 6 hours at 20 V B] Sample anodized for 6 hours at 15 V and C] Cross-section of sample anodized for 6 hours at 15 V, in an electrolyte containing 2.5 M NH ₄ NO ₃	200
Figure 100: UV-Vis absorption spectra of N doped TiO ₂ thin films	203
Figure 101: Photocurrent generation of samples A, B and C (of Fig. 98) under AM 1.5 illumination.	204

XV

LIST OF TABLES

Table 1: Average wall-thickness and tube-length of 10 V titania-nanotube arrays anodized at different bath temperatures	21
Table 2: Effect of pH and anodization time on tube-length in aqueous electrolytes	29
Table 3: Physical properties (measured at room temperature) of solutions of fluoride compounds containing selected cations in formamide containing 5% water	60
Table 4: Crystallographic ionic radii and limiting molar conductivities of selected cations in formamide and water.	60
Table 5: Limiting molar conductivities, Stokes radii, hydrodynamic radii and solvation shell volume of cations investigated	65
Table 6: Effect of the cation and anodization potential on the morphological features of TiO ₂ nanotubes	83
Table 7: Parameters obtained from the curve fits of Fig. 51 and Fig. 52.	107
Table 8: Surface area of nanotubes determined by dye desorption measurements	139
Table 9: Carbon content and chemical state information (from XPS)	182

ACKNOWLEDGEMENTS

Nine months after I embarked on my Ph.D., I was a "refugee" from my previous adviser and research group. At this critical juncture in my career, Prof. Craig Grimes took me into his fold, gave me an interesting research topic to work on and has been an unwavering source of encouragement during the course of this work. Through his dexterous management of the research group, he has created a truly joyful and good atmosphere for scientific research. Therefore, I would like to express my sincere gratitude and thanks to Professor Grimes.

I would also like to express my appreciation to Prof. Tom Mallouk for his guidance during this work and for the generosity shown by him and his group members, notably Paul Hooertz and Neal Abrams in allowing me to use their equipment and measurement systems. I would also like to thank Professors Jerzy Ruzyllo and Srinivas Tadigadapa as committee members whose constructive criticism and suggestions have been useful to my research and to me as a student. I would also like to thank Prof. Anthony Perrotta for his constant stream of new ideas, Prof. Venkat Gopalan for sharing optical equipment whenever required and Prof. Michael Grutzeck for providing me usage of his autoclaves. A special note of thanks to all the MRL and MCL staff for always providing help, when needed.

I would like to thank the fantastic people in the Grimes Research Group (both past and present) for the pleasant working environment and for always lending a helping

hand in practical problems. My friends outside of work carried me through the years-so thank you Amit Vaish, Anirudh Vengurlekar, Bobbie Sue Peno, Steven Gross, Jose Agraz, Parvez Syed, Sumoy Das, Beth Van Horn, Blessy Varghese, Vaidy Subramanian, Aravind Mohanram, Josh Petko, Raksha Nagaraj and anyone else I might have missed. Finally, I would like to thank my parents for their constant support and backing during my studies.

CHAPTER 1

INTRODUCTION

1.1 Nanostructured metal oxide architectures

Nanostructured materials are artificially synthesized materials that have constituent grain structures or morphological features modulated on a length scale less than 100 nm¹. The principal impetus towards fabricating nanostructured materials lies in the promise of achieving unique properties and superior performance due to their inherent nano-architectures. Titanium dioxide is a particularly versatile material with technological application as a photocatalyst, photovoltaic material, gas sensor, optical coating, structural ceramic, electrical circuit varistor, biocompatible material for bone implants, a spacer material for magnetic spin valve systems, and more. Therefore, the ability to control the architecture of titania down to nano-scale dimensions can be expected to positively impact a variety of economically important technologies.

Since the first reports of multiwall carbon nanotubes by Ijima² in 1991, the range of interesting optical, electrical and mechanical properties associated with carbon nanotubes stimulated efforts to synthesize nanotubular structures employing other elements and compounds. As such, there have been significant efforts to develop nanotubular titania, including sol-gel and template-based approaches^{3, 4}. Adachi et al.⁵ have fabricated Dye Sensitized Solar Cells (DSCs) with disordered TiO₂ single crystalline nanotubes (NTs)

(10 nm diameter, 30-300 nm length) using molecular assemblies to obtain efficiencies of 5%.

Fig. **1**



Figure : Field Emission Scanning Electron Microscope (FESEM) image of an array of titania nanotubes

There are several reasons to expect oriented nanotubular structures to exhibit superior performance in a range of devices. One reason is their potentially high surface areas as compared to conventional materials. The surface area to volume ratio of an array of nanotubes increases as the diameter of the tubes decreases. The porosity of the nanotubular architecture results in a large surface area available for interfacial reactions. Another reason is the possibility of vectorial charge transport through the nanotubular layer. Furthermore, due to light scattering within a porous structure, incident photons are more effectively absorbed than on a flat electrode⁶.

Highly ordered arrays of titania nanotubes (NTs) are formed by anodization of a starting titanium thick or thin film in fluoride ion bearing electrolytes. TiO₂ NTs fabricated by anodization are highly-ordered, high-aspect ratio structures with nanocrystalline walls oriented perpendicular to the substrate. The fabrication process is explained in greater detail in Chapters 2 and 3. The nanotubes have a well-defined and controllable pore size, wall thickness and tube-length. The anodization approach achieves good uniformity and conformability over large areas at low cost. Applications of this unique nano-architectured material are only beginning. Previously, titania nanotube-based resistive gas sensors have been reported, that exhibit an amazing 50,000,000,000% change in electrical resistance upon exposure to 1000 ppm of hydrogen gas at room temperature⁷.

1.2 Low cost metal oxide solar cells

The US Energy Information Administration (E.I.A.) estimated global energy demand in 2003 to be 421 quadrillion BTU (~ 1.23×10^{14} kW.hr). This demand is projected to rise to 722 quadrillion Btu in 2030, or a 71-percent increase over the 2003 to 2030 period. Fossil fuels account for more than 80 % of global energy consumption with crude oil and its derivatives alone accounting for a 38% share of world energy consumption. In an era of dwindling fossil fuel reserves, the sun remains the most abundant source of clean

energy. The solar constant, i.e. the amount of incoming solar radiation per unit area, measured on the outer surface of Earth's atmosphere, in a plane perpendicular to the rays reaching the earth from the sun⁸ is 1366 W m⁻². The solar constant includes all types of solar radiation, not just the visible light. Efficient conversion of sunlight into useful form will allow humanity to tap into this immense reservoir. For solar energy conversion to be a feasible alternative, the technology of energy conversion should be cheap in dollar terms as well as energy terms. This means that a) the photoconversion system should be inexpensive to fabricate and b) the amount of energy required to fabricate the system or device must be much smaller than the energy obtainable using the device over its lifetime. Thus, prospective devices need to be cheap and non-energy intensive to fabricate, have a high enough efficiency and need to be durable so as to have a large operating lifespan.

The intensity of solar light that reaches the earth's surface (after losses due to absorption and scattering in the atmosphere) has an incident power of about 1kW/m². The polychromatic light from the sun has different number of photons of several different wavelengths. The solar spectrum is shown in Fig. **2**. For the efficiency of conversion of sunlight into electricity, 10 % is a key figure of merit. It could be argued that efficiency is not that important, provided the cells are very cheap but reality has demonstrated that solar cells should have a minimum efficiency of about 10% in order to be useful⁹. A very cheap solar cell would be one wherein over the life span of the cell, a single produced watt cost as little as \$0.20, compared with the current \$4. This has to do with area related cost which constitutes a large part of the system's total cost. The solar cells have to be

hermetically encapsulated in modules which are held in support structures and require electric wiring. All these factors depend on area and have a strong influence on the cost of photovoltaic electricity. Therefore, both in research laboratories and in manufacturing, improvement of efficiency is a high priority⁹.

Single crystalline inorganic semiconductors such as Si and GaAs are the most commonly used materials in photovoltaic cells owing to their high production efficiencies of 12-17 % and lifetimes (typically twenty years). In laboratory testing, 20.2 % efficiency was reported in a 10 x 10 cm area Ga-doped Silicon photovoltaic cell, which is the highest reported efficiency for a single stage cell using Si as the active semiconducting material⁹. Currently, it costs about \$4 to produce a single watt (averaged over the lifetime of the cell) while only about \$0.80 using fossil fuels such as oil and natural gas. The huge dollar and energy expense involved in the manufacture of photoconversion devices based on crystalline inorganic semiconductors makes it unlikely that a large portion of the world's energy needs will ever be met by photoconversion devices will be based on these materials. Further, the poor stability of these crystalline semiconductors in aqueous solutions limits their use in photoelectrochemical cells.

Fig. 2



Figure : Solar Radiation Spectrum (from www.nasa.gov)

Among the various paths to cheap solar energy conversion, the following three approaches are the focus of intense research in the materials science community as well as relevant to the application of titania nanotube technology and will hence be briefly discussed.

1.2.1 Regenerative photoelectrochemical cell :

Also known as a liquid junction solar cell, this device converts light to electric power leaving no chemical change behind (see Fig. **3**). The cell consists of a cathode and an anode fixed in electrolyte solution. Either the cathode or the anode, or both are photoactive. The photoactive electrode(s) is a semiconducting material, in which

electron-hole pairs (majority and minority charge carriers) are generated upon irradiation by photons with energies exceeding the band-gap of the semiconductor. Minority carriers are scavenged by the redox species in the electrolyte, thus separating the electron hole pair and preventing them from recombining. Majority charge carriers travel through the semiconductor and then through the external circuit to the counter electrode, where they regenerate the redox species in the electrolyte. During this process, a photovoltage and photocurrent are generated and the light is converted into electricity. The most successful adaptation of this approach is the Gratzel cell¹⁰, in which efficiencies larger than 10% have been achieved. Further, the installed cost per unit area of these devices is expected to be less than one-fifth that of existing solar cell technologies. The Gratzel cell, also known as a liquid junction dye sensitized solar cell (DSC) is composed of two surfaces of transparent conductor (mostly a conducting oxide on glass), onto which a film of wide bandgap semiconductor is deposited. Energy conversion in a DSC is based on the injection of an electron from the photoexcited state of the sensitizer dye into the conduction band of the wide bandgap semiconductor (typically nanocrystalline titania). The liquid electrolyte (typically an iodide, triiodide redox-active couple dissolved in organic solvent) is used to reduce the dye cation. Regeneration of iodide ions occurs at a platinized counter electrode. The applications of TiO₂ nanotube arrays in DSCs are presented in Chapter 6.

Fig. **3**



Figure : Schematic of regenerative photoelectrochemical cell

Fig. **4**





1.2.2 Non-regenerative photoelectrochemical cell (water-splitting cell) :

This device operates on a similar principle except that there are two redox systems : one reacting with holes at the surface of the semiconductor photoelectrode and the other with electrons entering the counter electrode (see Fig. 4 and Fig. 5). When the photoelectrode is an n-type semiconductor, water is oxidized to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode. The energy of light is converted to chemical fuel, in the form of hydrogen. The simultaneous collection and storage of energy promises greater efficiency and lower cost than strategies where collection and storage are done sequentially such as in photovoltaic systems.

Fig. 5



Figure : Photograph of n-type semiconductor based water splitting cell

In 1972, Fujishima and Honda¹⁰ reported hydrogen generation by water photoelectrolysis in sunlight using n-type TiO_2 and the overall conversion efficiency was 0.3 % when illuminated. Since then, considerable efforts have focused on the development and application of photoelectrochemical cells using a variety of material

platforms, both oxide and non-oxide, in a variety of material architectures^{11, 12}. 30 years after the discovery of the Honda-Fujishima effect, the development of a useful, costeffective photochemically stable material system for water photoelectrolysis still faces two fundamental materials science challenges. One challenge is engineering the bandgap of the semiconductor in such a way that its absorption spectrum is optimized to harvest the greatest possible energy resident in the solar spectrum. Our efforts towards modifying the absorption spectrum by doping the TiO_2 are presented in Chapter 8. Semiconductors with bandgaps narrow enough for efficient absorption of visible light are unstable against photocorrosion and lack stability and durability. The width of the bandgap is a measure of the chemical bond strength. Wide bandgap semiconductors such as titanium oxide and niobium oxide exhibit exceptional stability under illumination, but their absorption edge occurs close to the ultraviolet and renders them insensitive to a large portion of the solar spectrum. An equally important challenge is that water photoelectrolysis requires a material architecture able to maximize light absorption, charge separation and charge collection so that the photo-generated electrons and holes are generated in sufficient numbers and then efficiently used to perform work splitting water, rather than simply recombining.

1.2.3 Organic heterojunction cell :

Organic materials have the advantage of being cheap and easy to process. They can be deposited on flexible substrates. The potential of organic solar cells is related to the idea of low cost photovoltaic materials such as polymers, which can be easily manufactured as large-area films, cut from rolls and installed onto permanent structures. The choice of materials is practically unlimited and specific parts of the solar spectrum can be absorbed. The other great advantage of this configuration is that it is a solid state device. Both the electron transporting and hole transporting materials are solids, but are grown as interpenetrating networks forming a heterojunction of large contact area¹⁰. A cell based on a spirobisfluorene-connected arylamine hole transmitter was reported to have a conversion efficiency approaching 5 % at full sunlight^{13, 14}.

1.3 Nanotubular vs. Nanoparticulate Architectures

To date, the most efficient photoelectrochemical energy conversion devices have consisted of porous crystalline nanoparticulate titania films several microns thick, obtained by casting a colloidal sol, with a three dimensional network of interconnected 15-20 nm sized nanoparticles. The use of porous nanocrystalline semiconductor films has led to substantial progress in the field of low cost photoelectrochemical energy conversion¹⁵⁻¹⁷. Liquid junction dye-sensitized solar cells using monolayers of dye molecules with efficiencies larger than 10% have been demonstrated¹⁸. A single molecular monolayer absorbs a very small amount of light and as a consequence, the efficiency of a solar cell based on a flat planar electrode coated with a self-assembled dye monolayer would be very poor. However in nanocrystalline films, the light incident on the electrode is absorbed not by a single molecule but by many thousand dye molecules in the path of the beam. The large internal surface area of the porous film enables efficient light harvesting and maximization of the photogenerated charge in

nanocrystalline electrodes. In conventional solar cells based on Si, the photogenerated charges are separated under the influence of the built-in potential of the p-n junction. In the absence of a mechanism of charge separation, the photogenerated carriers are lost to recombination processes. However, in nanocrystalline solar cells, the nanometer-sized particles are too small to sustain significant electric fields and fields are screened by charges in the electrolyte so that charge separation must be achieved by some other means; it so happens that electron-hole pairs generated in nanocrystalline electrodes by direct absorption are separated kinetically¹⁹ i.e. since the nanoparticle is small, the hole diffuses to the particle-electrolyte interface and is captured by a solution ion resulting in successful charge separation before the hole recombines with the electron within the body of the nanoparticle. Additionally, electron transport from the point of generation to the collector (back contact) is a limiting factor in the performance of porous nanocrystalline electrodes, hindering progress in achieving higher efficiencies. The structural disorder at the contact between two crystalline particles leads to an enhanced scattering of free electrons, thus reducing the electron mobility²⁰. This results in charge transport being limited by the hopping of electrons along a poorly formed network²⁰ of randomly distributed nanoparticles. Nanoparticulate TiO₂ (anatase) films, which promote efficient photooxidation of a large variety of organic molecules, exhibit in contrast poor IPCE for the splitting of water from both acidic and alkaline solutions^{21, 22}. In case of an anodically biased nanoparticulate TiO₂ electrode, unable to develop a depletion layer, the conduction band electrons may not only combine with photogenerated holes but may also react with intermediates of the photooxidation of H₂O. Wahl et al²³ have attributed the poorer behavior of nanoparticulate TiO₂ electrodes to the easy occurrence of the backcharge transfer reactions involving intermediates of the photooxidation of water and molecular oxygen. Chapter 5 discusses electron transport in the nanotubular architecture. Electron loss by recombination is lower in TiO_2 nanotubes and is manifested by a recombination time constant that is an order of magnitude higher than for nanoparticulate cells.

An ordered and strongly interconnected nanoscale architecture would eliminate randomization of the particle network, increase contact points for good electrical connection and decrease small necking points that have been shown to develop between adjacent-bound particles in the current nanoparticulate titania structure after sintering²⁴. Therefore, ordered nanostructures such as arrays of nanowires³, nanorods^{25, 26} and nanotubes²⁷ are the focus of exploratory research for potential enhancement of electron percolation pathways and light conversion as well as improved ion diffusion at the semiconductor-electrolyte interface. Sol-gel³, sonochemistry²⁸ and surfactant templating⁴-based approaches have been used to fabricate nanotubular structures, but in all the cases, the nanotubes are discrete and randomly oriented. For use as photoelectrodes in a photoelectrochemical cell, the discrete nanotubes need to be assembled, oriented and immobilized, which is a non-trivial exercise.

1.4 Scope of the thesis

The primary objectives of this project are to systematically probe the parameter space of variables that affect the architecture of TiO_2 nanotube arrays to obtain synthetic

control over the architecture, to explore the effect of the architecture on the finally photochemical properties and to demonstrate the feasibility of photoelectrochemical devices based on these nanotube arrays. A nanotube array length of about 20-30 µm is adequate for photoelectrochemical devices and hence formed the initial target of the fabrication process. Once nanotube arrays of this length were obtained reproducibly, the process of fabricating successively longer nanotube arrays was continued to explore the limits of nanotube fabrication; one such limit was found when the 250 µm thick starting Ti foil was fully consumed. Chapter 2 delves in great detail into the fabrication process and explains the use of anodization potential, anodization duration and electrolyte chemistry to control the architectural parameters. The cation conjugated to the active fluoride ion was found to profoundly influence the growth rate and aspect ratio of the architecture. The effect of the cation is discussed at length in Chapter 3. The superior growth rates in polar protophilic organic electrolytes are considered in terms of a growth model in Chapter 4. We seek to elucidate the effects of the unique nanotubular architecture on the properties of nanotube arrays enabling control and optimization of the photochemical and photocatalytic properties. Chapter 5 discusses electron transport in the nanotubular architecture while the applications of TiO2 nanotube arrays in DSCs are presented in Chapter 6. Chapter 7 examines the performance of photo-assisted water electrolysers constructed using TiO₂ NT arrays as the photoanode under band-gap illumination. Our efforts towards modifying the absorption spectrum by doping the TiO_2 are presented in Chapter 8. In summary, this work aims to enhance the present understanding of nanotechnology aided material design and be a significant contribution to the fields of nanostructured materials and photoelectrochemistry.

CHAPTER 2

FABRICATION OF TITANIA NANOTUBE ARRAYS

2.1 Fabrication of TiO_2 nanotube arrays in aqueous electrolytes

2.1.1 Experimental details

Fig. **6**



Titanium foils (0.25 mm thick, 99.7 % purity) were procured from Aldrich Corporation. Nanotube arrays were grown by potentiostatic anodic oxidation in aqueous electrolytes containing fluoride (F) ions. Fig. **6** shows the experimental set-up used for the anodization process. The anodization potential applied, the temperature of the electrolyte and its pH are key parameters in the anodization process and monitored as shown above. Short nanotubes (100-400 nm) are produced at a high throughput in electrolytes with a very low (acidic) pH while long nanotubes (1-7 μ m) are produced at lower throughput in electrolytes that are mildly acidic (higher pH). A typical bath used to grow short nanotubes consists of an aqueous solution of 0.5% hydrofluoric acid (HF) in de-ionized water mixed with pure glacial acetic acid in the ratio 7:1. On the other hand, an electrolyte containing potassium fluoride (KF ; 0.1 M), sodium hydrogen sulfate (1 M), trisodium citrate (0.2 M) and sodium hydroxide (variable amounts) was typically used to grow longer nanotubes.

The as-anodized tubes are amorphous²⁸. To induce crystallinity, they are subsequently annealed in an oxygen containing ambient at elevated temperature (350-650°C) for 6 hrs with heating and cooling rates, typically of 1°C/min.

The morphologies of the titania nanotubes are studied using a JEOL JSM-6300 field-emission scanning electron microscope (FESEM). The crystalline phases are detected and identified by glancing angle X-ray diffractometer (GAXRD) on a Phillips X'pert MRD PRO X-ray diffractometer (Almelo, The Netherlands). The ultraviolet (UV)-visible (vis) absorbance spectra of the samples are measured using a Hewlett-Packard HP-8453 diode-array UV-Visible spectrophotometer (1 nm resolution) as well as a Cary 100 UV-Visible spectrophotometer (Varian Instruments) in combination with a Labsphere RSA-HP-53 (North Sutton, NH) diffuse reflectance and transmittance integrator.

2.1.2 Control of Pore Diameter

The presence of fluoride (F^{-}) ions in the anodization bath is critical to the achievement of the nanotubular structure. In any given F^{-} containing electrolyte there is an optimal window of anodization voltages wherein nanotubular structures are obtained. In an aqueous electrolyte containing 0.5 wt % HF, random pores are obtained at a wide range of anodization potentials from 3 V to 75 V. At low anodizing voltages, a porous film with sponge-like morphology is obtained. On increasing the voltage, the surface

becomes nodular with an appearance similar to particulate films. On further increasing the voltage, the particulate appearance is lost, with the emergence of discrete, hollow cylindrical tube-like structures. The nanotubular structure is lost at anodizing voltages greater than 40 V and once again, a spongelike randomly porous structure is obtained. In more dilute HF solutions, larger anodization voltages are required to produce the tubular structure.

Fig. **7**



Figure : Top-view of nanotube array anodized at 10 V

Fig. 8



Figure : Top-view of nanotube array anodized at 20 V
The pore diameter increases with anodization voltage. For instance, the geometry of the tubes resulting from 10 V anodization in aqueous 0.5% HF is as follows: pore diameter = 22 nm with standard deviation (SD) 5 nm, wall thickness = 24 nm, SD = 2 nm, length (including barrier layer thickness) = 200 nm. The geometry of the tubes resulting from the 20 V anodization are pore diameter = 76 nm, SD = 15 nm, wall thickness = 17 nm, SD = 6 nm, length = 400 nm.

2.1.3 Control of Wall Thickness

Titania nanotube arrays were anodized at 10 V at four different electrolyte bath temperatures, 5°C, 25°C, 35°C and 50°C. Arrays were also formed by 20 V anodization at room temperature (25°C) and 0°C.



Figure : FESEM images of the top view of titania nanotube arrays anodized at 10V at A) 5°C B) 25°C C) 35°C and D) 50°C

Fig. **9** [A] through [D] are FESEM images of the morphology of titania nanotubes fabricated by anodization at 10 V at A) 5°C, B) 25°C, C) 35°C, and D) 50°C. The pore diameter is essentially the same (22 nm) for titania nanotube arrays fabricated at these different temperatures, whereas the wall thickness and tube-length are substantially changed. The wall thickness increases with decreasing anodization temperature from 9 nm at 50°C to 34 nm at 5°C. As the wall thickness increases with decreasing anodization

temperature the voids in the interpore areas fill; with the tubes becoming more interconnected the discrete tube-like structure approaches a nanoporous structure in appearance. The length of the nanotubes (corresponding to the thickness of the nanotube layer) increases with decreasing anodization bath temperature from 120 nm at 50°C to 224 nm at 5°C. Table 1 shows the variation in wall-thickness and tube-length with anodization temperature at 10V. Fig. 10 [A] and [B] are FESEM images of titania nanotubes fabricated by anodization at 20 V at A) 5°C and B) 25°C. Here, the nanotube wall thickness is clearly seen to increase from 17 nm at 25°C to 27 nm at 5°C, thus confirming the trend of increasing nanotube wall-thickness as a consequence of lower anodization temperature.

Table 1

Table : Average wall-thickness and tube-length of 10 V titania-nanotube arrays

anodized at different bath temperatures

Anodization	Wall thickness	Tube-length	
temperature	(nm)	(nm)	
5°C	34	224	
25°C	24	176	
35°C	13.5	156	
50°C	9	120	



Figure : FESEM images of the topview of titania nanotube arrays anodized at **A**) 5°C and **B**) 25°C

These changes can be explained within the context of the formation mechanism of titania nanotubes^{29, 30}. The chemical dissolution of titania in the HF electrolyte plays a key role in nanotube formation, and is the factor ultimately limiting nanotube length. The formation of inter-pore voids is caused by oxidation of the metal in the interpore-region followed by field-assisted dissolution. Wet chemical etching is a temperature dependent process, with etch rates typically being exponential functions of the temperature. The solubility product of ions in any given electrolyte is also a strong function of temperature. It is therefore reasonable to assume that etching by fluoride ions as well as dissolution of the oxide will be weaker at lower temperatures, thus accounting for the larger tube length and wall-thickness. The pore diameter is almost constant because it is primarily

determined by the applied anodization voltage, in this work kept constant at 10 V for all samples.

2.1.4 Formation of tapered nanotubes (nanocones)

Mor et al³⁰ first reported the formation of tapered nanotubes by the application of a time dependent linearly varying anodization potential. In that study, the anodization voltage was varied from 10-23 V at rates from 0.43-2.6 V s⁻¹. In the present study, the anodization voltage was varied from 7.5-23 V at a rate of 0.005 V s⁻¹. After the voltage ramp, the potential was kept constant at 23 V for two minutes. Our results are consistent with the findings of the earlier study³⁰. Nanocones are obtained with a larger diameter of the base than the top (see Fig. 11 and Fig. 12). The base diameter corresponds to the pore diameter that is obtained when anodization is conducted at a constant potential of 23 V. The diameter of the top aperture is given by the diameter obtained by a potentiostatic anodization at 7.5 V.



Figure : Nanocone array obtained by ramped anodization in 0.1 M NaF (7.5 V-23V)



Figure : Nanocone array obtained by ramped anodization in 0.5 % HF (10 V-23V)

2.1.5 Ridging-effect on nanotube sidewalls

The sidewall profile of TiO_2 nanotubes formed by anodization in aqueous electrolytes exhibit considerable thickness variations. While this is an irregularity in the geometry of structure, it may also have certain beneficial effects such as increasing the effective surface area of the nanotube walls. Consider a discrete nanotube of outer diameter D and length L with hemispherical ridges X nm thick spaced Y nm apart as shown in Fig. **13**.

Fig. 13



Figure : Schematic of a ridged nanotube

Where there is a hemispherical ridge, a flat surface of area πDX is replaced by the ridge whose outer surface area is $\pi DX(\pi/2)$. Also a fraction X/(X+Y) of the surface is covered by ridges. Hence, increase in the surface area of the nanotube of length L is given by Eq. 1

$$\pi DL\left(\frac{X}{X+Y}\right)\left(\frac{\pi}{2}-1\right)nm^2$$

When the ridges are adjacent to each other all along the length of the nanotube (Y=0), a 57 % increase in the area of the nanotube results.

Nanotube sidewalls with thick continuous ridges were obtained when the anodization electrolyte used was an unbuffered solution of NaF in water. Highly ridged nanotubes formed by anodization at 20 V for one hour in 0.05 M NaF (aqueous) are shown in Fig. **14**

Fig. 14



Figure : Nanotubes with continuous ridges by anodization in aqueous NaF

The ridging of the nanotubes occurs due to local spatial inhomogeneities in the dynamic reaction equilibria of oxide formation and dissolution, but primarily arises as a consequence of two phenomena. One phenomenon consists of local concentration variations and pH bursts during the anodization process³¹. Use of buffered electrolytes reduces ridging in aqueous electrolytes but does not eliminate it. Use of highly viscous

electrolytes such as glycerol ($\eta = 945$ cP at 25°C) has been reported to eliminate ridging and promote smooth sidewall profiles by suppressing local concentration fluctuations³¹. The second phenomenon causing ridges is the variation in the local electric field vectors that results from oscillations in the voltage source used during potentiostatic anodization. When the voltage applied to the electrochemical anodization cell is well regulated, oscillations constitute a minor effect, secondary to the effect of local concentration fluctuations. Nevertheless, in a process such as the formation of tapered nanotubes, wherein the voltage is being varied almost continuously, both phenomena can be significant. Thus, the ridging effect in the nanocones of Fig. **11** and Fig. **12** is quite prominent.

2.1.6 Control of nanotube length

The titania nanotubes discussed so far are formed by anodization of Ti foils using dilute hydrofluoric acid electrolyte. However these nanotubes are limited in length to about 500 nm, due to the restriction imposed by the high rate of chemical dissolution of TiO_2 in the HF-based electrolyte. At a constant temperature, anodization potential and fluoride ion concentration, we found the electrolyte pH to be the principal determinant of nanotube length in aqueous electrolytes. Mere dilution of the HF based electrolyte is not sufficient to create conditions favorable for long nanotube formation because of the pH variation during the oxidation process. However, when the fluoride ion containing electrolyte is buffered, the pH variation is greatly reduced and the control of the length is achieved. Sodium hydrogen sulfate mixed with tribasic sodium citrate in a 5:1 molar

ratio was employed to buffer the anodization electrolyte to produce solutions with pH in the range 1.0-5.0.

As shown in Table 2 below, longer nanotubes can be formed in higher pH solution and at high pH, the nanotube-length is time-dependent. For a constant potential of 10 V and a constant anodization time of 20 hours, with pH increasing from strong acidity (pH<1) to a pH of 4.5 (mildly acidic), the length of the nanotube-array increases from 0.28 µm to For a particular pH, the pore size increases with anodization potential. 1.1 μm. However, the pore-size is independent of the pH at a particular potential. At a constant pH of 3.8 and a constant potential of 10 V, the nanotube length is 0.8 µm after the first twenty hours, increasing to 1.8 µm after sixty hours and then to 2.3 µm after 90 hours. Our studies showed that the best pH range for the formation of the micron long nanotubes is between pH 3 and pH 5. Lower pH forms shorter but clean nanotubes, whereas higher pH values result in longer nanotubes that suffer from unwanted precipitates. Selforganized nanotube formation did not occur in alkaline solutions. Cross-sectional FESEM images of nanotubes formed in electrolytes of increasing pH are shown in Fig. 15, Fig. 16 and Fig. 17 respectively.

Table 2

рН	Potential (V)	Time (hrs)	D (nm)	L (µm)
<1	10	1	40 ± 5	0.28 ± 0.02
1.3	10	20	30 ± 5	0.32 ± 0.03
2.8	10	20	30 ± 5	0.59 ± 0.05
3.8	10	20	30 ± 5	0.80 ± 0.06
3.8	10	60	30 ± 5	1.8 ± 0.06
3.8	10	90	30 ± 5	2.3 ± 0.03
4.5	10	20	30 ± 5	1.05 ± 0.04
4.5	25	20	115 ± 5	4.4 ± 0.1
5	25	20	115 ± 5	6.6 ± 0.2

Table : Effect of pH and anodization time on tube-length in aqueous electrolytes



Figure : Cross-section of 0.2 μm nanotubes fomed at pH < 1





Figure : Cross-section of 2 μ m nanotubes fomed at pH = 2.8



Figure : Cross-section of 6.6 μm long nanotubes formed in at pH 5

2.1.7 Effect of Chloride ions



Figure : Disordered nanorods formed by anodization in an aqueous electrolyte containing 0.1 M NH₄F and 5 M NH₄Cl. (Top-right) Inset showing the top-view at a magnification of 90K

Titanium dioxide is far less vulnerable to chemical etching by chloride ions when compared to fluoride ions. With this fact in mind, we surmised that an anodization electrolyte containing some fluoride ions substituted by chloride ions might produce a similar degree of anodic dissolution while substantially reducing the amount of chemical dissolution. NH₄Cl (0.1 M to 5 M) was added to aqueous electrolytes containing 0.1 M NH₄F and used to anodized Ti foil samples. The presence of chloride ions produced very high anodization currents initially and the anodization currents did not decrease with time indicating that the formation of the passivating oxide layer on TiO₂ was being inhibited. Therefore, an alternative approach was attempted. A short potentiostatic pulse at 20 V was used to initiate etch pits and then constant current anodization was performed at 3 mA for 10 hours. Nanotubes did not form as a result of this process ; however disordered nanorods were obtained. This investigation showed the dynamic equilibrium between the processes of oxide formation, anodic dissolution and chemical dissolution to be unstable when perturbed by large amplitude changes in the relative rates of the dissolution processes. In the present experiment, the oxide formation rate was presumably unchanged. But the promotion of the anodic dissolution reaction at the expense of chemical dissolution resulted in a structure shift from ordered tubes to disordered rods as shown in Fig. 18. Another hypothesis for this behavior is that vigorous field directed etching by anions (F⁻ and Cl⁻) splits the incipient nanotubes along the longitudinal direction and causes tubes to disintegrate into rods during growth. Thus nanotube formation occurs in a rather small window of operating potentials and chemical ion concentrations.

2.1.8 Insight from the Effect of Oxidizing/Reducing agents

The maximum obtainable nanotube length in buffered aqueous solutions was found to saturate at a value of 6.6 μ m. While this was a substantial improvement from the 500 nm films that had hitherto been obtained, applications such as dye sensitized

solar cells still required films of atleast fifteen microns in thickness. In an effort to increase nanotube length beyond this limiting value, several strong oxidizing agents known not to corrode TiO_2 were added to the anodization electrolyte with the idea of providing oxygen bearing anionic species to the growing interface in order to promote the oxidation reaction of Ti without simultaneously increasing the rate of chemical etching. Hydrogen peroxide, ammonium persulfate, ammonium nitrate, ammonium dichromate and potassium permanganate were some of the oxidizing agents experimented with. However, the addition of oxidizing agents to the anodization electrolyte proved counterproductive as the resulting nanotube length (same as the thickness of the nanotube array film) decreased.

This prompted a detailed consideration of the rate limiting step in the anodic growth of nanotubes of higher length. A more extensive discussion of the growth mechanism follows in Chapter 4. Suffice to say that at this point, the reverse strategy of inhibiting the oxidation of titanium metal by addition of a reducing agent was attempted. Again, the reducing agents were chosen in such a way as to have minimal effect on the chemical etching process.

The first attempt using a reducing agent involved the addition of 6g of potassium iodide, which is a mild reducing agent, to 75 ml of an anodization electrolyte at pH 4 containing 1 M NaHSO₄, 0.2 M tribasic sodium citrate and 0.1 M KF before the start of the anodization process. The iodide ions cannibalized the anodic current and the oxidation of titanium was delayed since electrons at the Ti anode were preferentially

transferred to iodide ions oxidizing them to iodine. The electrolyte immediately turned yellowish brown due to the formation of free iodine. After the iodide was completely consumed, the titanium oxidation began and the anodization proceeded as usual and a final nanotube length of 2 μ m was obtained as shown in Fig. 19. Since the potassium iodide has been consumed, the reducing agent exercised no beneficial influence on the ongoing anodization process. Thus the first attempt was a failure.



[A]



[**B**]

Figure : Nanotubes formed at 25 V in an aqueous electrolyte at pH 4 containing 0.5 M KI A] Topview and B] Cross-section

The second attempt involved starting the anodization of titanium in the same electrolyte namely, 75 ml of an anodization electrolyte at pH 5 containing 1 M NaHSO₄, 0.2 M tribasic sodium citrate and 0.1 M KF. A barrier oxide layer began to form within

the first several seconds of the anodization process and was accompanied by a sharp reduction in the anodization current ; typically from a value of ~500 mA to less than 100 mA. The potassium iodide reagent was added approximately fifty seconds after the start of the anodization. At this stage in the process, the reducing action of the potassium iodide slowed down the growth of the barrier layer and enabled faster nanotube growth (See Chapter 4 for a more detailed discussion). Also, the iodide ions were not exhausted quickly and possessed enough potency to continue reducing the barrier layer. The resulting nanotubes were 7.7 μ m long. This was 285% higher than the nanotube length obtained during the first attempt and was also higher than the maximum length of 6.6 μ m hitherto obtained in buffered aqueous electrolytes.



Figure : Nanotubes formed at 25 V in an aqueous electrolyte at pH 4 containing 0.5 M KI added fifty seconds after the start of anodization

2.2 Fabrication of TiO₂ nanotubes in organic electrolytes

The results of the experiments described in the previous section involving the addition of KI, demonstrated that nanotube growth benefited from mildly reducing conditions in the electrolyte. It is known that in comparison to water, the donation of oxygen is more difficult in organic electrolytes³². Thus an organic electrolyte, is by nature, more reducing when compared to a purely aqueous electrolyte.

2.2.1 High permittivity amphiprotic protophilic solvents

Non-aqueous electrolytes have been used to perform the anodization of semiconductors such as Si^{33, 34} base metals such as Fe³⁵ as well as valve metals such as Ti, Nb, Zr, W and Mg³⁶. However, these studies have been primarily focused either on alcohols such as ethanol, ethylene glycol and glycerol or on polar aprotic solvents such as Dimethylsulfoxide (DMSO), *N*,*N*-Dimethylformamide (DMF), Acetonitrile (ACN) and Propylene Carbonate (PC). All of these solvents have a dielectric constant that is lower than of water. In comparison, the very high dielectric constant amide based amphiprotic solvents such as formamide (FA), *N*-methylformamide (NMF), *N*-methylacetamide and *N*-methylpropionamide have received much less attention. Solvents that belong to the family of amphiprotic solvents have both acidic and basic properties in terms of the Bronsted acid-base concept³⁷. But formamide and N-methylformamide are also protophilic, meaning they have a weaker acidity and a stronger basicity than water. Thus

they provide a solution environment that is more reducing in comparison to water³⁷ and both small cations such as H^+ and small anions such as F^- are easily solvated.

Nanotube formation in fluoride ion bearing electrolytes occurs as a result of the interplay between three simultaneously occurring processes, namely the field assisted oxidation of Ti metal to form titanium dioxide, the field assisted dissolution of Ti metal ions in the electrolyte and the chemical dissolution of Ti and TiO₂ due to etching by fluoride ions, which is substantially enhanced by the presence of H⁺ ions^{30, 38}. The same three processes govern the anodic formation of several other self-organized nanoporous metal oxides^{39.43}. The first generation TiO₂ nanotubes were formed in highly acidic aqueous electrolytes (pH \leq 1) wherein the etching action of fluoride ions was very aggressive and the chemical dissolution process limited the overall length of the nanotubes. In the second generation, buffered electrolytes were used to provide mildly acidic conditions (pH \sim 5). Under these conditions, chemical dissolution of the growing nanotubes was restrained and nanotube lengths increased to 7 micrometers. Further improvements in length required enhancing the rate at which the Ti-TiO₂ interface moves into the Ti metal, i.e. increasing the rate of the field assisted processes.

At first glance, enhancing the rate of field assisted processes would appear to warrant an increase in the electric field. However, larger electric fields also result in a thicker barrier layer that retards the solid state transport of Ti^{4+} ions outward from the titanium substrate and the inward transport of OH^{-} and O^{2-} ions. Furthermore, in aqueous electrolytes containing a large concentration of ions, the TiO_2 barrier layer experiences dielectric breakdown beyond a threshold level of the electric field. Subsequent to

dielectric breakdown, electronic conduction instead of the desirable ionic conduction contributes to almost all the anodization current.

Our approach was directed at mitigating both these effects. First, we limited the water content of our electrolytes to less than 5%. With organic electrolytes, the donation of oxygen is more difficult in comparison to water and results in reduced tendency to form oxide³². The reduction in water content allows for thinner or lower quality barrier lavers through which ionic transport may be enhanced. The incorporation of organic components from the electrolyte into the anodic oxide film is known to lower the relative permittivity of the film and increase its dielectric breakdown potential⁴⁴. The higher breakdown potential of the oxide in non-aqueous electrolytes allows a larger potential window for nanotube formation. Finally, formamide and N-methylformamide are highly polar, with dielectric constants of 111 and 182.4 respectively, that are much greater than that of water, which has a dielectric constant of 78.39^{37} . The higher polarity of the electrolyte allows HF to be easily dissolved and makes it chemically available at the TiO₂-electrolyte interface. The higher capacitance of the electrolyte causes more charges to be formed on the oxide layer for an identical value of the applied potential and improves the extraction of Ti⁴⁺ ions.







[**B**]

Figure : FESEM images of TiO_2 nanotubes grown in FA based electrolyte at 35 V showing A] Cross-section at lower magnification and B] Cross-section at high magnification



[A]



[B]

Figure : FESEM images of TiO₂ nanotubes grown in NMF based electrolyte at 40 V showing A] Cross-section at lower magnification B] Top-view.

The surface morphology was found to be a function of anodization potential with the pore diameter increasing with voltage while wall-thickness slightly decreased with anodization voltage. Field emission scanning electron microscopy (FESEM) images of the anodic TiO₂ films formed in the FA and NMF based electrolyte respectively are shown in Fig. 21 and Fig. 22. K1 contained 0.56 grams of Ammonium Fluoride in a solution mixture of 5 ml Deionized water + 95 ml Formamide. N1 was the same as K1 except that 95 ml of NMF was used instead of formamide. Fig. 21 shows nanotubes nearly 30 µm long grown in a FA based electrolyte by anodization for 88 hours at a constant potential of 40 V. The average outer diameter of these nanotubes was determined to be 210 nm with a wall-thickness of 17 nm resulting in an aspect ratio of 140. Nanotubes formed at 20 V in the same electrolyte had a length of 18 μ m, an outer diameter of 90 nm and a wall-thickness of 24 nm resulting in an aspect ratio of 200. At larger anodization voltages, the driving force for ionic transport through the barrier layer at the bottom of the pore is greater and results in faster movement of the Ti/TiO₂ interface into the Ti metal. We attribute the higher nanotube length obtained at larger anodization voltages to this enhanced pore deepening effect. We observe an increase in the diameter of the nanotubes in a particular electrolyte as the anodization voltage is increased. This observation agrees with the reported behavior of nanotubular TiO₂ as well as other anodically formed metal oxides²⁹. In addition, we also observe a pronounced effect of the electrolyte on the nanotube pore size. All else being equal, nanotubes with a smaller pore diameter are obtained when the electrolyte used is NMF rather than FA. Fig. 22 shows 18 µm long nanotubes formed by a 70 hour anodization at 40 V in NMF based

electrolyte. The average outer diameter was determined to be 166 nm with a wallthickness of 18 nm.

In FA/NMF based electrolytes, the range of applied anodization potentials which result in nanotubes, is significantly extended. Nanotubes were found to form at voltages between 8 V and 56 V. At 60 V, the anodization was found to be unstable with sharp fluctuations in the current. Anodization was not attempted at voltages below 8 V. The duration of the anodization was also an important variable. We observed that the length of the nanotubes increased with time until a certain maximum length is obtained, beyond which it declined. For instance, increasing the duration of the anodization at 35 V to 164 hours resulted in a smaller nanotube length of 10 μ m compared to the 30 μ m obtained after 88 hours of anodization. The time to maximum length is a function of the anodization voltage with the nanotubes reaching this maximum sooner at lower potentials.

Decreasing the concentration of NH_4F improves the quality of the nanotubes but also decreases the length. Although increasing the concentration of NH_4F results in longer nanotubes achieved in a shorter time, however there is a tendency for the tubes to be clogged due to precipitation from solution. For example, our K4 bath consisting of 1.2 g of NH_4F in the same solvent mixture gives much longer nanotubes at every voltage but there exists a tendency for the resulting tubes to be clogged as solubility in the solvent mixture becomes more difficult. Within the range for which nanotubes can be obtained, higher anodization potentials and larger F^- concentrations result in longer nanotubes. There is a diminishing marginal return on nanotube array length as F^- concentration is increased. At the maximum F^- concentrations the F^- levels are almost at the solubility limit in the solvent. Perhaps as a result, the tendency for pore clogging increases as the F^- concentration increases.

2.2.2 Dipolar Aprotic Protophilic Solvents

Unlike protic solvents, aprotic solvents do not have a hydrogen atom bonded to an electronegative atom. The hydrogen atoms in aprotic solvents are only bonded to carbon atoms. Therefore, aprotic solvents have very weak proton and hydrogen bond donating abilities. The protophilic members of this solvent family include Dimethyl formamide (DMF), Dimethylsulfoxide (DMSO), N-methylpyrrolidone (NMP) and Hexamethyl phosphoric triamide(HMPA) and have basicities that are stronger than that of water. These solvents easily solvate to small cations and are excellent proton acceptors whereas solvation to small anions is difficult. Strong oxidizing agents are unstable in dipolar aprotic protophilic solvents since the solvent itself acts as a mild reducing agent.

2.2.2.1 DMSO

The first studies of the anodic formation of TiO_2 nanotubes in DMSO were conducted by Ruan et al⁴⁵, who obtained 2.3 µm long nanotubes after anodizing a Ti metal foil for 72 hours at 20 V in an electrolyte containing 4% HF in a 1:1 mixture of DMSO and ethanol. Nanotubes were observed only 48 hours after anodization in contrast to aqueous electrolytes where nanotubes are formed in less than 1 hour²⁹. The nanotube arrays easily separated from the substrate when sonicated in aqueous solutions. Compared to aqueous electrolytes, the nanotubes formed in DMSO were relatively fragile, probably due to higher internal stresses in the film and poorer adhesion of the nanotube array to the Ti substrate.

Paulose et al obtained higher nanotube growth rates by eliminating ethanol from the anodization electrolyte and increasing the anodization voltages from 20 V to potentials as high as 60 V⁴⁶. Fig. **23** shows cross sectional, top and bottom FESEM images of a sample fabricated at 60 V, for 70 hr, in a DMSO electrolyte containing 2 vol% HF; the resulting nanotube array length is 93 μ m and the outer diameter is 200 nm, hence a length to outer diameter aspect ratio of ~465. For a 70 hour anodization at, respectively, potentials of 20V and 60V, an increase in length from about 10 μ m to 93 μ m was observed. Anodization in the range 20 V to 60 V yielded a regular, wellaligned nanotube-array architecture; the resulting pore diameters were, respectively, ~50 nm, 120 nm and 150 nm for 20, 40 and 60 V potentials. As the HF concentration varied from 1% to 4% the length of the nanotubes grown at 40 V increased from 13 μ m to 52 μ m. Further increases in the HF concentration decreased the nanotube lengths.

We note that the top-surface of the as-prepared samples are typically covered with broken tubes and other debris from the anodization bath that are easily removed by sonication of the sample. The solubility of the reaction products is low in DMSO allowing the reaction products to stay at the surface of the nanotubes. Under FESEM imaging the pores may appear clogged in such cases, although a complete clogging does not take place as this prevents the electrolyte species from reaching the bottom of the tubes thus terminating the anodization process.



Figure : Illustrative FESEM cross-sectional [A] and [B], top [C] and bottom [D] images of a nanotube array⁴⁶

2.2.2.2 DMF

Initial studies with DMF resulted in the formation of an irregular nanoporous structure of varying thickness (see **Fig. 24**). The nanoporous structure obtained in DMF had two interesting features, a larger internal surface area as measured by dye adsorption studies (to be explained in more detail in Chapter 6) and a much smaller pore diameter for similar fluoride ion concentrations. However, due to the fact that the growth rates obtained were unremarkable and because the pores were irregular, a more comprehensive investigation of nanotube formation in DMF based electrolytes was not undertaken.

Fig. 24



Fig. : Top-views of an irregular nanoporous structure formed at 20V in 0.1 M solution of NH₄F in DMF **[A]** Low magnification (5K) and **[B]** High magnification (50K)

2.2.3 High viscosity amphiprotic neutral solvents

The mono- and poly-hydroxy alcohols are members of this family of solvents whose relative acidities and basicities are similar to those of water. Anodization electrolytes with a high methanol content were found to be unstable during anodization and resulted in corrosion of the Ti substrate under the conditions employed (10-40 V; 0.1 M F⁻). However the more viscous dihydroxy and trihydroxy alcohols were found to be suitable for anodic formation of titania nanotubes.

2.2.3.1 Glycerol

Glycerol ($\eta = 945$ cP at 25°C) is one of the most viscous solvents in common use. Macak et al⁴⁷ reported a maximum nanotube length of 6.1 µm in an electrolyte containing 0.5 wt. % NH₄F in glycerol at 20 V after 72 hours of anodization. The high resistance of glycerol constrains the anodization currents to small values and the high viscosity of glycerol causes diffusion of reactants to be slow. Therefore, the nanotube growth rates in glycerol are relatively small. For instance, after 3 hours of anodization, an aqueous electrolyte containing 1M (NH₄)₂SO₄ + 0.5 wt. % NH₄F resulted in a 2 µm long nanotube array whereas 0.5 wt. % NH₄F/glycerol electrolyte produced a 1.3 µm long array⁴⁷. However, nanotubes fabricated in glycerol possessed a higher aspect ratio since the average pore diameter in the glycerol based electrolyte was 50 nm, almost half the 100 nm pore diameter obtained in the aqueous electrolyte at the same anodization voltage³¹. As mentioned previously, nanotubes formed in glycerol had very smooth sidewall profiles due to the suppression of local concentration fluctuations³¹.

2.2.3.2 Ethylene Glycol (EG)

EG has a viscosity of ~16 cP at 25°C, which is much lower than that of glycerol but higher than that of formamide and NMF. The anodization process in ethylene glycol has two distinctive features^{46, 48}. One is the extremely rapid nanotube growth rate of up to 15 μ m/ min which is nearly five times the maximum rate of nanotube formation in amide based electrolytes and an order of magnitude greater than the growth rate in aqueous solutions. Nanotube arrays up to 360 μ m in length maybe achieved by careful selection of the anodization parameters. Also, the rapid growth rate does not degrade the porous structure of the nanotubes in any way. The second distinctive feature is that nanotubes formed in EG exhibit long range order manifested in hexagonal close-packing and very high aspect ratios (~2181) as shown in Fig. **25**.



Figure : FESEM images of the bottom [A] and top [B] of a nanotube array sample grown at 60 V in an ethylene glycol electrolyte containing 0.25 wt% NH_4F^{48} .



Figure : Cross-sectional FESEM image of a TiO_2 nanotube array obtained by anodization of Ti foil for 96 hours at 60 V in an electrolyte containing 0.3% wt NH₄F and 2 vol % H₂O in ethylene glycol

Regular ordered nanotube arrays are achievable in EG electrolytes with water concentrations spanning 1% to 4%, ammonium fluoride concentrations spanning 0.1 wt % to 0.5 wt % and anodization potentials spanning 20-65 V⁴⁸. When extremely long nanotube array bearing films were ultrasonicated for a time in excess of five minutes, the nanotube layer peeled off to form self-standing films. Such films lend themselves to imaging of their backside as shown in Fig. **26** [**A**]. The nanotube array shown in Fig. **26** is 360 μ m long, with an average outer diameter of 160 nm and a wall-thickness of 25 nm. A trend of increasing nanotube pore diameter with increasing anodization potential is observed. Use of anodization voltages larger than 80 V resulted in corrosion of the starting Ti substrate.

2.2.4 Dipolar Protophobic solvents

The formation of nanotubes was generally unsuccessful in dipolar protophobic solvents. Solvents in this family have a basicity that is weaker than that of water. Because they are aprotic, their acidity is weaker as well. Thus, neither small anions nor small cations are well-solvated in these solvents rendering H^+ and F^- ions very reactive. Perhaps as a consequence of this, anodization in the potential range 10-40 V in electrolytes based on members of this solvent family, such as acetonitrile, propylene carbonate and acetone was found to be unstable. In the case of fluorinated acetonitrile and acetone, the Ti substrates corroded whereas in fluorinated propylene carbonate, the solvent appeared to decompose, leaving a thick black residue on the Ti substrate.

CHAPTER 3

EFFECT OF THE CATION ON THE FORMATION OF TITANIA NANOTUBES IN FORMAMIDE-WATER MIXTURES

Fabrication of high aspect ratio semiconducting metal oxide nanotubes with lengths extending into the several tens of micrometers is a challenge, but is key to boosting the performance of a variety of nanotube-based devices. The so-called first generation nanotubes anodized using an aqueous HF based electrolyte grew to a length of about 500 nm^{29,49}. While the nanotube length was increased to about 7 μ m in the second generation by controlling the pH of the anodization electrolyte and reducing the chemical dissolution of TiO₂ during anodization^{31, 50}, smoother more uniform nanotubes of similar length were synthesized in non-aqueous viscous electrolytes in the third generation by reducing thickness variations in the sidewall profile^{31, 51}. Recently, Paulose et al⁴⁶ reported fourth generation ultralong nanotubes grown for the first time to a thickness of 134 μ m by anodization in various organic electrolytes. In this Chapter we investigate the effect of five different cationic species on the formation of TiO₂ nanotubes with specific attention paid to the time of formation, the length and the aspect ratio of the resulting nanotubes.
3.1 Experimental Methods

Titanium foils (99.8% pure) approximately 250 μ m thick were cleaned in ethanol and subsequently anodized at room temperature in formamide (FA) and Nmethylformamide (NMF) solutions containing water and fluoride bearing species. For the purposes of this study, Hydrogen Fluoride, Ammonium Fluoride, Sodium Fluoride, Tetrabutylammonium Fluoride and Benzyltrimethylammonium Fluoride were the fluoride ion bearing species chosen. The cations in these compounds shall be referred to as H⁺, NH₄⁺, Na⁺, Bu₄N⁺ and BnMe₃N⁺ respectively in the reminder of this report. The molecular structures of Bu₄NF and BnMe₃NF are shown in Fig. **27** and Fig. **28** respectively.

Fig. 27.

$$\begin{array}{c} \mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_3\\ \overset{|}{}_+\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\\ \overset{|}{}_-\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_3\\ \overset{|}{}_{\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_3} \qquad \mathsf{F} \stackrel{-}{}_{\mathsf{XH}_2\mathsf{O}} \end{array}$$

Figure : Molecular structure of Tetrabutylammonium Fluoride





Figure : Molecular structure of Benzyltrimethylammonium fluoride

The conductivity of all solutions used was probed at 25°C under DC conditions using planar platinum electrodes with a measured cell constant of 1.25 ± 0.01 cm⁻¹ and readings were recorded when they became invariant with time. This data is shown in Fig. **29** and Fig. **30**. The viscosities of the solutions were measured using a falling ball viscometer (Gilmont) and are shown in Table **3**. Data regarding the crystallographic ionic radii^{37, 52-54} and limiting molar conductivities³⁷ of the selected cations in water and formamide are displayed in Table **4**. NH₄F possesses limited solubility in 95% formamide-5% water mixtures. The much higher solubility of Bu₄N⁺ allows higher concentrations to be employed in the anodization electrolyte. NaF has the poorest solubility among the compounds studied and a saturated solution of NaF was formed at a much lower concentration (~0.04 M) than the other compounds. The anodization process in NMF and formamide is fairly similar; however at identical anodization potentials, nanotubes formed in NMF are slightly longer¹³. All studies comparing the effect of different cations were conducted using formamide as the base electrolyte. NMF was only used to assess the maximum length that nanotubes could be grown to in this system and anodization in NMF was confined to the case where tetrabutylammonium cations were used in combination with a lower water content. The duration of the anodization varied, from 6 hours to 164 hours. From previous studies, we know as an-anodized anodic films to be amorphous and to be crystallized by a high temperature anneal⁵⁵. To induce crystallinity, the initially amorphous as-anodized films were subjected to a 3 hour anneal in oxygen at 580°C with heating and cooling rates of 1°C/min.



Figure : Current voltage behavior of different electrolytes probed using planar platinum electrodes with a cell constant of 1.25 in the low field regime





Figure : Current voltage behavior of different electrolytes probed using planar platinum electrodes with a cell constant of 1.25 in the high field regime.

 Table : Physical properties (measured at room temperature) of solutions of fluoride

 compounds containing selected cations in formamide containing 5% water.

Compound	Molar	Density	Viscosity		
	Concentration	$(g \text{ cm}^{-3})$	(cP)		
	(M)				
HF	0.27	1.10	2.76		
NaF	~0.04	1.09	2.61		
NH ₄ F	0.27	1.11	2.81		
Bu ₄ NF	0.27	1.10	3.40		
BnMe ₃ NF	0.27	1.09	3.12		

Table : Crystallographic ionic radii and limiting molar conductivities of selected cations in formamide and water³⁷

Cation	Crystallographic	Limiting molar	Limiting molar	
	ionic radius (pm)	conductivity in	conductivity in	
		water	formamide	
		$(S \text{ cm}^2 \text{ mol}^{-1}) 25^\circ C$	$(\mathrm{S} \mathrm{cm}^2 \mathrm{mol}^{-1}) 25^{\circ}\mathrm{C}$	
H^{+}	-	349.81	10.41	
Na ⁺	116	50.1	9.88	
$\mathrm{NH_4}^+$	148	73.55	14.94	
Bu_4N^+	391	19.5	6.54	

3.2 Effect of cation and water content on the anodic current transient



Figure : Real time observation of anodization behavior of a Ti foil (99.8 % pure) anodized at 20 V in a formamide solution containing 5 wt % H₂O and identical molar concentrations (0.27M) of fluoride ion bearing compounds with four different cationic species : Hydrogen (H⁺), Ammonium (NH₄⁺), Tetrabutylammonium (Bu₄N⁺) and Benzyltrimethylammonium (BnMe₃N⁺)

The growth of TiO_2 nanotubes was studied in fluoride bearing electrolytes containing different cations while maintaining similar and in some cases identical molar concentrations of the chemical species. This ensured that each electrolyte had the same concentration of fluoride ions thus allowing us to observe the effect of the cations on

nanotube growth in isolation. **Fig. 31** shows the real time potentiostatic anodization behavior of Ti anodized at 20V in 95% formamide-5% water solutions containing 0.27 M of NH₄F, Bu₄NF, HF and BnMe₄NF respectively. The crystallographic ionic radius of the cationic species⁵⁴ increases in the order

Eq. 2

$$H^+ < Na^+ < NH_4^+ < Bu_4N^+ < BnMe_4N^+$$

The binary mixture of water and formamide is reported to be a near-ideal system as indicated by the volume corrected preferential solvation parameters⁵⁶. Due to this ideality, we assume a linear dependence of the conductivity on the mole fraction and calculate the limiting molar conductivity in the mixed solvent as

Eq. 3

$$\lambda_{i,mixture}^{\infty} = \lambda_{i,water}^{\infty} X_{water} + \lambda_{i,formamide}^{\infty} X_{formamide}$$
 3

The Stokes radius of an ion in solution provides information about the solvation of the respective ion and is given by⁵³

Eq. 4

$$r = \frac{\left|z\right|F^2}{6\pi N\eta\lambda_i^0} \tag{4}$$

63

where z is the charge on the ion, F is the Faraday constant and N is the Avogadro number. Eq. 4 shows the Stokes-law radii r_s of ions to be inversely related to the product of the viscosity η and the limiting equivalent conductance λ_i^0 of the ion. Replacing the value of 6 by 4 in the denominator of Eq. 4 yields the hydrodynamic radius r_h of the ion. From the crystallographic radii r_c and the hydrodynamic radii r_h , the volume of the solvation shell surrounding the ions is given by

Eq. 5

$$V_{sh} = \frac{4}{3}\pi (r_h^3 - r_c^3)$$
 5

The values of the Stokes radii and volume of the solvation shell of the cations in the formamide-5 % water mixture were obtained by substituting the data of Table **3** and Table **4** in Eq. **3**, Eq. **4** and Eq. **5**. This data is displayed in Table **5**. For ions such as Et_4N^+ and Bu_4N^+ , the Stokes radius (r_s) obtained by Eq. **4** is usually less than the crystal radius (r_c). This contradiction is avoided by the use the Stokes-Robinson effective ionic radius (r_{eff}). For weakly solvated ions like tetraalkylammonium ions, the effective ionic radius must be equal to the crystal ionic radius r_c . If r_{eff} is equal to the real radius of the ion solvated in the solution, the solvation volume maybe estimated from :

$$V_{sh} = \frac{4}{3}\pi (r_{eff}^3 - r_c^3)$$
 6

Table 5

 Table : Limiting molar conductivities, Stokes radii, hydrodynamic radii and solvation

 shell volume of cations investigated

Cation	Limiting molar	Walden	Hydro-	Stoke	Volume of
	conductivity in	product	dynami	S	solvation
	formamide-5 %	$(\lambda_{i}^{\infty}\eta)$	с	radius	shell
	water binary	$(S cm^2)$	Radius	(pm)	(cm^3)
	mixture	mol ⁻¹ P)	(pm)		
	$(S \text{ cm}^2 \text{ mol}^{-1}) 25^\circ C$				
Na ⁺	13.9	0.36	340	227	3.8 x 10 ⁻²³
$\mathrm{NH_4}^+$	20.8	0.58	212	141	6.3 x 10 ⁻²⁴
Bu_4N^+	6.5	0.22	559	373	~0

Fig. 29 and Fig. 30 show that the current voltage plots of the electrolytes exhibited different slopes in the low field (up to 1 V) and high field (5V - 20V) regimes. In the low field regime, the conductivities of the various electrolytes increased in the order

64

Eq. 7

$$Bu_4N^+ < Na^+ < NH_4^+ < H^+ < BnMe_3N^+$$
 7

HF is a weak acid in aqueous solutions with a dissociation constant of 6.7×10^{-4} in water⁵⁷. Since HF is a weak acid, the actual concentration of H⁺ and F⁻ in aqueous solutions is much lower than the HF concentration. This means that the conductivity of this solution will be low relative to the tetraalkylammonium fluoride solutions. At the same time, in solvents with an OH group such as water, the conductivity of H⁺ is abnormally high due to the proton jump effect³⁷.

In the low field regime, the conductivity behavior shown by tetrabutylammonium, sodium and ammonium cations agrees very well with the calculated limiting molar conductivities shown in Table **5**. However, in the high field regime (which more closely approximates the anodization conditions), the conductivities of the various electrolytes increased in the order

Eq. 8

$$H^{+} < Na^{+} < Bu_{4}N^{+} < NH_{4}^{+} < BnMe_{3}N^{+}$$
8

The benzyltrimethylammonium fluoride solution was found to be the most conductive among all the electrolytes investigated in both the low field and high field regimes. The viscosities of the solutions increase with the size of the cationic species with solutions containing Bu_4N^+ and $BnMe_3N^+$ exhibiting much higher viscosities than solutions of the remaining cations (see Table 3).

Table **5** shows that the Na⁺ and NH₄⁺ cations have larger solvation shells than the Bu₄N⁺ cations. This is understandable considering that formamide is a polar protophilic solvent with good hydrogen bond donating ability³⁷. Because of the protophilicity, small ions such as H⁺ and Na⁺ ions are strongly solvated. Due to the hydrogen bond donating ability F⁻ ions are strongly solvated as well. From the solvent-berg model, the solvent molecules immediately adjacent to the ion are rigidly bound to it and thus the ion moves as this kinetic unit³⁷. Consequently, the conductivities of HF and NaF in the formamide-water mixture are limited by the mobility of the solvent molecules and the anodization current is relatively small. On the other hand larger ions such as Bu₄N⁺ and BnMe₃N⁺ are very weakly solvated and their higher ionic mobility translates into a higher anodization current. However, at high concentrations of these cations, the viscosity of the solution increases and the conductivity is reduced. This is because large cations such as Bu₄N⁺ and BnMe₃N⁺ follow Walden's rule whereby

Eq. 9

$$\lambda^{\infty}$$
. η = constant 9

where λ^{∞} is the limiting molar conductivity of the cation in the solution and η is the viscosity.



Figure : Real time observation of the effect of the water concentration on the anodization behavior of a Ti foil (99.8 % pure) anodized in an electrolyte containing 0.27 M NH₄F in N-methylformamide

Fig. 32 contrasts the real time potentiostatic anodization behavior of Ti anodized at 20 V in electrolytes containing an identical concentration of NH₄F (0.27M) but with different amounts of water ranging from 100 % water (no formamide) to 2.5 % water-97.5% formamide. In the 100% aqueous electrolyte, the anodization current drops sharply from a high initial value (>100 mA/cm²) in the first few seconds of anodization. This is attributed to the formation of an initial insulating oxide layer that reduces the current. Thereafter, pitting of the oxide layer by fluoride ions commences and the anodization current increases to reach a local maximum after about 5000 seconds of anodization. On the other hand, the anodization current in the electrolytes containing

formamide remains relatively constant in the first 100-1000 seconds of anodization and decreases monotonically thereafter. As a result, while the total charge passed after 500 minutes of the anodization process was similar for both kinds of electrolytes, a much larger amount of charge is passed in the formamide based electrolytes during the first 500 seconds of anodization. The region of stable current extends for a longer period of time in electrolytes containing a smaller concentration of water. The current plots are broadly similar in that they all exhibit a sigmoidal curve with an initial region of stable or near stable anodization current followed by a region of falling current of larger slope and a then a region where the current reaches a lower level and continues to decrease albeit with a smaller slope. During the initial period of high current, gas evolution at the anode is observable. Since gas evolution requires electronic charge transfer, this is indicative of electronic conduction dominating in the early part of the anodization. With organic electrolytes, the donation of water is more difficult in comparison to water and results in reduced tendency to form oxide³². The reduction in water content allows for thinner or lower quality barrier layers through which ionic transport may be enhanced. The greater ionic conduction allows faster movement of the Ti/TiO₂ interface into the Ti substrate allowing for a larger final nanotube length. Higher anodization voltages provide a greater driving force for both electronic and ionic conduction and are accompanied by higher anodization currents.

3.3 Effect of Cation on the Morphology of Titania Nanotubes

3.3.1 Morphologies obtained by anodization at 35 V and 20 V

The surface morphology is a function of anodization potential with the pore diameter remaining roughly constant in electrolytes containing different cations. Field emission scanning electron microscopy (FESEM) images of the anodic TiO_2 films formed at 35 V and 20 V in FA based electrolytes containing 5% water and 0.27 M HF are shown in Fig. **33** and Fig. **34** respectively. The images shown are of nanotubes grown to their maximum length at the particular anodization in the respective electrolyte.



Figure : Cross-sectional FESEM image of TiO_2 NTs formed at 35 V in formamide electrolyte containing 5 wt % water and 0.27 M HF. Upper-inset shows topview while lower inset shows enlarged cross-section



Figure : Cross-sectional FESEM image of TiO_2 NTs formed at 20 V in formamide electrolyte containing 5 wt % water and 0.27 M HF. Inset shows topview.



Figure : Cross-sectional FESEM image of TiO_2 NTs formed at 35 V in formamide electrolyte containing 5 wt % water and 0.27 M NH₄F. Upper-inset shows topview while lower inset shows enlarged cross-section



Figure : Cross-sectional FESEM image of TiO_2 NTs formed at 20 V in formamide electrolyte containing 5 wt % water and 0.27 M NH₄F. Upper-inset shows topview while lower inset shows enlarged cross-section



Figure : Cross-sectional FESEM image of TiO_2 NTs formed at 35 V in formamide electrolyte containing 5 wt % water and 0.27 M NaF. Upper-inset shows topview while lower inset shows enlarged cross-section



Figure : Cross-sectional FESEM image of TiO_2 NTs formed at 35 V in formamide electrolyte containing 5 wt % water and 0.27 M Bu₄NF. Upper-inset shows topview while lower inset shows enlarged cross-section



Figure : Cross-sectional FESEM image of TiO_2 NTs formed at 20 V in formamide electrolyte containing 5 wt % water and 0.27 M Bu₄NF. Upper-inset shows topview while lower inset shows enlarged cross-section

The length and aspect ratio increased when the cations in the electrolytes were larger. The shortest nanotubes were obtained when the cation was H^+ . At an anodization potential of 35V, nanotubes with outer diameters in the range 175-215 nm were obtained in all the electrolytes investigated. The longest nanotubes were obtained when the cation was Bu_4N^+ (Fig. **38** and Fig. **39**) with nanotubes of intermediate length formed when the cation was NH_4^+ (Fig. **35** and Fig. **36**). The Na⁺ containing electrolyte formed a saturated solution at a much lower concentration (~0.04 M) and nanotubes with an outer diameter

of 48 nm were obtained in this electrolyte (Fig. 37). After accounting for an average wall-thickness of 18 nm, an inner diameter of 12 nm results making these the nanotubes with the smallest pore opening reported thus far. Anodization in BnMe₃N⁺ containing electrolytes were unstable at anodization potentials larger than 20 V. The results at 15 V are shown in Fig. 40. Table 1 summarizes the effect of different cations, concentrations and anodization potentials on the morphology of TiO₂ nanotubes. A trend of decreasing wall-thickness at higher fluoride ion concentrations was discerned and is attributable to the enhanced chemical etching afforded by a higher F⁻ concentrations. During the course of our study, nanotubes with the smallest wall-thickness of approximately 6 nm were obtained in an electrolyte containing $0.5 \text{ M Bu}_4\text{NF}$ and are shown in Fig. 42. When the wall-thickness is this small, the nanotubes are rendered almost transparent to the electron beam used to perform the scanning electron microscopy. This effect is seen clearly in Fig. 42 where when looking at any particular nanotube, features belonging to the nanotube immediately behind it are visible within its contours. The longest nanotubes fabricated using the FA/NMF electrolyte system are shown in Fig. 41. The nanotubes in Fig. 41 were formed at 35 V in an NMF based electrolyte containing 1 % water and 0.27 M Bu₄NF with a length of 94 µm and an outer diameter of 180 nm resulting in an aspect ratio of 522. Nanotubes formed at 20 V in the same electrolyte had a length of 63 µm and an outer diameter of 90 nm resulting in an aspect ratio of 700. At larger anodization voltages, the driving force for ionic transport through the barrier layer at the bottom of the pore is greater and results in faster movement of the Ti/TiO₂ interface into the Ti metal. We attribute the higher nanotube length obtained at larger anodization voltages to this enhanced pore deepening effect. At the same time, we observe an increase in the

diameter of the nanotubes in a particular electrolyte as the anodization voltage is increased. This observation agrees with the reported behavior of nanotubular TiO_2 as well as other anodically formed metal oxides²⁹. At anodization potentials from 10 V to about 20 V, the nanotube length increases faster than nanotube diameter with increasing voltage resulting in an increasing aspect ratio. At potentials larger than 20V, the increase in length are less dramatic and are more than matched by increasing pore diameter. Consequently, as **figure 6** demonstrates, the highest aspect ratio nanotubes are obtained at 20 V in all the electrolytes investigated by us.



Figure : Cross-sectional FESEM image of TiO_2 NTs formed at 20 V in formamide electrolyte containing 5 wt % water and 0.27 M BnMe₃NF. Upper-inset shows topview while lower inset shows enlarged cross-section



Figure : Cross-sectional FESEM image of TiO_2 NTs formed at 20 V in formamide electrolyte containing 1 wt % water and 0.27 M Bu₄NF. Inset shows enlarged cross-section



Figure : FESEM images of nanotubes formed in 0.5 M solution of Bu_4NF in formamide electrolyte containing 5% water



Figure : Histogram showing effect of anodization potential, cation specie (0.27 M concentration), and water concentration on aspect ratio of the resulting nanotubes

Table 6

Table : Effect of the cation and anodization potential on the morphological features of TiO_2 nanotubes

Cation Molar Anodization Duration of Outer Wall Nanotube Thickness Voltage (V) anodization Length concentration Diameter of cation (M) (hr) (nm) (nm) (µm) H^+ 0.14 35 101 256 21 5.6 H^+ 0.27 20 48 99 22 2.9 H^+ 48 0.27 35 214 20 7.3 NH_4^+ 0.14 35 88 208 17 29.2 $\mathrm{NH_4}^+$ 0.14 90 19 20 55 14.4 110 29 NH_4^+ 0.14 15 81 8.2 NH4⁺ 0.27 35 30 159 15 37.4 NH_4^+ 0.27 90 20 24 17 19.6 Na^+ Saturated 35 48 48 18 9.6 solution (~0.04) Bu_4N^+ 0.27 35 48 190 22 68.9 Bu_4N^+ 0.27 20 34 90 16 35.2 Bu_4N^+ 0.27 15 46 80 15 20.0 BnMe₃N⁺ 0.27 7.2 15 42 70 18

3.4 Discussion

The maximum nanotube length obtained in formamide-5 %water mixtures with different cations increased in the following order :

Eq. 10

$$H^+ < Na^+ < NH_A^+ < Bu_A N^+$$
 10

Higher nanotube lengths were obtained in the Bu_4N^+ containing electrolytes. The maximal length was obtained with a shorter duration of the anodization process implying a faster growth rate. We attribute this behavior to the a) presence of a thinner interfacial oxide layer that promotes faster migration of the oxide-metal interface deeper into the oxide and b) a decrease in the rate of chemical etching and c) higher conductivity of the electrolytes containing larger cations. Quaternary ammonium salts effectively inhibit the acid corrosion of metals in the presence of halide $ions^{58}$. The inhibitory effect of quaternary ammonium salts is explained by structuring of the solvent in the diffuse part of the electrical double layer and by a decrease in the mobility of hydronium ions in the near-to-electrode laver⁵⁸. The inhibiting action of organic compounds containing polar groups such as nitrogen and sulfur is also based on the adsorption ability of the molecules where the resulting adsorbed film protects the metal from the corrodent⁵⁹. The chemical etching of TiO₂ is assisted by H^+ ions and has a marked pH dependency⁵⁰. Therefore, chemical etching of the TiO_2 is highest in the HF containing electrolyte. Chemical etching is also higher when the cation is NH_4^+ compared to Bu_4N^+ . This is because the ammonium ion is a stronger acid than tetrabutylammonium and can donate a proton more Comparing Eq. 8 to Eq. 10, the high field conductivity of various electrolytes easily.

correlates well with the maximum nanotube length obtained in those electrolytes suggesting that solution conductivity may also be a parameter determining the maximum length of the nanotubes. However, the behavior of the ammonium ions runs counter to the hypothesis that conductivity is the key parameter. The conductivity of the ammonium ion bearing solution is higher than the tetrabutylammonium containing solution and the anodic current transient is larger in the ammonium bearing electrolyte. Yet the growth rate and final formation length of TiO_2 nanotubes are much larger in the electrolyte containing tetrabutylammonium cations.

3.5 Summary

The effect of different cations and anodization potentials on the anodic formation of TiO_2 nanotubes was investigated in formamide-water mixtures and the results are as follows :

- (1) A smaller water content results in a faster nanotube growth process due to a thinner interfacial oxide layer.
- (2) The cation exerts a profound influence on the anodization process. Among the various cations investigated, quaternary ammonium ions result in the faster growth rates and the longest nanotubes. In particular, when tetrabutylammonium was the cation, nanotubes as long as 94 μm were obtained. We attribute this to the inhibitory effect of quaternary ammonium salts which again result in a thinner

interfacial oxide layer as well as to a lower rate of chemical dissolution of TiO_2 in these electrolytes.

- (3) In a saturated solution of NaF in formamide, nanotubes with an inner diameter of 12 nm were obtained. To the best of our knowledge, this is the smallest reported pore opening for anodically formed TiO₂ nanotubes.
- (4) The nanotube aspect ratio is a function of the anodization potential. In all the investigated electrolytes, a maximum in the aspect ratio was observed at 20 V. In particular when tetrabutylammonium was the cation and the water content was limited to 1 %, the highest aspect ratio of 700 was obtained.

CHAPTER 4

EVOLUTION OF THE NANOTUBULAR STRUCTURE

Anodization has been employed to fabricate nanotubular structures in Titanium Dioxide and more recently in several other oxide systems such Hafnium Oxide⁴³, Zirconium Oxide^{42, 60}, Niobium Oxide⁶¹ and Tantalum Oxide⁴¹. However, the formation of a nanoporous structure in Alumina (also aluminum oxide or Al₂O₃) has been studied since the fifties⁶²⁻⁶⁴ and precedes work in all the other oxide systems. Spatially regular, hexagonally ordered arrays of nanoscale pores in aluminum oxide can be formed by the anodization of aluminum in acidic electrolytes^{65, 66}. The theory behind the evolution of the nanoporous structure in porous alumina is relatively well-understood and will form the basis for the ensuing discussion of the evolution of the nanotubular structure.

4.1 Theory of evolution of porous structure in Alumina

During the anodization of aluminum metal, oxidation takes place and the oxide forms a porous structure due to oxide growth at aluminum/oxide interface and field enhanced chemical dissolution at the oxide/ electrolyte interface. When the anode is a valve metal (such as Ti, Ta, Zr, Hf, etc.) and the anodization is performed in an electrolyte containing fluoride ions, nanotube formation occurs as a result of the interplay between three simultaneously occurring processes, namely the field assisted oxidation of Ti metal to form titanium dioxide, the field assisted dissolution of Ti metal ions in the electrolyte and the chemical dissolution of Ti and TiO_2 due to etching by fluoride ions. The same three processes govern the anodic formation of several other self-organized nanoporous metal oxides. Such a delicate balance of reactions is achieved only when the process parameters such as pH, temperature, anodization potential and fluoride ion concentration occur in certain defined ranges, which are specific to the valve metal undergoing anodization.

Fig. 44



Figure : Schematic describing the evolution of the porous structure during the potentiostatic anodization of aluminum

The pioneering work of O'Sullivan and Wood⁶⁴ demonstrated conclusively that the barrier layer thickness, pore diameter, and interpore spacing all increase nearly linearly with the voltage of the electrochemical cell and decrease with increasing acid strength of the electrolyte. O'Sullivan and Wood suggested a basic mechanism to explain the pore formation and growth behavior observed in their experiments. They proposed that the steady-state barrier layer thickness is determined by the equilibrium between oxide growth at the metal-oxide interface and field-assisted dissolution at the pore bases. Pore formation is initiated by the concentration of the electric field in the barrier layer at the depressions of the oxide-electrolyte interface that start dissolving faster and become the precursors of well-developed pores.

As the voltage is switched on to start the anodization, process apparent nuclei or spots of thicker oxide (a few tens of nanometer in diameter) form that increase in number and size until they merge eventually, leaving thin areas of oxide between them⁶⁷. These thin areas rapidly transform into the situation with the scalloped pore base, the film then eventually penetrating more, not less, into the metal in these locations. As the current rises, the pore and cell diameters increase causing a smaller number of major pores to eventually propagate. A certain number of the incipient pores cease to function, and very large ones do not grow larger. Fig. **44** provides a schematic description of the four stages:

(I) Immediately after switching on the anodic bias a barrier oxide layer starts to grow (II) Relatively fine featured pathways are then revealed in the outer regions of the barrier oxide prior to any true pore formation (III) Further anodizing results in propagation of individual paths through the barrier oxide with their heads becoming enlarged

(IV) Finally, a steady state pore structure is formed by closely packed cylindrical cells, each containing a pore at the center and separated from the aluminum metal by a layer of scalloped hemispherical barrier oxide.



Figure : Schematic representation of three possible pore base situations, r_1 , r_2 and r_3 representing the radii of curvature at pore bases, b the constant barrier-layer thickness and ω the (constant) solid angle subtended from the center of curvature to the pore bases. r_2 is the steady-state radius of curvature under the prevailing anodization conditions [1]



different radii of curvature. Initially it is assumed for simplicity that the barrier layer thickness *b*, and the solid angle, ω , remain constant as the pore diameter varies. It is supposed that r_2 is the equilibrium pore base radius of curvature under the set conditions. The extent to which the field increases on passing from the cell base to the pore is measured approximately in the three cases by the ratio of the cell base area to pore base area, since the same current is passing through all the surfaces. Thus, a self-adjusting situation predominates, any tendency for the pore diameter to become too large or small being checked by a consequent increase or decrease in the radius of curvature of the pore base. The constant pore and cell sizes, proportional to anodization voltage, are a consequence of the equilibrium barrier layer thickness and pore base radius of curvature established. Measurements of the cell-wall thickness indicated that it was always 0.71 of the barrier-layer thickness under these conditions for the range of cell-voltages used. Thus the pore diameter is given by

Eq. 11

$$p = c - (2 \times 0.71d) \tag{11}$$

where p is the pore diameter, d is the barrier layer thickness and c is the cell diameter.

When the voltage is switched on, the initial current is dominated by barrier-layer growth. The drop from the maximum corresponds to the initial pores having a low radius of curvature, giving a high rate of field-assisted dissolution. As the pore base radius of curvature increases with the growth of the pore diameter, the dissolution at the pore bases slows down and the rate of current decrease declines until the pores and the barrier layer have reached their equilibrium dimensions. From the assumption that ω should be
constant for all pore radii of curvature, it follows that the pore and cell bases must remain of the spheres of which constant segments thev respectively form parts. The unoxidized metal close to the junction between two adjacent growing cells is acted upon by two components of the field, each component trying to pull the metal into different cells. When the pore and cell bases are almost hemispheres, these two fields almost cancel each other out so there is virtually no net field acting to pull ions through the oxide towards or away from the pore base. In the absence of moving ions there is less tendency for field-assisted dissolution to propagate the pore side-ways to enlarge them. As cell formation continues, however, the horizontal components of the field cancel out as before but the vertical components reinforce, causing film growth and balancing field-assisted dissolution to promote barrier layer and pore propagation into the metal. Therefore, if the segment becomes too small, the appropriate component of the field causes lateral spread of the pore, whereas if it is too large penetration into the barrier-layer predominates.

The diameter of each pore and the separation between the adjacent pores can be controlled by changing the anodization conditions. The pore size and pore spacing of these alumina membranes are proportional to the anodization voltage with proportionality constants of 1.29 nm V⁻¹ and 2.5 nm V⁻¹ respectively^{65, 68}. Thus by controlling the anodization voltage the pore size and distribution of the pores can be easily tailored. Pore densities of the order of 10^{10} - 10^{12} /cm² can be achieved.

4.2 Theories of the evolution of the nanotubular structure in Titania

Mor et al³⁰ proposed a mechanism for the anodic formation of nanotubular TiO₂ in aqueous acidified electrolytes based on their observation of the morphology of straight and tapered TiO₂ nanostructures 5s, 30s, 60s, 90s, 120s and 45 min into the anodization process in aqueous HF electrolytes. Chemical dissolution of titania in the HF electrolyte plays a key role in the formation of nanotubes rather than simple nanoporous structures. However, this dissolution also limits the thickness of the nanotube layer to a few hundred nanometers in strongly acidic aqueous environments. They contend that with the exception of chemical dissolution, which is nearly negligible in the case of alumina, the key processes responsible for the anodic formation of nanoporous alumina and titania appear to be the same and are as follows: (i) Oxide growth at the surface of the metal due to interaction of the metal with O^{2-} or OH^{-} ions and migration of these anions through then oxide layer after the formation of an initial oxide layer, and reaction with Ti at the Ti-TiO₂ interface. (ii) Ejection of the Ti⁴⁺ cations from the Ti-TiO₂ interface and migration of these cations through the oxide toward the oxide-electrolyte interface. (iii) Field-assisted dissolution of the oxide at the oxide-electrolyte interface. Due to the applied electric field, the Ti-O bond undergoes polarization and is weakened, promoting dissolution of the metal cations. Ti^{4+} cations dissolve into the electrolyte, and the free O^{2-} anions migrate toward the metal-oxide interface to interact with the metal (iv) Chemical dissolution of Ti and TiO₂ in the acidic electrolyte, which is critical for the self-organized formation of the nanotube arrays, reduces the thickness of the oxide layer (barrier layer)

keeping the electrochemical processes (field-assisted oxidation and dissolution) active. No nanotubes can be formed if the chemical dissolution is too high or too low. The chemical dissolution rate is determined by the F^- concentration and solution pH (Eq. 13). With increasing F^- and H^+ concentrations, chemical dissolution increases.



Figure : Schematic diagram^{30, 69} of the evolution of straight nanotubes at a constant anodization voltage, as follows: (a) oxide layer formation (b) pit formation on the oxide layer (c) growth of the pit into scallop-shaped pores (d) the metallic part between the pores undergoes oxidation and field-assisted dissolution and (e) fully developed nanotubes with a corresponding top view.



The mechanism proposed by Mor et al^{30} envisions the anodization process proceeding in a sequence of steps, a schematic of which is shown in Fig. 46. Almost immediately after the start of anodization, a thin layer of oxide forms uniformly on the titanium surface [Fig. 46(a)]. The overall reaction for the anodization of titanium can be represented as

Eq. 12

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+$$
 12

This oxide layer undergoes pitting due to attack by fluoride ions and localized dissolution of the oxide [Fig. **46(b)]** and , making the barrier layer at the bottom of the pits relatively thin, which, in turn, increases the electric-field intensity across the remaining barrier layer, resulting in further pore growth [Fig. **46(c)**]. The pits themselves act as pore forming centers.

Eq. 13

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O$$
 13

The pore entrance is not affected by electric-field-assisted dissolution and hence remains relatively narrow, while the electric field distribution in the curved bottom surface of the pore causes pore widening, as well as a deepening of the pore. The result is a pore with a scallop shape. Also, unanodized metallic portions initially exist between the pores. As the pores become deeper, the electric field in these protruded metallic regions increases, enhancing the field-assisted oxide growth and oxide dissolution, and simultaneously with the pores the well-defined interpore voids start forming, as shown in Fig. **46(d)**. Thereafter, both voids and tubes grow in equilibrium to finally yield a tubular structure shown in Fig. **46(e)**. Schmuki and colleagues^{70, 71} explained the effect of pH in the anodization process and refined the mechanism first proposed by Mor et al³⁰. They offered that at the stage of the anodization process represented by Fig. **46(c)**, a pH gradient is established between the pore tip and the bottom of the pore, where the dissolution due to the lower pH values leads to an accelerated TiO_2 dissolution and pore penetration into the Ti substrate. Also, they surmise that the transition from irregular to regular pores occurs due to competition between the pores for the total available current⁷¹. The author attempted to use a hydrophobic self-assembled monolayer of Octadecyltrichlorosilane (OTS) which is commonly used as a blocking layer, to reduce chemical etching. However, the monolayer of OTS caused all reactions to cease. An interesting idea involves using capping/chelating ligands such as glycolate and butylmalonate to selectively inhibit chemical etching and push the competing reactions more in the direction of forming pores such as in alumina rather than tubes.

4.2.1 Effect of Grain Size of Ti metal

When magnetron sputtered titanium thin films on conducting glass substrates are anodized (instead of the more typical Ti foil substrates), a relationship between grain structure and nanotube formation was found to exist. When the deposition temperature of the sputtering process was low (close to room temperature), Ti films with a smaller grain size were obtained and these films did not result in nanotubes upon anodization. Mor et al⁴⁹ observed a larger grain size in films deposited at 500°C compared to films deposited at 250°C. Also, the fine grained films deposited at 250°C yielded non-uniform nanoporous structures instead of well-defined nanotubular structures. When the deposition temperatures were higher than 400°C, the larger grained films thus obtained yielded nanotubes upon anodization. The grain size resulting from deposition at a certain temperature was not quantified; however it is clear that a minimum grain size of the starting Ti metal is necessary for nanotube formation and if this grain size does not exist, nanotube formation does not proceed. However once nanotube formation occurs, the properties of the nanotubes are independent of the starting grain size and are exclusively dependent on the morphology, structure and composition of the nanotube arrays themselves.

4.3 Anodic current transients in aqueous electrolytes

Fig. 47



Figure : Anodic current transient of a Ti foil sample anodized at 25V in a KF based buffered electrolyte of pH 5. The inset shows the period from 10^3 -2x 10^4 s in greater detail

The anodic current transient observed during the anodization of a Ti foil sample in a buffered aqueous electrolyte of pH 5 containing 0.1 M KF is shown in Fig. **47**. Upon application of the voltage, the measured current density reduced from 131 mA cm⁻² to a local minimum of 0.25 mA cm⁻² in about 500 seconds due to the field-assisted formation of a thin uniform insulating "barrier" oxide layer on the surface of the metal. The character of the current flow at the anode transitions from all-electronic to all-ionic as the barrier oxide layer is formed. At this stage, local attack by fluoride ions cause pits or cracks to form on the surface, which also act as pore nucleation sites. The reduced oxide layer thickness at these points results in an increase in the current. The local current maximum shown in the inset of Fig. **47** corresponds to the stage in the process where the crack/pit density has reached saturation. Beyond this point the current (which is nearly all ionic at this stage) gradually drops due to an increase in the thickness of the barrier layer accompanying the movement of the Ti/TiO₂ interface further into the Ti substrate.

The very formation of titania results in local acidification at the pore bottom per Eq. 12. When the H^+ concentration at the pore bottom reaches a certain threshold level, the thickness of the barrier layer reduces once again due to chemical etching and accounts for the second local minimum in the anodization process. Also, H^+ ions at the pore bottom gradually diffuse to the bulk of the electrolyte and any increase in the ionic current through the barrier layer is also accompanied by an increase in the dissolution rate of the nanotube array. A quasi-steady state is thus reached due to the balancing of competing reactions. The maximum length of the nanotube array corresponds to the point in the anodization process when the rate of formation of fresh oxide and the rate of loss of oxide to dissolution processes become equal.

4.4 Anodic current transients in organic electrolytes

Fig. 48



Figure : Real time observation of anodization behavior of a Ti foil (99.8 % pure) anodized at 25 V in A] Electrolyte containing 0.5 wt % NH₄F and FA/NMF in the ratio 8:5 B] Aqueous electrolyte containing 0.5 wt % NH₄F and C] Aqueous electrolyte containing 0.5 wt % KF. Inset : region of local maxima in anodization current for aqueous solutions.

Fig. **48** compares the real time potentiostatic anodization behavior of Ti anodized at 25 V in an electrolyte consisting of formamide and N-methylformamide in the ratio 8:5 to the same process occurring in aqueous solutions of 0.5 wt % NH₄F and KF respectively. The difference is stark. In aqueous electrolytes, the anodization current drops sharply from a high initial value (>100 mA/cm²) in the first few seconds of anodization. This is attributed to the formation of an initial insulating oxide layer that reduces the current. Thereafter, pitting of the oxide layer by fluoride ions commences and the anodization current increases to reach a local maximum (see inset in Fig. 48) after about 500 seconds of anodization. In complete contrast, the anodization current in the FA/NMF based organic electrolyte remains relatively constant in the first 100 seconds of anodization and decreases monotonically thereafter. As a result, while the total charge passed after 500 minutes of the anodization process was similar for both kinds of electrolytes, a much larger amount of charge is passed in the FA/NMF based electrolyte during the first 100 seconds of anodization. In Fig. 48, 2 coulombs of charge accompanied the anodization of Ti in the FA/NMF based electrolyte after 100 seconds while 0.3 coulombs of charge were passed in the KF based aqueous electrolyte. Fig. 49 shows the anodic current transients obtained at three different anodization potentials, namely 10 V, 20 V and 25 V in an FA based electrolyte containing 0.4 wt % NH₄F. The region of stable current extends for a longer period of time at lower anodization potentials. The pitting process in the FA based electrolyte is very quick and occurs contemporaneously with electronic conduction. Even after just 600s of anodization, the outline of a nanotubular structure is already formed. Since the electronic current is much larger than the ionic current at this stage, the pitting current which is much smaller in comparison is not clearly visible in the anodic current transients whereas the pitting current is very visible in the anodic current transients of aqueous electrolytes. The current plots are broadly similar in that they all exhibit a sigmoidal curve with an initial region of stable or near stable anodization current followed by a region of falling current of larger slope and a then a region where the current reaches a lower level and continues to decrease albeit with a smaller slope. During the initial period of high current, gas evolution at the anode is observable. Since gas evolution requires electronic charge

transfer, this is indicative of electronic conduction dominating in the early part of the anodization. We attribute this to the formation of a thinner or lower quality initial oxide layer in the non-aqueous electrolyte which allows substantial electronic conduction through field emission. The higher anodization voltages provide a greater driving force for both electronic and ionic conduction and are accompanied by higher anodization currents. In the second region, the transition electronic conduction to ionic conduction, which is a much slower process requiring the solid state transport of ions, occurs causing a reduction in the anodization current. Also, nanotube formation occurs causing the effective surface area for anodization to contract and the current to decrease while pore deepening occurs in the third and final region of anodization.

Fig. 49



Figure : Real time observation of anodization behavior of a Ti foil (99.8 % pure) anodized in an electrolyte containing 0.4 wt % NH₄F in FA electrolyte



Figure : Voltage dependent current – time behavior during the first 30 minutes of anodization of Ti samples in an electrolyte comprised of 0.3 wt % NH_4F , and 2 vol % H_2O in ethylene glycol.

Fig. **50** shows the current-time behavior during potentiostatic anodization of Ti samples in a 0.3 wt % NH₄F, 2 vol % H₂O ethylene glycol electrolyte as a function of potential during the first 30 minutes of the anodization process. The current plots are broadly similar to the anodic transients for formamide (Fig. **49**) in that they all exhibit a brief initial region of stable or near stable anodization current followed by a region of falling current of larger slope and then a region where the current reaches a well-defined plateau and continues to decrease albeit with a smaller slope.

4.5 Growth Models

The nanotube growth rates in both formamide and ethylene glycol are almost an order of magnitude larger than the growth rate in aqueous solutions. EG in particular exhibits growth rates as large as 15 μ m per hour in the first four hours of the anodization process. Furthermore, the rapid growth rate does not degrade the porous structure of the nanotubes in any way. In fact, the nanotubes formed in formamide have pore shapes that approach the shape of a circle for the most part while nanotubes formed in EG exhibit long range order manifested in hexagonal close-packing and very high aspect ratios (~2181).

The rate of reaction was studied by anodizing titanium foil samples at 60 V, in a fresh (un-used) solution of 0.3% wt NH₄F and 2 vol % H₂O in ethylene glycol for different durations. The samples anodized for 4 hr, 17 hrs, 21 hrs, 48 hrs and 96 hrs exhibited a length of ~ 58 μ m, 164 μ m, 188 μ m, 289 μ m and 360 micron respectively. The lengths obtained at various intervals up to 21 hours are proportional to the charge passed during those time intervals indicating the current efficiency to be a constant. After accounting for the porosity of the structure and the titanium dioxide dissolved during the formation of the nanotubular structure, the effective current efficiency for TiO₂ formation is close to 100 % indicating almost no side-reactions during the anodization and negligible bulk chemical dissolution of formed TiO₂ nanotube arrays. This is confirmed by the report of Macak and Schmuki⁴⁷, who also observe a near 100% current efficiency for the anodization reactions in glycerol and ethylene glycol. The

proportionality between the charge passed and the length of formed TiO_2 nanotubes, when adjusted for their respective porosity factors, was also found to hold for anodization potentials lower than 60 V. The reason the proportionality holds is that when the rate of chemical dissolution is low and the barrier layer thickness is small in comparison with the length of the porous (nanotubular) structure, the main result of the anodic current is growth of the porous oxide layer. Using Faraday's law, the increase of the layer thickness (nanotube array length) *L* with time t is given by

Eq. 14

$$\frac{dL}{dt} = \frac{M}{P_{ox}\rho_{ox}nF}i$$
14

Where *M* is the molecular weight of the oxide, P_{ox} is the porosity factor, ρ_{ox} is the density of the oxide, *n* is the number of electrons needed to form one molecule of oxide (4 for TiO₂) and *F* is the Faraday number. For contiguous nanotubes with circular pores, the porosity factor p_{ox} is given by⁷²

Eq. 15

$$P_{ox} = 1 - \frac{2\pi}{\sqrt{3}} \frac{\left(DW + W^2\right)}{\left(D + 2W\right)^2}$$
 15

In order to find an equation that provides analytical insight into the experimental results, a great number of semi-empirical expressions for the anodic ionic current were applied using non-linear regression. By far, the best fitting among them was found to be given by the expression Eq. 16

$$j \times t^{\gamma} = \text{constant}$$
 16

The anodization current during the first 10 minutes of the anodization process in the formamide (FA) based electrolyte is mostly electronic and hence not relevant to our investigation of the growth model in the ionic current regime. The first and second derivatives (w.r.t. time) of the anodization current were plotted and the inflection point in these plots was judged to be the transition point from electronic to ionic conduction. Fig. **51** shows the results of the fit for anodization in formamide based electrolytes. The same procedure was applied to the transients in EG based electrolytes and the results are shown in Fig. **52**.

Fig. **51**



Figure : Anodic current transients in FA based electrolyte fit to Power Law (Eq. 16)





Figure : Anodic current transients in EG based electrolyte fit to Power Law (Eq. 16)

The standard error of the fits were smaller than 1% and the R factors of the fit were very high as shown in Table 7. γ values were obtained in the range 0.30 to 0.56.

The following mechanisms are relevant to anodization phenomena in valve metals in the determination of the rate limiting step and the applicability of each to the case of nanotubular growth in formamide and EG based electrolytes will be considered.

Table 7

Electrolyte	Potential (V)	γ	R
EG based	20	0.48	0.918
	40	0.34	0.975
	50	0.36	0.997
	60	0.30	0.983
	65	0.33	0.996
FA based	15	0.56	0.983
	25	0.53	0.989

Table : Parameters obtained from the curve fits of Fig. 51 and Fig. 52.

Diffusive Mass Transport Control

The two main arguments supporting this explanation are :

1) In the existing literature on the fast formation of porous structures by anodization, mass transport is sometimes cited as the rate limiting step. For alumina obtained by hard anodization, the gradual decrease of the ionic current with time was attributed to the diffusion controlled mass-transport of oxygen containing anionic species from the bulk reservoir to the oxide/metal interface³². Based on the increase in nanotube length at higher temperatures, Macak et al³² claimed that diffusion of the reactants from the poretip or of reaction products away from the pore tip was the dominant growth limiting factor in the anodic formation of TiO₂ nanotubes in viscous electrolytes. 2) γ values close to 0.5 are typical of diffusive mass transport⁷³. Indeed, the transient response of a diffusion limited system is given by⁷⁴

Eq. 17

$$i_d(t) = \frac{nFAD_o^{0.5}}{2t^{0.5}} [C_o^* - C_o(x=0)]$$
 17

where *n* and *F* are the same as in Eq. 14, $i_d(t)$ is the diffusion limited current, *A* is the electrode area, D_O is the diffusion coefficient of oxygen bearing species, *t* is the time, C_O^* is the concentration of oxygen bearing species in the bulk and C_O^* is the concentration of oxygen bearing species at the surface.

The arguments against the mass transport explanation are as follows :

- A problem with the mass transport explanation as applied to the anodization process in ethylene glycol is the strong dependence we observe, of the nanotube growth rate on anodization voltage, in both formamide based and EG based electrolytes.
- 2) When the process is diffusion controlled, the diffusion coefficient is inversely proportional to the viscosity as per the Stokes-Einstein relation :

$$D = \frac{k_B T}{6\pi\eta a}$$
 18

Eq. 18 indicates that all else being equal, the growth rates in more viscous solutions should be lower. However, much higher growth rates are obtained in the much more viscous EG based electrolytes than in the formamide based electrolytes. Also, in section **3.3** we observed that the higher viscosity formamide solutions of bulkier cations such as tetrabutylammonium exhibited higher nanotube growth rates compared to lower viscosity solutions of smaller cations such as ammonium and sodium. Also, when the concentration of tetrabutylammonium fluoride was increased, clearly no new sources of oxygen bearing anionic species were added to the electrolyte. The viscosity of the solution increased and the growth rate increased as well.⁷⁵

Potential Controlled Processes

For voltage controlled processes, the growth rate depends on whether the rate limiting step is solid state transport of ions through the oxide barrier layer or the availability of ionic species at the oxide-electrolyte interface. Hypotheses assuming that the film growth rate is limited by migration of ionic species through the film under the effect of a high electric field constitute the High Field Model (HFM). When a potential dependent interface reaction is assumed to be rate determining, the Interface Model (IFM) results.

High Field Model

The movement of the $Ti-TiO_2$ interface into the Ti metal involves ion transport under the influence of an electric field, either by transport of (i) metal cations in the direction of the solution, or (ii) oxygen ions (and probably some incorporated anions) in the direction of the metal. For valve metals, under the high field approximation, the ionic current *i* is related to the anodization potential and the thickness of the barrier layer by an equation of the form⁷⁶⁻⁷⁸ :

Eq. 19

$$i = A \exp\left(\frac{\beta \Delta U}{X_{barrier}}\right)$$
 19

Where ΔU is the potential drop across the oxide layer, $X_{barrier}$ is the thickness of the barrier layer and A and β are constants.

Diagnostic test between High Field Model and Interface Model

Macdonald et al have proposed diagnostic criteria to distinguish between different film growth regimes⁷⁹. For conditions with negligible dissolution under a constant polarization, the HFM was shown to give the relation :

$$\frac{\sqrt{-di}}{i} = k \ln i - k \ln A$$
20

Where *i* is the anodization current and *A* is the high field pre-exponent from Eq. 19. k is

given by $\frac{1}{nF}\sqrt{\frac{V_{ox}RT}{\alpha^{hf}sU}}$ where n is the valence, *F* is Faraday's constant, V_{ox} is the oxide molar volume, *R* is the ideal gas constant, *T* is the temperature, *U* is the applied potential, s is the high field half-jump distance and α^{hf} is the high field symmetry factor⁸⁰.

Eq. 20 results in a linear relationship with a positive slope when the function

$$f(i,i') = \frac{\sqrt{\frac{-di}{dt}}}{i}$$
 is plotted against *ln i*.

For interfacial kinetics (IFM), the corresponding equation is

Eq. 21

$$\frac{\sqrt{\frac{-di}{dt}}}{i} = \sqrt{\frac{V_{ox}\alpha E}{RT}}$$
21

Where E is the electric field in the barrier layer and α is a fit parameter for interfacial kinetics. The right hand side of equation 3 is a constant. Therefore, a horizontal line

results when $f(i,i') = \frac{\sqrt{\frac{-di}{dt}}}{i}$ is plotted against *ln i*. Thus, plotting f(i, i') vs *ln i* provides a diagnostic tool to identify the rate limiting step. The results are shown in Fig. **53**. The dashed colored lines represent the values of f(i, i') while the solid black lines are linear fits to the same. At constant potential, in the current decay phase, the points in the f(i, i') vs. *ln i* fall close to a straight line and indicate the high field model to be applicable.

The slopes of the plots in Fig. **53** at low potentials (20-50V) and high potentials (60-65 V) differ considerably. The slopes are ~18 at 20 V and ~6 at 65 V. Since the slopes in the f(i,i') vs ln (i) plot equate to half-jump distances in the high field model^{79, 80} and since anionic incorporation can cause the half-jump distance to vary by a factor of two, the slope maybe expected to vary by a factor of two. However, in the present case, the slope is clearly varying by a factor of three with a consistent trend of lower slopes at higher anodization potentials.

At higher potentials, ionic transport (which is exponentially dependent on potential per the Guntherschulze-Betz relation of Eq. **19**) is sufficiently fast for the interface reaction to become more significant. However when the film grows very thin (a phenomenon observed only at voltages above 60 V) after several hours of anodization, it is unlikely that the interface reaction becomes rate-determining and here is why. It is the *slowest step* that determines the rate. When the film thickness is thin during double sided anodization, Ti³⁺ ions are pulled in opposite directions, the electric field provided less impetus for ion transport inside the oxide, then diffusive transport of ions through the oxide becomes the rate-limiting step not the interfacial potential. The interface reactions are still not solely rate-determining during the first 30 hours of the anodization process during which the current is monitored, considering the presence of a clear positive slope in Fig. **53** even at 60V and 65 V and much clearer evidence of HFM being applicable at potentials 20 V-50 V.



Figure : f(i,i') versus ln i for potentiostatic anodization of Ti in EG based electrolyte.

The arguments in favor of the High Field Model are as follows :

- 1) Results of the diagnostic test (Fig. 53) support the HFM.
- The power law dependence of the current density on time is also characteristic of the HFM⁸¹.
- The increase in nanotube growth rate with decreasing water content is consistent with the HFM
- HFM explains the strong dependence seen in both formamide and EG based electrolytes of the nanotube growth rate on the potential employed for anodization.
- The nanotube growth behavior in electrolytes of different viscosity is not in contradiction with the HFM

6) During the galvanostatic growth of porous alumina, the results of Patermarakis and Moussoutzanis confirmed that the rate limiting step was the solid state charge transport across the barrier layer⁸².

The arguments against the HFM are as follows :

- 1. When HFM is the operating mechanism, the value of γ is closer to 1 than to 0.5^{73} . However, the value of 1 for γ results from derivation of the high field equations arising from assumptions of compact anodic films and are not necessarily true for porous films.
- Processes with a negative exponent n (oxide growth) are dominant only in short periods of time. Later, the influence of time-independent processes (e.g. corrosion) becomes more and more important.

The results of the diagnostic test(Fig. **53**) eliminate the Interface model as a candidate mechanism in the first thirty hours of anodization. Between the High Field Model and Diffusive Mass-Transport Control, a case may be made for both. Clearly, more investigations such as studying the temperature dependence of the anodization reaction, quantification of the transport numbers of the ions in the solid state oxide and Transmission Electron Microscopy studies of the thickness and composition of the barrier layer should help provide additional insight about the exact operating mechanism controlling the formation of titania nanotubes hundreds of microns in length. But the weight of evidence collected by us at the present moment favors the High Field Model.

CHAPTER 5

ELECTRONIC TRANSPORT IN TIO₂ NANOTUBULAR FILMS

5.1 Importance of Electron Transport

Electron transport and recombination are major determinants of solar cell efficiency. Hence, study of the electron transport characteristics of TiO_2 nanotube array photoelectrodes is important from the point of view of evaluating the suitability of use of NTs in solar cells.





Figure : : Schematics of the cross-section (left) and top-view (right) of the vertical TiO_2 nanotube/barrier layer structure

Electron transport is a limiting factor in the performance of porous nanocrystalline electrodes, hindering progress in achieving higher efficiencies⁸³. The

structural disorder at the contact between two crystalline particles leads to an enhanced scattering of free electrons, thus reducing the electron mobility. This results in charge transport being limited by the hopping of electrons along a poorly formed network of randomly distributed nanoparticles⁸³. An ordered and strongly interconnected nanoscale architecture would eliminate randomization of the particle network, increase contact points for good electrical connection and decrease small necking points that have been shown to develop between adjacent-bound particles in the current nanoparticulate titania structure after sintering. An architecture consisting of oriented one-dimensional structures, such as nanotubes aligned perpendicular to the substrate could potentially improve the charge collection efficiency by promoting faster transport and slower recombination.

5.2 Electronic band structure in TiO₂ nanotubes

Electron-phonon interactions, ionized impurities and grain boundaries are the principal factors affecting electron transport in polycrystalline semiconductors. Grain boundaries typically contain a high density of surface states which can trap or scatter free carriers, generate potential barriers or generate depletion regions within the grain⁸⁴. Depending on the geometry of the material and the intrinsic properties of the bulk materials, the following three situations can be distinguished with respect to the conduction band in a grain in the walls of a nanotube (see Fig. **55**). The wall-thickness of the nanotube is denoted by t. The charge density trapped in surface states is given by n_t while N_0 is the bulk doping concentration, L_d is the Debye length and N_c is the density of

states in the conduction band. The other physical parameters considered are the trap depth of the surface states (E_c - E_t) and the grain boundary potential Φ_b .



Fig. 55

Figure : Band structure of a grain in the nanotube wall

1] $n_t < N_0 \cdot t$

Band bending is limited to the interface region. A thin depletion layer is formed at the surface of the grains. In this case, the mobility is thermally activated and the carrier concentration n is constant within the bulk of the grain, namely : $n = N_0$

The Debye length is given by

$$L_{d} = \sqrt{\left(\frac{\varepsilon \cdot kT}{N_{0} e^{2}}\right)}$$
 22

And the grain boundary potential is

Eq. 23

$$\Phi_b = \frac{e^2 n t^2}{8\varepsilon \cdot N_0}$$
 23

The mobility is a function of the grain size and the carrier effective mass and is given by Eq. 24

$$\mu_0 = e \cdot t \sqrt{8\pi m^* kT}$$

2] $n_t < N_0 \cdot t$ and $L_d < t/2$

The grains are partially depleted and the electron transport is inhibited by the potential barrier. The carrier concentration n and the mobility μ are both thermally activated by the grain boundary potential, and are given by :

Eq. 25

$$N = \sqrt{2\pi} \left(\frac{L_d}{t}\right) \left[\frac{N_0 N_c}{\frac{N_t}{t} - N_0}\right] \exp\left[-\frac{\left(E_c - E_t - \Phi_b\right)}{KT}\right]$$
25

$$=\mu_0 e^{-\frac{\Phi_b}{KT}}$$
 26

3] $n_t = N_0 \cdot t$ and $L_d > t/2$

The Debye length is large compared with the grain size, the grains are fully depleted of free carriers and this results in conduction and valence bands with flat edges i.e. a flat band condition within the grain. In this case, there are no potential barriers to the current flow and the carrier concentration within the grain is thermally activated because of carrier excitations from the trap level E_t into the conduction band. Therefore, the carrier concentration is given by :

μ

Eq. 27

$$N = \left(\frac{N_0 N_c t}{N_t}\right) \exp\left[-\frac{\left(\mathbf{E}_c - \mathbf{E}_t\right)}{\mathbf{kT}}\right]$$
 27

While the mobility is $\mu = \mu_0$. In this regime, the injection of electrons from the crystallite surface into the conduction band is fast.

An optimal combination of parameters such as smaller wall-thickness, fewer grain boundaries and a more perfect stoichiometry (fewer structural defects) can improve the transport characteristics of a photoelectrode that employs TiO₂ nanotubes.

119

5.3 Transport and recombination in TiO₂ nanotube photoelectrodes and other low dimensional structures.

The slow percolation of electrons through a random polycrystalline network and the poor absorption of low-energy photons by available dyes are two of the major factors limiting further improvement in the photoconversion efficiencies achievable using nanocrystalline dye sensitized solar cells⁸³. The use of thicker nanocrystalline films (beyond 10 µm) to improve this absorption is counteracted by the slow electron diffusion through the nanoparticle network⁸³. The randomness of these films results in almost a doubling of the length of the electron pathway⁸⁵. Arrangement of ordered titania nanotubes perpendicular to the surface permits the vectorial charge transfer from the solution to the conductive substrate, thereby reducing the losses incurred by the hopping of charges across the grain boundaries of nanoparticles⁸⁶. Electron transport in oriented one dimensional structures such as nanotubes and nanowires is expected to be superior to electron percolation through a random polycrystalline network. Therefore, a onedimensional architecture with a similar surface area to a nanoparticle anode might be expected, upon optimization to yield a higher overall efficiency through superior carrier collection. Easier access to the film surface and better control of the interface are facilitated as well. Hence, this morphology has been deemed to be very desirable for DSSCs^{5, 87}. The enhancement in the electronic transport also allows for enhancement of the light harvesting. Adachi et al⁸⁸ reported the formation of single crystal-like anatase TiO₂ nanowires formed in a network structure by surfactant assisted self-assembling processes at a low temperature. Use of this oriented nanowire photoelectrode resulted in

dye sensitized solar cells with a reported overall conversion efficiency of 9.3 % close to the record result of 10.4 % obtained using nanoparticulate titania by Gratzel and colleagues¹⁸. A DSSC efficiency of 6.2% was reported using a photoelectrode composed of single crystalline nanorods prepared from electrospun fibers⁸⁹. Thicker films can be used to increase the optical density and thus improve the absorption of low energy photons in the red and infrared without losing the additionally harvested charge carriers to recombination⁸³. In the course of studies on TiO₂ nanotubes fabricated by anodization, the length of synthesizable nanotubes has been increasing resulting in thicker nanotube array films^{31, 38, 50, 60, 90}. From an initial tube-length of 200 nm which is insufficient for complete light absorption, arrays with nanotubes as long as 94 µm have been achieved. However a film thickness (corresponding to nanotube length) of about 20-30 µm is adequate for most photoelectrochemical applications.

5.3.1 Open circuit voltage decay technique: theory and application

Open circuit voltage decay (OCVD) is a powerful technique to study the electron lifetime in dye sensitized metal oxide semiconductor films. Developed by A.Zaban, M.Greenshtein and J.Bisquert⁹¹, OCVD probes the kinetics of recombination by monitoring the transient of V_{oc} during the relaxation from the illuminated quasiequilibrium state to the dark equilibrium. The electron lifetime so obtained does not correspond to the free carrrier lifetime but consists of an average of characteristic times for survival of free and trapped electrons. This technique is experimentally much simpler than the frequency and steady-state methods to obtain the electron lifetime; the treatment of the measured data is simpler as well. The ensuing discussion of the OCVD technique follows the treatment provided by Zaban et al⁹¹. A key assumption underlying the following treatment is that recombination occurs primarily with electrolyte species.

When a liquid junction dye sensitized solar cell is illuminated at open circuit, the free electron density in the semiconductor nanostructure (n) is affected by two main processes, namely the generation and recombination of electrons. Generation occurs by electron injection from the photoexcited dye anchored to the surface of the semiconductor into the semiconductor conduction band and the generation rate is given by :

Eq. 28

$$G = \alpha_{abs} I_0$$
 28

Recombination of the photogenerated electrons occurs by reaction with electrolyte species and the recombination rate which is a function of the electron density is given by Eq. 29

$$R = U(n)$$
²⁹

The rate of change of the electron concentration is equal to the difference between the rates of generation and recombination and can be expressed as :

$$\frac{dn}{dt} = -U(n) + \alpha_{abs} I_0$$
 30

The open circuit potential V_{oc} of a solar cell corresponds to the increase of the quasi-Fermi level of the semiconductor (E_{Fn}) with respect to the dark value (E_{F0}) and is given by :

Eq. 31

$$V_{oc} = \frac{\left(E_{Fn} - E_{F0}\right)}{e} = \frac{kT}{e} \ln\left[\frac{n}{n_0}\right]$$
 31

The starting point for the OCVD measurement is the illuminated quasi-equilibrium state. The illumination is interrupted and V_{oc} is monitored as a function of time while the cell is kept at open circuit. Under these conditions, the excess electrons are removed by recombination only, and the rapidity of the decay of the photovoltage is directly related to the electron lifetime. During the decay, the electron concentration n evolves from the initial steady state value to the dark equilibrium value of n_0 . In the absence of the illumination induced generation, this transient is described by the equation :

$$\frac{dn}{dt} = -U(n) \tag{32}$$

Assuming the recombination process to be a linear system, the electron lifetime is defined as the rate constant for this system and is given by :

Eq. 33

$$\tau_n^{-1} = -\frac{1}{n} \frac{dn}{dt}$$
 33

While this definition is exact only for a linear system, Zaban et al⁹¹ show that it is generally justified for the decay in non-linear solar cells as well.

Eq. 34

$$\tau_n = \frac{n}{U(n)}$$
 34

It follows then that

Eq. 35

$$\tau_n = -\frac{kT}{e} \left[\frac{dV_{oc}}{dt} \right]^{-1}$$
35

If the recombination rate is non-linear, its dependence on the free electron concentration maybe expressed as

$$R = -k_r n^\beta$$

where k_r is the recombination rate constant and n is the free electron concentration⁹². The effective recombination order β given by

Eq. 37

$$\beta = 1 + \frac{d\tau_n}{dt}$$
37

where τ_n is the electron lifetime. β has been found to be nearly constant and is hence a convenient way to describe the lifetime dependence in dye sensitized solar cells^{91, 93}.

The V_{oc} transient was recorded during relaxation from an illuminated quasi-equilibrium state to the dark equilibrium for the back-side and front-side illuminated DSSCs; this data, and for comparison the response time data for TiO₂ nanoparticles⁹³ (front-side illuminated) are shown in Fig. **56** and Fig. **57** respectively. For all samples investigated, the dye used was the Ruthenium based dye N-719. The nanotubes described as short had a length (same as film thickness) of 360 nm. The nanotubes described as long had a length of 6 µm. The samples were illuminated using AM 1.5 simulated sunlight for five minutes prior to recording the photovoltage decay. In comparison to reported open circuit photovoltage decay measurements of nanoparticulate TiO₂ based DSSCs^{91, 93}, the nanotube-arrays exhibit superior recombination characteristics. The longer lifetimes seen in the nanotube-array films indicate relatively fewer recombination centers. Recombination parameter β of the nanotube-array samples is constant at about 1.2, versus 1.3-1.6 as reported for the nanoparticulate DSSCs.



Figure : Photovoltage decay measurement of a TiCl₄ treated transparent nanotube array dye sensitized solar cell at 100% sun

Fig. 57


Figure : Electron lifetimes determined by open circuit photovoltage decay measurements for TiO_2 nanotube array DSSCs, as well as response times for TiO_2 nanoparticle DSC replotted from Fabregat-Santiago et al⁹³. Only the transparent nanotubes were subjected to front-side illumination; all foil samples were backside illuminated.

The data of **Fig. 57** indicates that back-side illuminated nanotube arrays resting atop a Ti thick film have superior charge transfer properties than their FTO connected counterparts. We believe this difference in charge transfer properties is due to differences in the back contacts, TiO_2 to FTO versus TiO_2 to Ti, and in architecture differences with the longer tubes having larger pore diameters and wall thicknesses.

5.3.2 Electrical Impedance Spectroscopy (EIS)

Electrical impedance spectroscopy is another small-signal technique for studying transport and recombination in dye-sensitized TiO₂ nanocrystalline films⁹⁴. Impedance spectroscopy provides a broad view of different parameters such as resistance and capacitance of the materials and interfaces in the solar cell. EIS measures the current response to a modulated applied bias superimposed on a constant applied voltage. The impedance is defined as the ratio of the voltage modulation to the current response and is typically modeled by an equivalent electrical circuit⁹⁴. The modulation of voltage imposed by the external source in the EIS technique induces a variation of the Fermi level of the nanocrystalline TiO₂ electrode⁹³. This has two effects:

- (i) it changes the occupancy of electronic states of electrode and
- (ii) it promotes a recombination current across the interface.

In the EIS experiment, effect (i) corresponds to the chemical capacitance C_{m} , and (ii) corresponds to a charge-transfer (recombination) resistance R_{ct} . The product of these quantities defines a time constant, $\tau_n = R_{ct}C_{m}$, which corresponds to the observed electron lifetime. Interpretation of the impedance spectra using such an equivalent circuit can provide direct information about the recombination time of electrons with the redox electrolyte at any bias, the electrical and electrochemical potential distribution, and the energy distribution of surface or other trap states in illuminated cells^{94, 95}.

5.3.3 Intensity modulated spectroscopies

Unlike OCVD, which is a large perturbation measurement technique, IMPS and IMVS are small signal techniques. IMPS which stands for Intensity Modulated Photocurrent Spectroscopy is an electrochemical technique where the working electrode is illuminated by a sinusoidally modulated source⁹⁶. The modulated light intensity is superimposed on a base (bias) light intensity, which produces a steady-state photocarrier density. The IMPS function is the complex ratio of the current response ΔJ to the incident light intensity modulation $\Delta \Phi_0$. An AC photocurrent may be generated by the fluctuating level of illumination. The harmonic response of the photocurrent to the illumination may be phase shifted. This photocurrent may be analysed as a function of the modulation frequency of the light source. IMVS, which stands for Intensity Modulated Photovoltage Spectroscopy measures the modulation of the photovoltage in response to the modulation of the incident light intensity⁹⁷. It has been shown that IMPS and IMVS can provide information about charge transfer and recombination at the illuminated semiconductor-electrolyte junction^{96, 98}. At low modulation frequencies, the IMPS function can be expressed in terms of a single equation 95 :

Eq. 38

$$\frac{\Delta J}{e\Delta\Phi_0} = A \frac{1}{1 + i\omega\tau_c}$$
38

Where τ_c is the time constant for electron collection at short circuit (transport time) in the absence of recombination and when electron transfer across the TiO₂-substrate interface is much faster than electron transport.

When IMPS is used to probe the electron lifetimes, both nanoparticulate and nanotubular cells display response curves given by Eq. **38** which represents a semicircle in the complex plane. The transport time τ_c is given by

Eq. **39**

$$\tau_c = \frac{1}{2\pi f_c}$$
39

where f_c is the characteristic frequency minimum of the IMPS imaginary component and f_r is the characteristic frequency minimum of the IMPS imaginary component. Similarly, the recombination time τ_r is given by

Eq. 40

$$\tau_r = \frac{1}{2\pi f_r}$$
 40

Electron transport in porous TiO_2 layers can be described by an effective diffusion coefficient, which is measured by photocurrent transients excited in porous electrodes immersed in electrolyte^{19, 99-101}. The time constant for electron collection is related to the electron diffusion coefficient by the expression :

$$\tau_c \approx \frac{d^2}{2.35D_n}$$

Where *d* is the thickness of the film and D_n is the effective electron diffusion length.

5.4 Charge collection efficiency

If charge collection is much faster than charge recombination, then the chargecollection efficiency will be high because the electrons are collected before they have time to recombine¹⁰²⁻¹⁰⁴. As the time constants approach each other, the charge-collection efficiency declines. For reasonable charge collection efficiencies ($\eta > 50\%$), the transport time constant (τ_c) and recombination time constant (τ_r) can be used to estimate the charge collection efficiency according to the expression^{95, 103}:

Eq. 42

$$\eta = 1 - \left(\frac{\tau_r}{\tau_c}\right)^{-1}$$
⁴²

Zhu et al⁷² used intensity modulated spectroscopies to compare the dynamics of electron transport in nanoparticulate films and films consisting of oriented nanotube arrays. They found the recombination in the NT films to be 10 times slower than in the NP films and

the transport times for both film morphologies to be similar. Consequently, the charge collection efficiency for NT electrodes was 25% larger than for the NP films.

For nanoparticulate films, the transport time is a function of the film thickness and the following relation holds for weakly absorbed light :

Eq. **43**

$$\tau_c \propto L^{2\alpha}$$
 43

In contrast, in NT films, the transport time constant τ_c exhibited only a minimal dependence on film thickness. This manifests itself in a linear increase of the short circuit photocurrent density (J_{sc}) with the roughness factor of the NT films with the slope (*the rate of increase of J_{sc}with roughness factor*) larger than that for NP films. Using an electrode consisting of oriented ZnO nanowires, Greene et al¹⁰⁵ constructed dye sensitized solar cells that showed a linear increase in J_{sc} with increase in roughness factor. Once again, the slope was higher than for NP films and provided strong evidence for an equally high collection efficiency for nanowire cells with wires as long as 25 µm.

The higher charge collection efficiency of oriented NT films and the minimal dependence of the transport time with nanotube length (same as film thickness) has an important implication for solar cells. It means NT films can be made much thicker than NP films for a given recombination loss, and this would allow for a higher light harvesting efficiency especially at the long-wavelength end of the solar spectrum.

CHAPTER 6

Dye Sensitized Solar Cells Using Titania Nanotubes

6.1 Surface area of TiO₂ nanotube array photoelectrodes

Fig. 58



Figure : Idealized unit cell of TiO_2 nanotube array with inner diameter D, wall-thickness W, a = D+W

The roughness factor i.e. the physical surface area of the film per unit of projected area measures the internal surface area of the electrode and is of crucial significance in applications such as sensing and catalysis. Assuming an idealized nanotubular structure shown in Fig. **58** with inner diameter D, wall-thickness W and tube-length L, the purely geometric roughness factor is calculated as^{48,72}

$$1 + \left[\frac{4\pi L(D+W)}{\sqrt{3}\left(D+2W\right)^2}\right]$$
44

Eq. 44 assumes all surfaces of the nanotubes to be perfectly smooth. In reality, the surfaces are not smooth and the actual roughness factor is higher due to the ridging effect. Fig. 59 is a plot of the calculated geometric roughness factor for nanotubes with three different geometries. The plot shows that higher surface area is more easily obtained with nanotubes of smaller pore size. This is because even though each single nanotube of a smaller pore diameter has a smaller surface area than a nanotube of the same length with a large pore diameter, more of the smaller nanotubes may be packed in an equivalent area.



Fig. 59

Figure : Calculated geometric roughness factor as a function of nanotube length

134

6.2 Dye desorption measurements to determine surface area of TiO₂ nanotube arrays

The candidate dye for desorption measurements should preferably have absorption peaks in the 450-700 nm range to avoid overlapping signal with TiO_2 absorption below 420 nm. It should also possess an appropriate binding group(s) such as –COOH or –NC or –PO₃H to anchor the dye molecule on the surface of TiO_2 . We used ruthenium bipyridine based dye N-719 (Solaronix) (Fig. **60**) and N-749, also known as "Black Dye"(Fig. **61**).

Fig. **60.**









Figure : Molecular structure of Black Dye

Described below is a sequence of steps to obtain the surface area of any ansorbing electrode using dye desorption measurements based on the procedures described by Nishimura et al¹⁰⁶. All optical absorption measurements were performed using a Cary 100 spectrophotometer in transmittance mode using standard non-absorbing cuvettes.

- Calculate the projected planar area of the dye molecule anchored on the surface of TiO₂ (lets say *P1*)
- 2. Form a self-assembled monolayer of the dye on TiO_2 nanotubes by immersion in a non-aqueous dye solution (ethanol or acetonitrile) for atleast 24 hours. Measure the planar area of the TiO_2 nanotube sample exposed to dye solution (*P2*)

- 3. Measure the peak absorbance (*A1*) of a solution of the dye in KOH, (1M in 1:1 ethanol : water recommended), of known molar concentration *C1*.
- 4. Measure the peak absorbance (A2) of a solution of the dye in the same alkaline solvent as above, but of a different known molar concentration C2
- 5. From Beer-Lambert's law, absorbance A is given by

Eq. 45

$$A = \varepsilon bc \tag{45}$$

where ε is the extinction coefficient of the dye (calculated to be ~14200 M⁻¹cm⁻¹ at 535 nm), *b* is the optical path length and *c* is the concentration. Confirm A1/C1 = A2/C2 to verify the measurement.

- Desorb the dye monolayer on nanotubular sample by immersion for 5 minutes in KOH solution (described in step 5) of known volume V.
- 7. Place the entire volume V_d of KOH solution containing the desorbed dye in a single cuvette and measure the absorbance A_d .
- 8. Now calculate the molar concentration C_d of desorbed dye :

Eq. 46

$$C_d = \left(\frac{A_1}{C_1}\right) A_d \tag{46}$$

9. Roughness factor R of nanotube sample is given by :

Eq. 47

 $R = C_d V_d N_A \left(\frac{P_1}{P_2}\right)$ 47

Where N_A is the Avogadro number 6.02 x 10^{23} /mole





Figure : UV-Vis absorption spectra of caustic solutions of N-719 and Black dye.

Table 8

138

Electrolyte	Anodic	Inner	Length	Surface dye	Effective	Geometric
	Potential	diameter	(µm)	coverage	roughness	roughness
	(V)	(nm)		(nmol cm^{-2})	factor	factor
Aqueous 0.5	10	22	0.2	5.25	52	38
% HF						
Aqueous	10-23	-	0.4	1.75	17	-
0.5 % HF	(Nano-					
	cones)					
Aqueous	25	110	6.6	50	496	252
buffered 0.1M						
KF (pH~5)						
0.1M NH ₄ F in	15			30	296	136
1:1 DMF:H ₂ O	Porous	-	-			
0.15M NH ₄ F	10	12	3.6	55	546	325
+5% H ₂ O in						
Formamide						
0.15M NH ₄ F	15	29	5.4	79	784	390
+ 5% H ₂ O in						
Formamide						
0.15M NH ₄ F	20	70	14.4	181	1797	778
+ 5% H ₂ O in						
Formamide						
$0.22M \text{ NH}_4\text{F}$	35	180	30	277	2750	928
+ 5% H ₂ O in						
Formamide						
0.27M NH ₄ F	20	65	19.6	304	3019	1224
+ 5% H ₂ O in						
Formamide						
0.3% NH ₄ F in	30	45	9	57	566	544
$EG + 1\% H_2O$						
0.3% NH ₄ F in	40	70	12	66	655	609
$EG + 1\% H_2O$						
0.3% NH ₄ F in	65	135	30	116	1152	1018
$EG + 1\% H_2O$			<u> </u>			

Table : Surface area of nanotubes determined by dye desorption measurements

6.2.1 Light harvesting efficiency (LHE)

LHE is a measure of the utilization of photons at any wavelength and is given by¹⁰⁷

Eq. 48

$$LHE = 1 - 10^{-\Gamma\sigma(\lambda)}$$
 48

Where Γ is the number of moles of sensitizer per square centimeter of projected surface area (column 2 in above table) and σ is the absorption cross-section of the dye determined by the UV-Vis measurements shown earlier in this report. At 535 nm (the absorption maximum for N-719), $\sigma = 1.42 \times 10^7 \text{ cm}^2/\text{mol}$. For 6.6µm long nanotubes fabricated in aqueous solutions. $\Gamma = 50$ nano-moles/cm² = 50 x 10⁻⁹ mol/cm² as indicated in Table 8. Hence LHE at 535 nm = 0.8 implying 80 % to be the maximum obtainable Quantum yield (collected photoelectrons/incident photon) at 535 nm. At half the absorption maximum, which provides an estimate for the obtainable IPCE over the overall absorption spectrum of the dye, LHE = 56 %. Eq. 48 shows that higher surface area nanotube arrays extend the maximum obtainable quantum yields by increasing the light harvesting efficiency. Fig. 63 is a plot of the calculated LHE vs. wavelength for two distinct nanotube arrays, one being a 14.4 μ m long nanotube array with a pore size of 70 nm and a roughness factor of 778 formed in formamide electrolyte while the other is a 6.6 µm long nanotube array with a pore size of 110 nm and a roughness factor of 252 formed in aqueous electrolyte. Fig. 64 is a plot of the calculated LHE vs. N-719 dye loading for two different wavelengths (535 nm and 600 nm).

Fig. 63



Figure : Light harvesting efficiency of nanotube arrays as a function of wavelength

Fig. **64**



Figure : Light harvesting efficiency as a function of amount of dye adsorbed

6.3 Liquid Junction Dye Sensitized Solar Cells using TiO₂ Nanotubes

6.3.1 Cell Configurations

This section describes the application of highly-ordered TiO_2 nanotube arrays, oriented perpendicular to the substrate, as the working electrode in liquid junction dyesensitized solar cells (DSCs) under both front-side (Fig. **65**) and back-side (Fig. **66**) illumination. The non-transparent TiO_2 nanotube arrays are formed by the potentiostatic anodization of a Ti metal foil. The resulting nanotubes remain anchored to the Ti metal substrate, which is opaque. As a result, nanotubes grown on Ti foil can only be subjected to backside illumination. Backside illumination is not optimal in DSCs since the platinized counter electrode partially reflects light, while iodine in the electrolyte absorbs photons at lower wavelengths (400 nm-600 nm). Only transparent nanotubes on conducting glass substrates permit use of the frontside illumination geometry.



Fig. 65

Figure : Integration of transparent nanotube array architecture into front-side illuminated dye solar cell architecture

For the front-side illuminated DSSC a 360 nm long (46 nm pore diameter, 17 nm wall thickness) optically transparent nanotube-array is fabricated on an FTO coated glass substrate that serves as the negative electrode⁴⁹. The nanotube array is made by anodization of a Ti film rf sputtered onto the FTO-glass substrate; attempts to fabricate

longer nanotube-arrays for the front-side illuminated DSSCs have been limited by our inability to coat the FTO-coated glass substrates with a Ti film of a sufficient quality and thickness.



Fig. 66

Figure : Illustration of backside illuminated nanotube-array dye solar cell architecture

6.3.2 Experimental Details

Several annealed samples were placed in 0.2M TiCl₄ solution for 60 min at room temperature within airtight bottles, then rinsed in ethanol and annealed in air at 450°C for 30 minutes. The nanotube samples were immersed overnight in 0.3 mM ethanolic solution of N-719. The electrolyte contained 0.5M LiI, 0.05M I₂, 0.6 M N-methylbenzimidazole, 0.10 guanidinium thiocyanate, 0.5 M tert-butylpyridine in

methoxypropionitrile (MPN). A conductive glass slide sputter coated with 25 nm of Pt was used at the counter electrode in the fabricated cells. The average area of particulate electrodes was 1 cm². Both the electrodes were spaced by ParafilmsTM 120 μ m in thickness and pressed by clamps. Electrolyte was introduced into the clamped electrodes by capillary action.

Photocurrent (I) and photovoltage (V) of the cell were measured using simulated sunlight at AM-1.5 produced by a 150W Oriel Solar Simulator. The illumination intensities were measured using a Molectron thermopile detector. The intensities were further verified and standardized using an NREL calibrated silicon solar cell. The I-V characteristics of the film were measured using a Keithley 2400 Source Meter. The front-side illuminated DSSCs, although the transparent nanotube-array negative electrode is only 360 nm thick, show an AM 1.5 photocurrent of 7.87 mA/cm², open circuit voltage of 0.74 V, 0.49 fill factor, and 2.9% efficiency as shown in Fig. 67. Typically, the effect of the TiCl₄ treatment is an increase in the short circuit current and the fill factor and a slight decrease in the open circuit potential of the resulting solar cell. We note that this efficiency is 5 times the efficiency of non-TiCl₄ treated nanotubes; we hypothesize that the TiCl₄ treatment increases the number of active surface sites for dye adsorption and facilitates improved bonding between the TiO_2 and dye molecule, resulting in improved charge transfer. Another possible reason is that there exist "dead" regions of TiO₂ in the nanotube array film that are not electrically connected to the anode. The effect of the $TiCl_4$ may be to electrically reconnect some of the dead TiO_2 to the anode.

6.3.3 Performance of TiO₂ NT Array based Solar Cells

Fig. 67



Figure : Current-voltage characteristics of transparent nanotube array DSCs, under 100% AM-1.5 frontside illumination¹⁰⁸

Fig. 68 shows the photocurrent versus photovoltage plots under AM 1.5 backside illumination of a DSC constructed using the irregular nanoporous TiO_2 alluded to in Section 2.2.2.2 and shown in Fig. 24. The plot show the effect of electrode area on the solar cell fill factor. The open circuit potential (V_{oc}) and short circuit photocurrent density (J_{sc}) are relatively unchanged when the electrode area is larger whereas the fill factor significantly decreases when the electrode area is increased. Fig. 69 and Fig. 70 show the effect of nanotube length and geometry on the performance of dye sensitized solar cells. The nanocone geometry performs more poorly compared to nanotubes. The length of the nanotube arrays is directly proportional to the surface area available for dye

adsorption according to Eq. **44** and since the photocurrent is a function of the amount of adsorbed dye molecules, we find the photocurrent to increase with nanotube length. The surface areas of the respective nanotube arrays and their dimensions are provided in Table **8**.

Fig. 68



Figure : Effect of electrode area on the current-voltage characteristics of DSCs using non-transparent porous TiO₂ formed in fluorinated 1:1 DMF-H₂O, under 100% AM-1.5 backside illumination

The highest efficiency liquid junction dye sensitized solar cells using the back illumination geometry were obtained using 19 μ m long nanotube arrays wherein an open circuit voltage of 0.817 V, a short circuit current density of 12.72 mA/cm², and a fill

factor of 0.663 were achieved resulting in an overall conversion efficiency of 6.89 %. Consistently high V_{oc} values (0.8-0.84 V) are obtained by us employing nanotube arrays in N-719 based DSCs. Our short circuit photocurrents are limited by "dead" regions in the TiO₂ that are not electrically connected to the anode, the series resistance of the Ti/TiO₂ contact and absorption of incident light by the electrolyte due to the backside illumination geometry. In comparison to N-719 (Fig. **60**), Black dye (Fig. **61**) has a lower extinction coefficient but is photosensitive to a larger range of wavelengths (Fig. **62**), that in theory should result in a higher overall photoconversion efficiency for solar cells constructed using Black Dye. However, as shown in Fig. **71**, Black Dye sensitized solar cells consistently exhibited lower fill factors than those obtained for N-719 and as a result, lower efficiencies were obtained when Black Dye was used.





Figure : Effect of nanotube array length & geometry on DSC (N-719 dye) performance



Figure : Effect of nanotube length & geometry on DSC (using N-719 dye) efficiency

Fig. 71



Figure : Current-voltage characteristics of DSCs constructed using 19 μ m long nanotube arrays sensitized with Black Dye, under 100% AM-1.5 backside illumination



Figure : Current-voltage characteristics of DSCs constructed using 19 μm long nanotube arrays sensitized with N-719, under 100% AM-1.5 backside illumination

6.4 Solid State Dye Sensitized Solar Cells using TiO₂ Nanotube Arrays : Proof of Concept

Liquid junction dye sensitized solar cells, also known as Gratzel cells, suffer from several practical problems related to the presence of a liquid electrolyte¹⁰⁹. The problems include desorption of the dye, leakage and evaporation of the liquid electrolyte and the corrosive action of the iodide/iodine redox couple. Therefore, there is growing interest in solid state heterojunction solar cells, where both the electron and hole conducting materials are solids, but are grown as interpenetrating networks forming a heterojunction of large contact area. 4% is the highest efficiency solid state DSC reported thus far¹¹⁰

and was obtained by using the molecular organic hole conducting material Spiro-OMeTAD (see Fig. **73**). We used Copper thiocyanate (CuSCN) as the hole conducting layer in this first application of TiO₂ nanotubes in solid state DSCs. Inside the interpenetrating p-n heterojunction formed by nanotubular TiO₂ and CuSCN, only the dye layer absorbs visible light. After the dye absorbs a photon, the excited-state dye is quenched by electron injection into the TiO₂ conduction band¹¹¹. The photooxidized dye is then regenerated by the capture of an electron from the valence band of CuSCN, a process also referred to as hole injection. The two photoseparated charges then percolate separately through the two phases and, in the absence of recombination, reach the front and back contacts, respectively. Recombination consists of either (a) reduction of the oxidized dye by an electron from the TiO₂ before hole injection into the CuSCN regenerates the dye or (b) recombination of an electron from the TiO₂ with a hole in the CuSCN¹¹².

Fig. 73



Figure : Molecular structure of hole conducting organic compound Spiro-OMeTAD



Figure : Current-voltage characteristics of a solid state DSC using sol-gel deposited CuSCN as the hole conductor, under 100% AM-1.5 frontside illumination

To make the CuSCN solution, 0.12 g of CuSCN (Aldrich) was dissolved in 10 mL of dipropyl sulfide (also from Aldrich). A 200 nm long (46 nm pore diameter, 17 nm wall thickness) optically transparent nanotube-array fabricated on an FTO coated glass substrate served as the negative electrode. The dye used was N-719, a monolayer of which was formed on the TiO₂ electrode by immersion in a 0.3 mM solution of the dye in acetonitrile for 48 hours. The p-type material (CuSCN) was incorporated into the DSC using a procedure similar to that described by O'Regan et al.¹¹¹ The TiO₂/dye electrode was placed in an enclosed chemical hood on a hot plate at 80°C. Very thin films of CuSCN were formed by spreading 6 μ L drops onto the surface of the electrode and then allowing the surface to dry. This procedure was repeated 10 times to increase the film thickness. Subsequently, to fabricate the top contact to the DSC, a 40 nm thick gold film was evaporated onto the CuSCN film through a shadow mask containing clearly defined features of known area. The I-V characteristics of such a DSC are shown in Fig. **74**. The

principal factors limiting the performance of this solid state solar cell are the poor conductivity of CuSCN-thus causing a large series resistance at the hole contact, inadequate pore-filling of the nanotubes by the p-type organic semiconductor (CuSCN in our case) and low yield for the hole transfer reaction from the dye molecule to CuSCN leading to the loss of carriers by interfacial recombination. A CuSCN film of average thickness 1 µm formed by dipcoating on glass substrates has a sheet resistance of 120 $M\Omega/\Box^{113}$. Stoichiometric excess of SCN produces p-type conductivity and can be induced in CuSCN films by exposing them to gaseous halogens. In particular, CuSCN films exposed to Cl₂ attain a much lower sheet resistance of $0.5M\Omega/\Box$ in a short time¹¹³. The problem of non-optimal pore filling may be addressed in two ways. One way involves insitu polymerization inside the nanotubes. Monomer molecules such as thiophene and aniline are small and easily soluble in several organic solvents. Hence, delivering the monomer molecules to the insides of the nanotubes is relatively simple. If these monomer molecules inside the nanotubes were to be polymerized, they would then provide superior pore filling characteristics. The other route involves annealing the hole transporter film after coating onto the nanotube/dye electrode at an elevated temperature of about 150°C. The idea here to induce plastic deformation of the hole transporter that would enable the material to penetrate further into the pores and produce better pore filling. The danger however is the high temperature degradation of the electronic properties of the dye and the hole transport material. The hole transfer yield depends on the dye and the material used. Spiro-OMeTAD has a superior hole transfer yield from Ruthenium bipyridyl dyes (such as N-719) in comparison with other hole transport materials and accounts for its use in high efficiency solid state solar cells¹⁰⁹.

CHAPTER 7

Photo-assisted Electrolysis of Water Using TiO₂ Nanotubes Under Bandgap Illumination

7.1 Band-structure at the Semiconductor/Electrolyte Interface



Fig. **75**

Figure : Energy band diagram for photoelectrolysis of water with n-type TiO₂ and Pt

In Fig. 75, E_c and E_v refer to the conduction and valence bands of TiO₂ respectively, e is the electron charge, $E_{c,s}$ and $E_{v,s}$ are the respective band-edges at the

surface, E_g is the band-gap, $F_{H2/H2O}$ and $F_{H2O/O2}$ are the redox levels for the half-cell reactions constituting the electrolysis of water, $\boldsymbol{\Phi}_{sc}$ is the potential drop across the space-charge region in the semiconductor and η_c is the overpotential of the reaction on the metal(Pt) cathode.

The following conditions must hold for the photoelectrolysis of water¹¹⁴ :

- 1. The incident photon energy should exceed the band-gap of the semiconductor i.e. $hv > E_g$.
- 2. The band-gap of the semiconductor E_g should exceed ΔG , the change of the Gibbs' free energy of reaction in the cell given by

Eq. 49

$$\Delta G = F_{H_2/H_2O} - F_{H_2O/O_2} = 1.23eV$$
49

- 3. The flat band potential of n-type semiconductors (photoanodes) should be more negative than the reversible potential of the hydrogen electrode reaction. Otherwise, the energy of majority carriers will be insufficient for the partial reaction to proceed on the metal electrode of the cell.
- 4. The valence band edge on the n-type photoanode surface should be below the electrochemical potential level of the water oxidation reaction.

Eq. 50

$$E_{V,s} < F_{H_2O/O_2}$$
 50

5. The semiconductor photoanode should not photocorrode in the electrolyte.

The efficiency of photoassisted electrolysis is estimated by allowing for the consumption of energy from the external source of voltage and is given by the expression¹¹⁴

Eq. 51

$$\eta = \frac{j_{ph} \left(\frac{\Delta G}{e} - \varphi_{ext}\right)}{P_i} \times 100$$

Where P_i is the power density of light incident on the photoelectrode, ΔG is the free energy change of the water photolysis reaction in Eq. 49, j_{ph} is the incident photocurrent density and φ_{ext} is the actual difference of potentials between the illuminated photoelectrode and counter-electrode when the photocurrent flows through the cell. Upon substituting for ΔG and φ_{ext} in Eq. 51, we obtain¹¹⁵

Eq. 52

$$\eta = \frac{j_{ph} \left(1.23 - \left| E_{meas} - E_{oc} \right| \right)}{P_i} \times 100$$
 52

Where E_{meas} is the electrode potential (vs Ag/AgCl) of the working electrode at which the photocurrent was measured under illumination, and E_{oc} is the electrode potential (vs Ag/AgCl) of the same working electrode at open circuit condition under same illumination and in the same electrolyte.

7.2 Experimental Details

The electrochemical measurements were performed in a standard three-electrode configuration with a Pt mesh counter electrode and a saturated Ag/AgCl reference The photocurrent at the TiO₂ electrode, i.e. the working electrode, was electrode. measured using a scanning potentiostat (CH Instruments, Model CHI 600B). The potential was swept linearly at a scan rate of 20 mV/sec. The illuminated area of the working electrode was 1 cm^2 . An electrical contact was taken from the backside of Ti foil after removing the oxide layer by mechanically scribing. An electrically insulated copper wire was attached on the backside using conductive silver-epoxy adhesive. The backside of the sample was fixed to the glass substrate using a nonconductive epoxy, which also covered the edges of the foil. 1 M KOH purged with N₂ was used as the electrolyte. A 50 W metal halide lamp (EXFO Lite) was used as the UV light source. The light was passed through broadband optical filters, which allowed only wavelengths between 320 nm and 400 nm to be incident on the TiO₂ photoanode at a measured intensity of 100 mW/cm^2 to provide band-gap illumination of TiO₂. Photocleavage of water was studied at a potential of -0.4 V vs. Ag/AgCl. The gaseous photoproducts were identified and measured by a SRI 8610C gas chromatograph (GC) equipped with a thermal conductivity The quantum efficiencies at selected wavelengths are determined using detector. interference filters from Edmund Industrial Optics.

Fig. 76



Figure : TiO₂ nanotube photoanode under band-gap illumination

7.3 Effect of Architecture on Photoelectrochemical Properties

7.3.1 Effect of Nanotube Array Pore Diameter

Plots of photocurrent density versus applied potential of both 22 nm (10 Vanodized) and 76 nm (20 V-anodized) pore diameter TiO2 nanotubes, on a Ti substrate, annealed at either 350 or 500 °C are shown in Fig. 77. Monochromatic Ultraviolet (UV) light of 365 nm wavelength and an incident intensity of 146 mW/cm² were used to illuminate the samples. The shape of the curves is typical for a photoelectrochemical cell with an n-type semiconductor photoanode. The photo-responses of the annealed samples are compared with that of an as-anodized amorphous 22 nm titania nanotube sample. The dark current densities of all samples are negligible. With UV exposure, the photocurrent onset potential is found in the range -1.0 to -0.8 V versus an Ag/AgCl reference electrode in a 1.0 M KOH solution. For both the 22 nm and 76 nm samples, there is a negative shift in the open circuit potential with the increase in annealing temperature from 350 to 500 °C. The plots reveal there is little difference between samples in their photoanodic currents at higher applied voltages. However, at lower applied potentials, the 22 nm, 350°C sample shows a relatively steeper rise in anodic current. Compared to the annealed nanotubes, amorphous nanotubes show an extremely weak photoresponse, e.g., a photocurrent density of approximately of 0.08 mA/cm² at 1.0 V. The photocurrent is determined by subtracting the dark current from the measured illuminated value.





Figure : Photocurrent density as a function of measured potential (vs. Ag/AgCl) for 22 nm diameter nanotubes (annealed at 350 and 500°C), 76 nm diameter nanotubes (annealed at 350 and 500°C) and as-anodized amorphous samples

As light passes through a semiconductor, its intensity decreases due to absorption as¹¹⁴:

Eq. 53

$$J = J_0 \exp(-\alpha x)$$
 53

Where *x* is the thickness of the film from the surface downward, J_0 is the intensity of light incident on the semiconductor surface (*x*=0), α is the linear absorption coefficient. α^{-1} is a measure of the depth of penetration into the semiconductor since it is the distance over which the incident light attenuates e times.

The higher length of the larger nanotubes allows the resulting nanotubular film to be thicker, thus allowing for the absorption of a larger amount of the incident light per Eq. **53**. Inspite of this fact, nanotubes with a smaller pore diameter exhibit a higher photocurrent as shown in Fig. **77**. The higher activity towards the oxygen evolution reaction (OER) of 22nm titania nanotubes can be explained by an increase in the electrode surface area. Each individual 22 nm nanotube has half the height of a 76 nm diameter nanotube and a diameter about 3.45 times smaller, having thus a surface area 6.9 times smaller than a 76 nm diameter nanotube. However, the same electrode surface area can accommodate 12 times more 22 nm nanotubes. Finally, taking into account the void area between the nanotubes, the net increase in surface area moving from a 76 nm to 22 nm diameter nanotubes is approximately a factor of two. This increase in surface area overwhelms the smaller absorption and results in 22 nm nanotubes yielding maximum photocurrents 15% higher than the 76 nm nanotubes.

7.4 Effect of Nanotube Wall-Thickness on Photochemical Properties

Fig. 78



Figure : A variation of photocurrent density as a function of measured potential [vs. Ag/AgCl] is plotted for 10V samples anodized at four temperatures [i.e. 5°C, 25°C, 35°C and 50°C]

Fig. 78 shows the *I-V* characteristics of the titania nanotube-array electrodes, photocurrent density versus potential, measured in 1 M KOH electrolyte. The photocurrent density increases with decreasing anodization bath temperature. As mentioned in section 2.1.3, a higher anodization temperature results in a lowernanotube wall-thickness. At 1.5 V the photocurrent density of the 5°C anodized sample is more than three times the value for the sample anodized at 50°C. The lower anodization temperature also increases the slope of the photocurrent-potential characteristic. For crystalline semiconductors, under certain limitations such as not too high absorption coefficients and not too high band-bending, the squared photocurrent is a linear function of the applied bias¹¹⁶.



Fig. 79

Figure : Photocurrent squared-potential curves for 10 V samples anodized at four temperatures [i.e. 5°C, 25°C, 35°C and 50°C]

In Fig. **79**, squared photocurrent is plotted against electrode potential and the plots obtained closely approximate a straight line at low values of applied bias. This is indicative of photogenerated charges being separated by the electric field of the depletion layer^{117, 118}. At high anodic polarizations, the squared photocurrent-potential plot deviates from linearity for all the samples since the band-bending is too high. As can be seen in **Fig. 79**, the sample anodized at 5°C adheres to linearity for the largest bias range.
With increasing anodization temperature, the range of potentials over which linearity prevails is smaller.

It is known that during the growth of an anodic oxide, the electric field extends to the full film thickness¹¹⁹. Since the nanotubular structure is grown by anodization, it allows significant electric fields to be sustained. However, when immersed in solution the electrostatic potential along the length of the nanotubes is constant. This is because, the highly ordered nanotubular structure enables the conductive electrolyte (1M KOH in most of our experiments) to permeate the entire internal and external surfaces. For the titania nanotubes, long-range electronic transport is dominated by diffusion rather than drift. In addition, the architecture of titania nanotube arrays results in a large effective surface area in close proximity with the electrolyte thus also enabling diffusive transport of photogenerated holes to oxidizable species in the electrolyte. The photoelectrochemical properties of titania nanotubes are studied at bias voltages much lower than those used during the anodization process. Under these conditions, the depletion approximation is valid for the titania barrier layer¹²⁰ and in the presence of a depletion region, the separation of photogenerated charges occurs under the action of the electric field. Minority carriers generated within a distance from the surface equal to the sum of the width of the depletion layer and the diffusion length, escape recombination and reach the electrolyte contact¹²¹. The relevant size of the structures in titania-nanotubes is smaller than 35 nm, which is comparable to the retrieval length in this material 122 ~100nm for TiO₂. The majority of photogenerated holes are within the retrieval length and as a result, bulk recombination is greatly reduced and the quantum yield is enhanced¹²³. J. van de

Lagemaat et al. observed a spectacular enhancement of the quantum yield in SiC made nanoporous by anodic etching in HF solution¹²¹. Furthermore, due to light scattering within the porous structure, the photons are more effectively absorbed than in a flat $electrode^{6, 124}$.

While bulk recombination is reduced for the nanotubular structure, significant surface recombination can still exist. In the nanotubular structure, minority carriers are always photogenerated close to the semiconductor surface, where they can be trapped in surface states. According to the model proposed by Lubberhuizen at al. to explain recombination of photogenerated charge carriers in nanoporous GaP, photogenerated charge carriers are instantaneously and effectively separated by the capture of holes in surface bonds¹²³. In this model, subsequent recombination between the separated electrons and holes depends sensitively on the band-bending potential that the electrons have to overcome to reach the surface where recombination takes place. Greater the band-bending potential, greater the barrier to be overcome and smaller the recombination. The titania crystallite size in the direction parallel to the length of the nanotubes is larger than 35 nm and is limited by the wall-thickness in the lateral direction⁵⁵. Transmission Electron Microscopy of TiO₂ nanotubes reveal each nanotube to be constituted by 3-4 crystallites⁵⁵. The potential drop within the wall across a single crystallite is Eq. 54

$$\Delta \Phi_0 = \frac{kTr_0^2}{6eL_D^2}$$
 54

Where r_0 is half the thickness of the wall, *e* is the electronic charge, *k* is Boltzmann's constant, *T* is the temperature and L_D is the Debye length given by Eq. 55

$$L_D = \sqrt{\frac{\varepsilon_0 \varepsilon kT}{2e^2 N_D}}$$
55

where ε_0 is the permittivity of free space, ε is the relative permittivity of the TiO₂ crystallite and N_D is the number of ionized donors per cm³.

The wall-thickness and hence, the lateral crystallite size are smaller with increasing anodization temperature. It is well-known from the study of particulate nanocrystalline photoelectrodes that a depletion layer cannot be formed in nanoparticles with sizes of a few nanometers¹⁵. In general, in the nanometer regime, as the size of the particle or grain decreases, so does its ability to sustain a significant amount of band-bending. As a consequence, the titania nanotube-array that has a wall-thickness of 34 nm can experience more band-bending than a similar array with 9 nm wall-thickness. The additional band-bending decreases the surface recombination and increases the photocurrent. The nanotubes fabricated at 5°C are also longer than those at 50°C. However, the changes in absorption due to variation in length (120 to 224 nm) are not significant enough to produce the observed difference in the photoresponse of the nanotube array electrodes. The photocurrent density for the nanotube array fabricated at 5°C (average wall-thickness =34 nm) is more than three times that obtained for an array fabricated at 50°C (average wall-thickness=9nm).

The presence of band-bending inside the nanotube walls is of immense significance. In dye sensitized solar cells, because electron diffusion is the rate limiting step in the recombination process, the positive impact of faster electron motion is negated by the higher recombination¹⁰⁴. Therefore, attempts to replace TiO_2 with an oxide in which electrons move faster have failed¹⁰⁴. Faster transport can be expected to improve collection efficiency only when it does not trigger proportionally faster recombination. As discussed in **Chapter 5**, a potentially very interesting feature of TiO_2 nanotube arrays is the decrease in recombination for comparable electron transport.

Law, M. et al^{104} constructed ZnO-TiO₂ core shell nanowires where a radial surface field exists within each nanowires, similar to the band-bending in the nanotube walls suggested by our results with nanotubes of different wall-thickness. The radial electric field in the core-shell nanowires assisted carrier collection by repelling photoinjected electrons from the surrounding electrolyte. Similarly in our nanotubular structure, we suggest that the upward band-bending at the surface of each nanotube reduces the surface recombination velocity regardless of the speed at which the electrons move.

7.5 Effect of Nanotube Length on Photochemical Properties

Fig. **80** shows the *I-V* characteristics of the titania nanotube-array electrodes of different tube-lengths annealed at 500°C, photocurrent density versus potential, measured

in 1 M KOH electrolyte. Both the photocurrent magnitude (Figure 20 a) and photoconversion efficiency (Figure 20 b) are seen to increase with length.





Figure : Effect of nanotube-length on photoresponse **[A]** Photocurrent Density and **[B]** Photoconversion efficiency as a function of potential (1M KOH electrolyte and 98mW/cm² ultra-violet illumination)⁹⁰

However, the best results to date have been obtained using high aspect ratio nanotube arrays of $\sim 30 \ \mu\text{m}$ length formed in formamide based electrolytes. Fig. **81[A]** shows the measured photocurrent density of nanotube array samples fabricated using a formamide electrolyte, our so-called K1 bath of 0.56 grams of Ammonium Fluoride in a solution mixture of 5 ml de-ionized water + 95 ml formamide, at 15 V, 20 V, and 25 V anodization potentials. Prior to photocurrent measurement all samples were annealed at 525°C for 1 hour in oxygen.

Fig. 81



Figure : **[A]** Photocurrent density and **[B]** corresponding photoconversion efficiency, of annealed nanotube array samples fabricated using a formamide electrolyte, our so-called K1 bath of 0.56 grams of Ammonium Fluoride in a solution mixture of 5 ml de-ionized water + 95 ml formamide, at indicated anodization voltages.

Fig. **81**[B] shows the corresponding photoconversion efficiency of the three nanotube array samples. The use of different anodization voltages resulted in variation of nanotube array length and tube outer diameter (hence packing fraction): 15 V resulting in a nanotube array 8.2 μ m long, 80 nm outer diameter; 20 V resulting in a nanotube array 14.4 μ m long, 94 nm outer diameter; 25 V resulting in a nanotube array 16 μ m long, 140 nm outer diameter. The 20 V sample, 14.4 μ m long 94 nm outer diameter, achieves a photoconversion efficiency of 14.42%. Too short a nanotube array and the light is not fully absorbed; too long a nanotube array and the photoconversion efficiency suffers from recombination of the photogenerated electron-hole pairs.

Fig. 82



Figure : **[A]** Photocurrent density and **[B]** corresponding photoconversion efficiency of nanotube array samples fabricated in an electrolyte of 1.2 g of NH₄F in a solution of 5 ml de-ionized water + 95 ml formamide at 35 V. The samples were annealed at indicated temperatures for 1 hour in oxygen prior to measurement. The resulting nanotube array samples were 30 μ m in length, with an outer diameter of 205 nm

Fig. **82[A]** shows the measured photocurrent density of nanotube array samples fabricated in an electrolyte of 1.2 g of NH₄F in a solution of 5 ml de-ionized water + 95 ml formamide at 35 V. The resulting nanotube array samples were 30 μ m in length, with an outer diameter of 205 nm. The samples were annealed at 525°C and 580°C for 1 hour in oxygen prior to measurement. The 580°C annealed sample had an open circuit voltage V_{OC} of -0.925 V (vs. Ag/AgCl); the 525°C annealed sample had an open circuit voltage V_{OC} of -0.80 V (vs. Ag/AgCl). Fig. **82[B]** shows the corresponding photoconversion efficiency of the two samples.

7.6 Hydrogen Generation Rates of Titania Nanotubes



Fig. **83**

Figure : Hydrogen photoproduction in a photoelectrochemical cell consisting of a 200 nm long 22 nm diameter nanotube array annealed at 500°C with a wall-thickness of 34 nm

Hydrogen generation experiments were done at constant voltage bias, determined by the peak position in the photoconversion efficiency curve with respect to the applied potential. The area of the illuminated sample was fixed at 1cm². Illumination consisted of Ultraviolet radiation from 320-400 nm from an EXFO metal halide lamp at an incident intensity of 100 mW/cm². Fig. **83** shows hydrogen generated as a function of time (mL) using a 200 nm long nanotube array with a pore diameter of 22 nm and a wall-thickness of 34 nm. Fig. **84** shows the effect of nanotube-array length on hydrogen evolution rate. Gas chromatographic analysis was used to verify that the volume ratio of the evolved hydrogen and oxygen was 2:1, which confirmed water-splitting. In both Fig. **83** and Fig. **84**, the graphs have not been drawn to include the origin of the respective plots. In Fig. **83** for instance, the hydrogen generated in the first 400 seconds is very small, lower than the detection limit of the gas chromatograph. Similarly, in Fig. **84**, the hydrogen generated by nanotube arrays of length $< 1.8 \mu m$ is too small for detection and quantification purposes.





Figure : The rate of hydrogen generation from crystallized nanotube arrays of different lengths annealed at 500°C

7.7 Quantum Yield of TiO₂ Nanotube Array Photoanodes



Fig. 85

Figure : The 337 nm and 365 nm photocurrent wavelength photocurrent generated from a 6 μ m nanotube array annealed at 600° C

Fig. **85** shows the behavior of 6 μ m nanotube-array samples when exposed to individual wavelengths of 337 nm (3.1 mW/cm²) and 365 nm (89 mW/cm²). The incident photon-to-current efficiency (quantum yield) was calculated using the relation

Eq. 56

$$\eta(\lambda) = \frac{hc}{e} \frac{j_{\rm p}(\lambda)}{I_0 \lambda}$$
 56

where j_p is the photocurrent density, I_0 is the power density of light and $h,c,e,and \lambda$ are respectively Planck's constant, speed of light in vacuum, elementary charge and wavelength of the incident light. The quantum efficiency was calculated to be 81% and 80% respectively for the 337 nm and 365 nm. The high quantum efficiency demonstrates that titania nanotubes offer a near-optimal architecture for photoelectrochemistry that utilizes >80% of the incident photons with wavelengths within the photosensitive region of the material.

CHAPTER 8

ANIONIC DOPING OF TITANIA NANOTUBES

8.1 Introduction

 TiO_2 exists in three crystalline polymorphs, namely rutile (Eg=3.05 eV), anatase $(E_g=3.23 \text{ eV})$ and brookite $(E_g=3.26 \text{ eV})$. The bandgap of titanium dioxide lies in between 3.0-3.5 eV depending on the phase composition, nano-architecture, and method of material preparation¹²⁵⁻¹²⁷. Since the discovery of photoelectrochemical water-splitting on TiO₂ electrodes in 1972¹⁰, TiO₂ remains the most investigated semiconductor photocatalyst. TiO₂ is a large bandgap (3.0-3.2 eV) semiconductor that primarily absorbs the ultraviolet portion of the solar spectrum. The large electronic bandgap of titania renders it sensitive only to wavelengths in the ultraviolet region, which constitute less than 5% of the solar spectrum energy. The achievement of practical photoconversion efficiencies for the solar radiation induced electrolysis of water using titania, in the range of 10%, can only be achieved if a method is found to extend the photoresponse of titania into the visible portion of the solar spectrum. Modifying the band structure of titania to make it more responsive to visible wavelengths has been an enduring effort, with mixed results. External sensitizers such as organic dyes and polymers have been successfully employed to increase photoconversion efficiencies in photovoltaic cells^{17, 128, 129}. Such an approach, based on separating the processes of charge generation and charge transport, has been used in Gratzel cells¹⁰⁷ to obtain efficiencies exceeding 10%. However, the

sensitizers may detach from the TiO₂ surface in aqueous media and these organic sensitizers degrade in corrosive and highly oxidizing environments. For applications such as photoelectrochemical water-splitting, and photocatalytic degradation of organic compounds, where the photoelectrode is subject to prolonged exposure to an aqueous medium, the external sensitizer approach is not feasible. Thus in applications where the incident solar flux is utilized not to produce electricity but to perform work in-situ, such as the photo-splitting of water, modification of the material properties to achieve the desired visible-spectrum sensitization is necessary. This approach involves manipulating the chemical composition of titania towards modifying its electronic structure. Cationic doping of TiO₂ with transition metals such as V and Cr has been extensively studied¹³⁰⁻ ¹³². While there is an improvement in the optical absorption for visible wavelengths, there is also an increase in thermal instability¹³³ and a decrease in carrier lifetimes¹³¹. The presence of transition metal ions have been found to inhibit the photocatalytic activity of TiO₂; commonly as the visible-spectrum response improved with doping, the lifetimes of the photogenerated electron-hole pairs decreased, thus keeping the overall efficiencies at similar levels^{130, 134}.

Anionic doping of TiO₂ has been receiving attention only recently. Asahi et al¹³⁵ performed densities of states (DOSs) calculations on the effect of substitutional doping of C, N, F, P, or S for O in the anatase crystal. They identified Nitrogen as the most effective dopant due to its comparable ionic radius¹³⁶. However, Lee at al¹⁴ contradict this assessment in their report, where their density functional calculations indicate that while nitrogen doping produces isolated N 2p states above the valence band maximum of

TiO₂, the mixing of N with O 2p states is too weak to result in appreciable bandnarrowing. Theoretical calculations have suggested that smaller bandgaps might also be achieved by incorporating anionic dopants such as Sulfur^{137, 138} and Nitrogen^{31, 136} into anatase as well as rutile by substitution in oxygen lattice sites. The narrowing of the bandgap results from an increase in the width of the valence band due to mixing of the delocalized p-states of the anionic dopants with the O-2p and Ti-3d orbitals constituting the valence band. There also competing reports which argue that anionic doping does not produce bandgap narrowing¹³⁹. Di Valentin et al¹⁴⁰ used experimental data from X-ray Photoelectron Spectroscopy (XPS) and calculations using Density Functional Theory (DFT) to suggest that nitrogen impurities form localized states above the valence band and promote the formation of oxygen vacancies. Recent experimental studies focusing on Nitrogen¹⁴¹⁻¹⁴³ and Sulfur^{144, 145} doping of titania report a shift of the titania optical absorption edge to lower energies and a concomitant enhancement of the visiblespectrum photoresponse. Several other encouraging experimental efforts have attempted to use other anionic dopants, such as Fluorine¹⁴⁶ and Carbon^{147, 148}. However, Serpone¹⁴⁹ attributes the redshift of the absorption edge not to bandgap narrowing but to the advent of color centers that absorb the visible light irradiation.

There has recently been a surge of interest in this area documenting different experimental approaches towards nitrogen doping of titania¹⁵⁰⁻¹⁵². When vacuum techniques such ion beam assisted deposition¹⁵¹, pulsed laser deposition¹⁵² and reactive sputtering¹²⁷ in a nitrogen ambient are used to dope TiO₂, nitrogen atoms occur as β -N and are bonded to Ti atoms in substitutional lattice sites to form TiO_{2-x}N_x. On the other

hand, when wet chemical methods are used, a substantial portion of the doped nitrogen is not directly bound to Ti¹⁵³. In N,F-codoped TiO₂ powders synthesized by spray pyrolysis, the doped N atoms formed a localized energy state above the valence band of TiO2, whereas doped F atoms themselves had no influence on the band structure^{151, 154}. Band structure calculations made for F doped TiO₂ indicate that the F 2p levels do not mix with the existing bands and hence are not expected to contribute to optical absorption spectra¹⁴⁶. However, it is also noted in the same report that F-doping modifies the DOS near the conduction band minimum so that the resulting effect is similar to the creation of oxygen vacancies.

8.2 Conceptual Routes for Doping TiO₂ Nanotubes

The processing steps involved in the fabrication of titania nanotubes allow for the introduction of dopants in several different ways as listed below

8.2.1 Pre-Anodization

The starting material for the formation of TiO_2 nanotubes is Ti metal foil. However, this is not the only conducting substrate that lends itself to nanotube formation. Ti metal sputtered onto Indium Tin Oxide (ITO) conducting glass substrates can also be used to form titania nanotubes under the appropriate conditions. Transition metal dopants can be introduced by co-sputtering them with Ti onto ITO substrates. Transition metal dopants can also be sputtered onto Ti metal foils and subsequently heated to allow homogenization. Anionic dopants such as nitrogen can be introduced by reactively sputtering the titanium metal in an ambient containing nitrogen. For carbon, the reactive sputtering may require a CO /CO₂ ambient. Another alternative would be to start with a foil of Titanium Carbide (TiC) or Titanium Nitride (TiN). It is not being claimed that these titania nanotubes can be anodically formed on all these exotic substrates. It is merely being pointed out that there exist several avenues for exploration with regards to the substrate used for the anodization process.

8.2.2 Modifying the Anodization Bath Chemistry

During anodization, Ti metal is positively biased with respect to the platinum counter electrode. Under the influence of this positive bias, negative ions will get oxidized at the anode and some of these ions can get incorporated into the growing oxide film. In less conducting electrolytes, the ionic species are not completely dissociated and positive ions follow the negative ions to the anode and can get incorporated into the film. The advantage of this method is the versatility it provides in the design of the ion-bearing species. For instance if carbon doping were to be considered, there is a bewildering variety of carbocations and carbanions that can be used in attempts to dope the film with carbon.

8.2.3 Pre-Annealing Treatments

After anodization, the TiO₂ film formed is amorphous and annealing is necessary to introduce crystallinity. Before annealing, ion-implantation maybe used to introduce dopants into the surface and subsurface region and the subsequent annealing can be used to relieve implantation damage and homogenize the distribution of the dopants in the film. Yet another idea would be to coat the nanotube film with several layers of a material containing the desired dopant with the added condition that the material pyrolyze at the elevated temperatures encountered during the annealing process, thus freeing the dopant atoms to diffuse into the still-crystallizing film. Also, the same reactive sputtering techniques discussed in Pre-Anodization Treatments could be used again at this stage of the fabrication process to form thin films of dopants or dopant bearing compounds. For instance, TiS₂ could be reactively sputtered onto amorphous TiO₂ and the subsequent annealing process could be optimized to yield TiO_{1-x}S_x.

8.2.4 Annealing Treatments

The basic annealing step involves heating the amorphous as-anodized sample loaded in alumina or quartz boats in a tube-furnace with an oxygen ambient at a ramp rate less than 5°C/min upto to an elevated temperature (400-650°C) where the sample dwells for several hours before cooling down to room–temperature again at a rate not exceeding 5°C/min. Several variations on this theme are possible. The ambient can be changed to vacuum or a gas carrying atoms of the desired dopant species. The process maybe

conducted in a high-pressure autoclave instead of a tube-furnace. An even more exotic variation involves soaking the amorphous samples with a combustible mixture containing dopant atoms and then heating the samples in an autoclave. The combustion products then provide the annealing ambient in the autoclave. Yet another idea is to use Rapid Thermal Annealing (RTA) to activate dopant atoms that are already incorporated while avoiding diffusion and phase-modification. A further extension of the annealing concept involves striking a plasma in a low-pressure ambient containing dopant species.

8.3 Carbon Incorporation through Flame Annealing

8.3.1 Why Flame Anneal?

A recent report¹¹⁵ indicated that annealing titanium metal foils and titanium oxide films in a hydrocarbon flame forms carbon doped titania with a significantly enhanced photoresponse resulting in remarkable photoconversion efficiencies of up to 8%. However, there is some controversy over the nature of this enhancement. On annealing Ti metal foils in a natural gas flame at 850°C, Khan and co-workers found the diffuse reflectance spectra of these samples to be significantly changed¹¹⁵. In addition to a shift in the primary absorption threshold from 414 nm to 440 nm, a second optical absorption threshold appeared at 535 nm, which was used to extract a bandgap of 2.32 eV. However, on flame annealing their samples using a propane/butane-oxygen mixture, Augustynski et al¹⁵⁵ described a shift of the primary band-edge of the spectral photoresponse into the visible region up to 425 nm but their samples did not exhibit a secondary band edge and the photoconversion efficiency was much smaller. Both groups found carbon in their samples upon chemical analysis as well as an enhancement in the photocurrents.

8.3.2 Flame Annealing of Titania Nanotube Arrays

The titania nanotubes investigated in this report were of two different geometries. The first geometry consisted of nanotubes with an average pore size of 22 nm, an average wall thickness close to 20 nm and a length of ~200 nm. This geometry is representative of nanotubes with a smaller aspect ratio (~10), henceforth referred to as short nanotubes. The long nanotubes had a pore size of 100 nm, a wall thickness close to 20 nm and a length of 4.4 microns giving rise to an aspect ratio of ~44. Flame annealing of samples was performed in air after the crystallinity-inducing annealing step by exposing them to the reductive region of a propane burner for 3 min. The temperature of the titania surface while exposed to propane flame, determined using both optical and IR pyrometers, was found to be $1020^{\circ}C \pm 25^{\circ}C$. The duration of the anneal was kept short to preserve the nanotubular structure, which is destroyed upon prolonged exposure to temperatures in excess of 650°C. For comparison, a piece of titanium metal foil, identical to that used to form the nanotubes, was subjected to the propane flame anneal without any prior processing.

Table 9

	Binding	C1s	285.3	286.5	289
	Energy (eV)				
Sample	Depth	Total C	C-C	C-O	COO
	(nm)	(atom %)			
Short	0	0.7	-	-	-
NT	100	0.3	-	-	-
Flame	0	3.3	2.5	0.4	0.5
annealed	100	2.8	1.9	0.6	0.3
short					
NT					
Flame	0	5.6	3.9	0.8	0.9
annealed	100	5.2	3.8	0.9	0.6
long NT					
Long	0	3.5	2.3	0.5	0.7
NT	100	3.0	1.9	0.6	0.5

Table : Carbon content and chemical state information (from XPS)

Carbon was found in all samples and a summary of the carbon content and carbon state information is provided in Table 9; signals were assigned to peaks based on prior studies^{147, 148}. In addition to carbon, about 5 atom % sodium was present in the long NT samples. Fluorine was present in all samples, at a surface concentration of nearly 2 atomic percent, decreasing to about 0.2 atom % in the interior. The presence of both sodium and fluorine are directly related to the chemistry of the anodizing baths. Based on the analysis of the C1s peak, incorporated carbon was present in C-C, CO, COO (carbonate) and C-N bonds. The Ti-C signal at 281.9 eV was not observed. The carbon content of the short nanotubes, which is initially quite small, becomes appreciable upon flame annealing. A significant amount of carbon ($\sim 3\%$) is present in the long nanotube sample even prior to flame annealing. We attribute this to the presence of a large number of organic ions such as citrate and tetrabutylammonium in the anodizing bath. In long nanotubes, flame annealing introduces additional carbon into a structure where carbon preexists in appreciable quantities. Hence, flame annealed long NTs have the highest carbon content (>5 %) of the samples studied.

Fig. 86



Figure : Photocurrent vs. wavelength plots for TiO_2 photoelectrodes recorded in 1 M KOH at anodic bias of 0.8 V





Figure : Photocurrent action spectra for TiO_2 photoelectrodes recorded in 1 M KOH at anodic bias of 0.8 V

Fig. **86** shows the wavelength dependent photocurrent spectra, and Fig. **87** the photocurrent action spectra of all samples with and without flame annealing at an applied bias of 0.8 V. All nanotube samples exhibit local maxima in their photocurrents from 600-700 nm, but this enhancement of the photocurrent for wavelengths in the red is much greater for the flame annealed samples. In the ultraviolet region of the spectrum, it was the long NT sample not subjected to flame annealing that exhibited the largest photocurrents with a maximum IPCE of 38% at 365 nm. Fig. **88** is the spectral photoresponse from 400nm to 700 nm; here the enhancement of the photoresponse due to flame annealing is clearly seen. The IPCEs of nanotube samples for visible wavelengths increase from near negligible values to a few percent upon flame annealing. It is highest for the flame annealed Ti metal foil sample, which exhibits a secondary threshold in the spectral response at 625 nm.

Fig. 88



Figure : Incident photon-to-current efficiency for TiO_2 electrodes in the visible wavelength region



Figure : The optical absorption spectra (obtained by diffuse reflectance measurements) of TiO₂ electrodes in the visible wavelength region

A similar improvement is also seen in the optical absorption spectra of the samples, shown in Fig. **89**. Again, the flame annealed short NT sample has a significantly enhanced absorption for visible wavelengths with a broad absorption maximum centered on 520 nm. The long NT sample exhibits sharply increasing absorption for wavelengths shorter than 425 nm as well as a trend of gradually decreasing absorption for shorter wavelengths. This dual behavior results in an absorption minimum at 430 nm. The behavior of the flame annealed long NT sample is very similar with a

modest enhancement in the optical absorption. The flame annealed Ti metal foil sample exhibits a featureless uniform absorbance across the entire visible spectrum.



Fig. **90**

Figure : Photocurrent vs. Applied potential curves for the TiO_2 electrodes recorded in 1 M KOH solution, under simulated solar AM 1.5 illumination at an intensity of 100 mW/cm² (scan rate = 10 mV s⁻¹)

The key test for any photoelectrode is its behavior in sunlight. Fig. **90** shows the photoresponse of nanotube photoanodes with and without flame annealing upon full spectrum (1 sun) illumination while scanning the applied bias potential. The applied potential is obtained as $E_{meas} - E_{oc}$, where E_{meas} is the electrode potential at which the photocurrent was measured and E_{oc} is the electrode potential at open circuit in the same electrolyte and at the same illumination. A dramatic improvement in the photocurrents is

obtained for the short NTs upon flame annealing. This is contrast to the long nanotubes where only a small increase in the photocurrent is obtained. At applied potentials of 0.72 V and higher photocurrent densities in excess of 1 mA/cm² are obtained for the flame annealed long NTs. For both long NT samples the photocurrent does not achieve saturation in the range of applied anodic potentials. As the applied potential is scanned in the positive direction, the slope of the photocurrent characteristic changes from steep values to a gently rising characteristic for potentials higher than 0.8 V. This behavior is clarified by Fig. 91, which plots the action spectra of long nanotubes at different values of applied bias. There is a large change in the maximum IPCE (at \sim 365nm) from 27% at short circuit to about 38% at 0.8 V. On further increasing the anodic bias the IPCE values remain clustered around 40%. Even at the relatively high anodic bias of 2.4 V the IPCE is 43%, suggesting that near-saturation of the ultraviolet photoresponse occurs at about 0.8 V. Contrary to this, the photoresponse to visible wavelengths continues to increase significantly with applied bias and is responsible for the region of gently increasing slope seen in Fig. 90. Fig. 90 also shows a markedly smaller slope for the flame annealed short nanotube sample wherein the photocurrent is less responsive to increases in anodic polarization.

Fig. 91



Figure : Incident photon-to-current efficiency vs. wavelength plots for the long nanotube photoelectrode as a function of anodic bias

Fig. **92**



Figure : FESEM image of the top-view of 6 μ m long titania nanotube arrays anodized at

25 V before flame annealing



Figure : FESEM image of the top-view of 6 μ m long titania nanotube arrays anodized at 25 V after flame annealing

The morphology of samples is significantly altered by the flame anneal. The short duration of the anneal ensured that the nanotubular structure was not destroyed. On flame annealing the short NTs, the interpore areas filled and the discrete nanotubes became more interconnected to form a nanoporous-like structure. The resulting structure was similar to the thick walled nanotubular structure grown by anodization at lower bath temperatures.

A key difference, however was that in the flame annealed samples, there were also vacant areas containing no nanotubes probably as a result of the shrinkage experienced due to fusion of adjacent nanotubes. For the long NTs, a similar thickening of the walls ensued but in addition, an interesting transformation occurred in the shape of the aperture of the nanotubes, from circular pores to square- and rectangular shaped pores with near perfect right angles. The sharp contrast in the morphology of the long NTs before and after the flame anneal is depicted in Fig. **92** and Fig. **93** respectively.

Annealing titania nanotubes for even a short duration of 3 min in the reductive zone of a propane flame results in the incorporation of carbon. Carbon can also be introduced by employing the appropriate bath chemistry. The studies of the spectral photoresponse of various TiO₂ electrodes reveal that flame annealing results in an enhancement of the photocurrents induced at wavelengths in the visible part of the solar spectrum. This enhancement of the visible photoresponse is not accompanied by any deterioration of the photoresponse in the ultraviolet. In the case of short nanotubes, a dramatically improved optical absorption as well as an increase in the incident-photon-to current efficiency of the photoelectrodes accompanied this enhancement. Flame annealing increased the IPCE for visible wavelengths at an anodic bias of 0.8 V to a few percent from negligibly small values. This enhancement was subdued for long NT samples, which had appreciable carbon content even before flame annealing.

8.4 Nitrogen doped nanostructured TiO₂ thin films : An electrochemical strategy to incorporate anionic dopants

We investigated an electrochemical method to incorporate anionic dopants, specifically nitrogen, by an anodization process that allowed simultaneous nanostructuring of the anodic film. The nanostructuring of the films is key for photocatalytic applications wherein an optimal material architecture that limits recombination of photogenerated charge carriers is required³⁸. Titanium foils (99.8% pure) approximately 250 µm thick were anodized in electrolytic solutions containing 0.07 M HF and varying concentrations of NH₄NO₃ from 0.2 M to 2.5 M, with ammonium hydroxide added to adjust the pH to 3.5. Such an anodization chemistry restricts the electrolytic ions to nitrogen and fluorine bearing species, allowing control of the possible elements that can be incorporated into the anodic titania films. The as-anodized films were amorphous. The films were subjected to a 3 hour anneal in air at 600°C with heating and cooling rates of 4°C/min to induce crystallinity. Depending upon the sample, the duration of the anodization varied, from 17 seconds to 6 hours.

Fig. 94



Figure : Real time observation of anodization behavior of a Ti foil (99.8 % pure) anodized at 25 V in an electrolyte of pH 3.5 containing 0.07 M HF and 0.4 M NH₄NO₃.

Fig. 94 shows real time observation of anodization behavior of Ti anodized at 25 V in an electrolyte of pH 3.5 containing 0.4 M ammonium nitrate and 0.07 M hydrofluoric acid. Sample A was removed after 17 s of anodization while Sample B was anodized for 4 min. Sample C (not shown in Fig. 94) was anodized for 6 hours at 20 V in an electrolyte of pH 3.5 containing 2.5 M NH₄NO₃ and 0.07 M HF. The maximum current at the onset of the anodization was limited by the compliance of the power supply $(\sim 0.5 \text{ A})$ used to perform the anodization. In the first 25 seconds, after application of the voltage, the measured current density reduced from $> 120 \text{ mA/cm}^2$ to a local-minimum between 80 and 100 mA/cm², with the field-assisted oxidation of the Ti metal surface reducing the current. In the potential range under consideration, this behavior is typical for the anodization of Ti in fluoride ion containing acidic electrolytes¹⁵⁶. However, the magnitude of the anodization currents is much higher. We attribute this to the stronger oxidizing and etching action of the nitrate ion containing electrolyte. Indeed, the anodization is unstable with enormous volatility in the anodization currents, if points of high electric field concentration on the samples (edges and air-liquid) interface are exposed. Localized breakdown of the growing anodic films occurs with a characteristic hissing sound. To ensure stability during the anodization, the edges and interfaces of the samples were sealed with a chemically resistant epoxy and further protected with teflon tape.

The composition of the films was examined using X-ray photoelectron spectroscopy (XPS). XPS spectra were obtained on a Kratos Axis Ultra spectrometer with a

monochromated Al K α source (1486.6 eV) at a take-off angle of 45° and an eight-channel detector. For depth profiles, the depth was estimated from the sputtering rate of SiO₂. XPS quantification was performed by applying the appropriate relative sensitivity factors (RSFs) for the Kratos instrument to the integrated peak areas. A survey scan was initially recorded for each sample to identify elements present. Composition as well as chemical states were determined from the charge corrected hi-resolution scans.





Figure : N 1s XPS spectra for samples A-C with respective nitrogen doping levels [x]

Fig. 95 shows the high resolution N 1s XPS spectra of samples A through C. XPS confirmed that all the incorporated nitrogen was substitutional, with the oxygen site being substituted. The nitrogen peak at 396.8 eV was observed and assigned to atomic β -N, indicating a chemically bound N⁻ state^{157, 158}. Fluorine was present in as-anodized samples but the concentration of incorporated F⁻ was found to be sensitive to the annealing conditions. Annealing processes (in air) lasting greater than six hours at temperatures above 600°C resulted in fluorine atoms being completely resubstituted by oxygen. The XPS depth profile of a 250 nm thick film with a surface nitrogen concentration x = 0.05 is shown in **Fig. 96**. The doping of nitrogen is inhomogeneous with the maximum nitrogen being incorporated close to the surface with nitrogen content diminishing linearly with increasing depth inside the film.



Fig. **96**

Figure : XPS depth profile of a N-doped anodic TiO_2 film showing nitrogen concentration as a function of depth





Figure : FESEM images of sample removed after 4 minutes of 25 V anodization in an aqueous electrolyte containing 0.4 M NH₄NO₃



Figure : FESEM images of sample removed after 6 hours of 25 V anodization in an aqueous electrolyte containing 0.4 M NH₄NO₃

Fig. **98**



[A]



Figure : FESEM images of A] Sample anodized for 6 hours at 20 V B] Sample anodized for 6 hours at 15 V and C] Cross-section of sample anodized for 6 hours at 15 V, in an electrolyte containing $2.5 \text{ M NH}_4\text{NO}_3$

The potential and pH regimes chosen were such as to facilitate the formation of nanotubes. The surface morphology is a function of the duration of the anodization. The time required for the evolution of the nanotubular structure depends on the concentration of F ions in the anodization electrolyte and the pH of the electrolyte. The growth of nanotubes to their maximum length requires an equilibration of the processes of chemical dissolution and electrochemical oxidation and etching (field assisted oxidation and dissolution)⁵⁰. Field emission scanning electron microscopy (FESEM) images of the surfaces of the doped anodic TiO₂ films are shown in Fig. 97, Fig. 98 and Fig. 99. Fig. 97 and Fig. 98 show the effect of anodization duration on samples fabricated in 0.4 M NH₄NO₃ containing electrolyte while Fig. 99 shows the effect of the anodization potential on samples fabricated in an electrolyte containing 2.5 M NH₄NO₃. Sample B Fig. 97 underwent anodization for only 4 minutes, which was insufficient for nanotube formation. However, small pits formed by local dissolution are present. The number and size of pits increases with anodizing time. When the Ti foil underwent anodization for 6 hours (Fig. 98), which was sufficient for the complete evolution of the nanotubular structure. In the electrolyte containing a higher concentration of ammonium nitrate, 20 V anodization for six hours (Fig. 99 [A]) results in a partially formed nanotubular structure whereas at 15 V (Fig. 99 [B] and [C]), the nanotubular structure is completely formed. The precise reactions involving the decomposition of ammonium ions and nitrate ions at the anodic surface to form N-doped titania are currently unclear. However, the anodization of aluminum in nitric acid has been studied previously and is known to be relatively complex¹⁵⁹. A study of the interaction of aluminum with nitrate ions in thin oxide films formed in nitrate ion containing electrolytes indicated that the adsorption of
nitrate ions on the oxidized surface of aluminium was followed by their reduction inside the oxide film¹⁶⁰. Parhutik et al¹⁶¹ reported the incorporation of electrolyte anions in the anodic film formed by anodization of Al in HNO₃ solution. Furthermore, it was reported that the anion concentration, in growing oxide, reaches a maximum value at the moment when intensive pore growth starts and the oxide is thin, i.e. when the anodizing time is very small^{159, 161} and the surface relief strongly depended upon the applied forming conditions. We observed very similar behavior for Ti anodization in the current study with the maximum nitrogen incorporation occurring in a film anodized for a mere 17s. Thus, a trade-off exists between the morphology and the level of nitrogen doping. Shorter anodization periods result in higher concentrations of incorporated nitrogen whereas longer anodization periods are required for the evolution of a desirable nanotubular architecture and result in thicker films. Higher anodization potentials were found to result in thicker films but the very large anodization currents observed at higher voltages (> $1A/cm^2$ at 25 V) resulted in excessive anodic oxygen evolution which disrupted the formation of the nanotubular architecture.

The optical properties were determined by measuring the diffuse reflectance of the films using a Cary 100 UV-Vis-NIR spectrophotometer equipped with a Labsphere DRA-CA-30I internal accessory at room temperature in the wavelength range 250-700 nm. The UV-Vis spectra of the doped TiO_2 thin films are shown in Fig. **100**. The presence of fluorine in TiO_2 thin films was not found to effect a discernable change in optical absorption whereas N-doped films exhibited enhanced optical absorption in the wavelength range from 400-510 nm. The optical absorption is a function of both film thickness and nitrogen concentration. The film with the highest nitrogen concentration (x=0.23) is also the thinnest film owing to the fact that it was anodized for only 17s. As a result, the improvement in optical absorption is manifested most clearly for films of similar thickness. It can be seen in Fig. **100** that in comparison with an undoped TiO₂ film (x = 0), the N-doped TiO₂ film (x= 0.09) exhibits a second absorption threshold at 510 nm. All N-doped films also exhibit a shift in the primary absorption threshold and the magnitude of this shift increases with the concentration of incorporated nitrogen.





Figure : UV-Vis absorption spectra of N doped TiO₂ thin films



Figure : Photocurrent generation of samples A, B and C under AM 1.5 illumination.

Fig. **101** shows the photocurrent-potential characteristics of the nitrogen doped TiO_2 samples A, B and C in 1 M KOH aqueous solution under full spectrum solar illumination. The photoelectrochemical measurements were performed using a CHI electrochemical analyzer (CH Instruments, Dallas, TX) in a standard three-electrode cell with 1M KOH as the electrolyte, a platinum plate counter electrode, a saturated Ag/AgCl reference electrode and TiO_2 working electrode (photoanode). The samples were mounted on a glass base and electrical contacts were taken from the titanium substrate using copper leads and silver epoxy after removing the oxide layer at the titanium surface. A Newport Oriel Solar Simulator with an illumination intensity of 1 sun (AM 1.5, 100 mW/cm²) was used as the light source. Photocurrents were calculated from the

currents measured during AM 1.5 illumination by subtracting the respective dark currents. As seen from Fig. 101, higher nitrogen doping levels result in superior electrode photoactivity. The photocurrent onset potentials are -0.85 V vs Ag/AgCl for samples A and B, and -0.95 V for sample C. Sample B with nitrogen doping level x = 0.09 exhibits only a slightly smaller photocurrent than Sample A with the higher doping level of x = 0.23. We attribute this to the larger thickness of Sample B which underwent anodic oxidation for a longer duration than Sample A.

CHAPTER 9

CONCLUSIONS

In this thesis, the interaction of electrolyte composition and anodization conditions and the morphology of TiO_2 nanotubes are established. The morphology and the surface area of the nanotube are characterized systematically in various ways. One of the most important contributions of this study has been on improving the length, aspect ratio and time of formation of TiO_2 nanotubes. The improvements in length and aspect ratio dramatically improved the photoelectrochemical properties of the nanotubes. It has been demonstrated that anodic nanotube formation is superior in moderately reducing solution ambients. Such ambients are produced using mixtures of water and high permittivity organic solvents. An unprecedented degree of control over the architectural parameters of the nanotube array structure has been achieved. By carefully varying the TiO_2 nanotube array fabrication parameters, pore diameters may be varied from 12 nm to 250 nm, wall-thickness from 5 nm to 30 nm and tube-lengths from 0.1 µm to 100 µm.

The nanotube lengths and the growth rate of the array structure are strongly dependent on the character of the cations present in the anodization electrolyte. The electrolytes containing the larger cations were found to be more conductive on average and more viscous as well. Larger cations that are less easily solvated in amide-water mixtures such as tetrabutylammonium result in much faster nanotube growth rates and final nanotube array lengths compared to smaller cations such as hydrogen and sodium, that are easily solvated. On the other hand, the pore diameter is almost exclusively a function of the anodization potential.

The observations of the anodic current transients, the effect of cations on growth rates and the formation of TiO_2 nanotubes in different electrolytes are used to examine the mechanism responsible for fast growth of titania nanotube arrays. Diffusive mass-transport controlled growth, Interface Potential (IFM) controlled growth and the High Field Model (HFM) are the candidate mechanisms to explain the fast formation of very long high-aspect ratio TiO_2 nanotube arrays. Diagnostic tests eliminated the IFM. Among the remaining two phenomena, there are pieces of experimental evidence to support each of the theories. However, the weight of evidence at the present moment favors the High Field Model as the likely explanation of the observed formation behavior.

The applications of TiO_2 nanotube arrays in photoelectrochemical applications such as water-photolysers and dye-sensitized solar cells are considered. Electron transport in the nanotube architecture is critical to the performance of photoelectrochemical devices and hence, the electron transport in TiO_2 nanotube arrays are investigated. Open circuit voltage decay experiments revealed that the electron recombination lifetimes in titania nanotube array photoelectrodes are superior to those in nanoparticulate electrodes of similar thickness and as a consequence, the nanotubular electrodes are expected to have superior charge collection efficiencies. Under band-gap illumination, 30 μ m long TiO₂ nanotube array based photoanodes performed photo-assisted water splitting at an efficiency as high as 16.25 %. Anionic doping of TiO₂ nanotube arrays has been investigated as a technique to extend the photoresponse of titania into the visible region with emphasis on the carbon and nitrogen as dopants. In the case of carbon, flame annealing has been employed to produce an extension of the photoresponse and improvement in the photoelectrochemical properties of the flame annealed samples. However it is found that the carbon merely forms disordered aggregates within the structure of TiO₂ without occupying oxygen sites in the lattice of titania. On the other hand, nitrogen doping is performed through an electrochemical route and found to occupy substitutional sites in the TiO₂ lattice. But, the resulting extension of the photoresponse and the change in the photoelectrochemical properties are modest for nitrogen doping.

TiO₂ nanotube arrays 19 μ m in length and with a pore diameter of 90 nm are found to have an internal surface area 3000 times that of a planar unstructured film. Dye sensitized solar cells using different architectures and dyes have been constructed and photoconversion efficiencies as high as 6.9 % have been demonstrated. The feasibility study of photoconversion devices based on TiO₂ NT arrays is significant because photoelectrochemical devices based on nanotubular titania are simple and relatively inexpensive because (1) the starting material is titanium metal which is universally abundant and (2) the fabrication process uses a low-cost process, anodization and has relatively few high-vacuum steps.

BIBLIOGRAPHY

- Siegel, R.W. Synthesis, Structure and Properties of Nanostructured Materials. (World Scientific Publishing Company, 1994).
- 2. Iijima, S. Helical Microtubules of Graphitic Carbon. *Nature* **354**, 56-58 (1991).
- Zhang, M., Bando, Y. & Wada, K. Sol-gel template preparation of TiO2 nanotubes and nanorods. *Journal of Materials Science Letters* 20, 167-170 (2001).
- 4. Peng, T.Y., Hasegawa, A., Qiu, J.R. & Hirao, K. Fabrication of titania tubules with high surface area and well-developed mesostructural walls by surfactant-mediated templating method. *Chemistry of Materials* **15**, 2011-2016 (2003).
- Adachi, M., Murata, Y., Okada, I. & Yoshikawa, S. Formation of titania nanotubes and applications for dye-sensitized solar cells. *J Electrochem Soc* 150, G488-G493 (2003).
- Marin, F.I., Hamstra, M.A. & Vanmaekelbergh, D. Greatly enhanced subbandgap photocurrent in porous GaP photoanodes. *J Electrochem Soc* 143, 1137-1142 (1996).
- Paulose, M., Varghese, O.K., Mor, G.K., Grimes, C.A. & Ong, K.G.
 Unprecedented ultra-high hydrogen gas sensitivity in undoped titania nanotubes.
 Nanotechnology 17, 398-402 (2006).
- 8. Gueymard, C.A. The sun's total and spectral irradiance for solar energy applications and solar radiation models. *Sol Energy* **76**, 423-453 (2004).
- 9. Goetzberger, A., Hebling, C. & Schock, H.W. Photovoltaic materials, history, status and outlook. *Materials Science & Engineering R-Reports* **40**, 1-46 (2003).

- 10. Fujishima, A. & Honda, K. *Nature* **238**, 37 (1972).
- Bolton, J.R. Solar photoproduction of hydrogen: A review. *Solar Energy* 57, 37-50 (1996).
- Aroutiounian, V.M., Arakelyan, V.M. & Shahnazaryan, G.E. Metal oxide photoelectrodes for hydrogen generation using solar radiation-driven water splitting. *Sol Energy* 78, 581-592 (2005).
- Schmidt-Mende, L. et al. Organic dye for highly efficient solid-state dyesensitized solar cells. *Adv Mater* 17, 813-+ (2005).
- Ma, W.L., Yang, C.Y., Gong, X., Lee, K. & Heeger, A.J. Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology. *Advanced Functional Materials* 15, 1617-1622 (2005).
- 15. Gratzel, M. Photoelectrochemical cells. *Nature* **414**, 338-344 (2001).
- Gratzel, M. Dye-sensitized solar cells. *Journal of Photochemistry and Photobiology C-Photochemistry Reviews* 4, 145-153 (2003).
- Gratzel, M. Conversion of sunlight to electric power by nanocrystalline dyesensitized solar cells. *Journal of Photochemistry and Photobiology a-Chemistry* 164, 3-14 (2004).
- Nazeeruddin, M.K. et al. Engineering of efficient panchromatic sensitizers for nanocrystalline TiO2-based solar cells. *Journal of the American Chemical Society* 123, 1613-1624 (2001).
- Cao, F., Oskam, G., Meyer, G.J. & Searson, P.C. Electron transport in porous nanocrystalline TiO2 photoelectrochemical cells. *Journal of Physical Chemistry* 100, 17021-17027 (1996).

- deJongh, P.E. & Vanmaekelbergh, D. Trap-limited electronic transport in assemblies of nanometer-size TiO2 particles. *Phys Rev Lett* 77, 3427-3430 (1996).
- Wahl, A., Ulmann, M., Carroy, A. & Augustynski, J. Highly Selective Photooxidation Reactions at Nanocrystalline Tio2 Film Electrodes. *J Chem Soc Chem Comm*, 2277-2278 (1994).
- Santato, C., Ulmann, M. & Augustynski, J. Photoelectrochemical properties of nanostructured tungsten trioxide films. *Journal of Physical Chemistry B* 105, 936-940 (2001).
- Wahl, A. et al. Photoelectrochemical Studies Pertaining to the Activity of Tio2 Towards Photodegradation of Organic-Compounds. *Journal of Electroanalytical Chemistry* 396, 41-51 (1995).
- Chou, T.P., Fryxell, G.E., Li, X.S. & Cao, G. in Nanophotonic Materials, Vol.
 5510. (eds. D.L. Andrews, G.Z. Cao & Z. Gaburro) 129-137 (SPIE, Denver, CO, USA; 2004).
- 25. Limmer, S.J., Chou, T.P. & Cao, G.Z. A study on the growth of TiO2 nanorods using sol electrophoresis. *Journal of Materials Science* **39**, 895-901 (2004).
- Chou, T.P., Limmer, S.J. & Cao, G. in Nanomaterials and Their Optical Applications, Aug 5-7 2003, Vol. 5224 53-61 (The International Society for Optical Engineering, San Diego, CA, United States; 2003).
- 27. Adachi, M., Murata, Y., Harada, M. & Yoshikawa, S. Formation of titania nanotubes with high photo-catalytic activity. *Chem Lett*, 942-943 (2000).

- 28. Zhu, Y.C., Li, H.L., Koltypin, Y., Hacohen, Y.R. & Gedanken, A. Sonochemical synthesis of titania whiskers and nanotubes. *Chem Commun*, 2616-2617 (2001).
- Gong, D. et al. Titanium oxide nanotube arrays prepared by anodic oxidation. J Mater Res 16, 3331-3334 (2001).
- Mor, G.K., Varghese, O.K., Paulose, M., Mukherjee, N. & Grimes, C.A.
 Fabrication of tapered, conical-shaped titania nanotubes. *J Mater Res* 18, 2588-2593 (2003).
- Macak, J.M., Tsuchiya, H., Taveira, L., Aldabergerova, S. & Schmuki, P. Smooth anodic TiO2 nanotubes. *Angew. Chem.-Int. Edit.* 44, 7463-7465 (2005).
- Foll, H., Langa, S., Carstensen, J., Christophersen, M. & Tiginyanu, I.M. Pores in III-V semiconductors. *Adv Mater* 15, 183-+ (2003).
- Christophersen, M., Carstensen, J., Voigt, K. & Foll, H. Organic and aqueous electrolytes used for etching macro- and mesoporous silicon. *Phys. Status Solidi A-Appl. Res.* 197, 34-38 (2003).
- Harraz, F.A., Kamada, K., Kobayashi, K., Sakka, T. & Ogata, Y.H. Random macropore formation in p-type silicon in HF-containing organic solutions - Host matrix for metal deposition. *J Electrochem Soc* 152, C213-C220 (2005).
- Prakasam, H.E., Varghese, O.K., Paulose, M., Mor, G.K. & Grimes, C.A.
 Synthesis and photoelectrochemical properties of nanoporous iron (III) oxide by potentiostatic anodization. *Nanotechnology* 17, 4285-4291 (2006).
- Melody, B., Kinard, T. & Lessner, P. The non-thickness-limited growth of anodic oxide films on valve metals. *Electrochemical and Solid State Letters* 1, 126-129 (1998).

- 37. Izutsu, K. Electrochemistry in Nonaqueous Solutions. (Wiley-VCH, 2002).
- Mor, G.K., Shankar, K., Paulose, M., Varghese, O.K. & Grimes, C.A. Enhanced photocleavage of water using titania nanotube arrays. *Nano Letters* 5, 191-195 (2005).
- Parkhutik, V.P. & Shershulsky, V.I. Theoretical Modeling of Porous Oxide-Growth on Aluminum. *Journal of Physics D-Applied Physics* 25, 1258-1263 (1992).
- 40. Sieber, I., Hildebrand, H., Friedrich, A. & Schmuki, P. Formation of self-organized niobium porous oxide on niobium. *Electrochemistry Communications* 7, 97-100 (2005).
- 41. Sieber, I.V. & Schmuki, P. Porous tantalum oxide prepared by electrochemical anodic oxidation. *J Electrochem Soc* **152**, C639-C644 (2005).
- Tsuchiya, H., Macak, J.M., Taveira, L. & Schmuki, P. Fabrication and characterization of smooth high aspect ratio zirconia nanotubes. *Chemical Physics Letters* 410, 188-191 (2005).
- Tsuchiya, H. & Schmuki, P. Self-organized high aspect ratio porous hafnium oxide prepared by electrochemical anodization. *Electrochemistry Communications* 7, 49-52 (2005).
- 44. Ue, M. et al. Anodization of Al-Nd alloy films in nonaqueous electrolyte solutions for TFT-LCD application. *Electrochimica Acta* **47**, 217-223 (2001).
- Ruan, C.M., Paulose, M., Varghese, O.K., Mor, G.K. & Grimes, C.A. Fabrication of highly ordered TiO2 nanotube arrays using an organic electrolyte. *Journal of Physical Chemistry B* 109, 15754-15759 (2005).

- 46. Paulose, M. et al. Anodic Growth of Highly Ordered TiO₂ Nanotube Arrays to
 134 μm in Length. J. Phys. Chem. B 110, 16179-16184 (2006).
- 47. Macak, J.M. & Schmuki, P. Anodic growth of self-organized anodic TiO2 nanotubes in viscous electrolytes. *Electrochimica Acta* **52**, 1258-1264 (2006).
- 48. Shankar, K. et al. Highly-ordered TiO₂ nanotube arrays up to 220 μm in length: use in water photoelectrolysis and dye-sensitized solar cells. *Nanotechnology* 18, 065707 (2007).
- Mor, G.K., Varghese, O.K., Paulose, M. & Grimes, C.A. Transparent highly ordered TiO2 nanotube arrays via anodization of titanium thin films. *Advanced Functional Materials* 15, 1291-1296 (2005).
- 50. Cai, Q.Y., Paulose, M., Varghese, O.K. & Grimes, C.A. The effect of electrolyte composition on the fabrication of self-organized titanium oxide nanotube arrays by anodic oxidation. *J Mater Res* **20**, 230-236 (2005).
- Shankar, K., Zeng, K.F., Ruan, C.M. & Grimes, C.A. Quantification of ricin concentrations in aqueous media. *Sensors and Actuators B-Chemical* 107, 640-648 (2005).
- Coates, R.V. & Woodard, G.D. An X-Ray Diffractometric Study of Ammonium Nitrate-Potassium Nitrate System. *Journal of the Chemical Society*, 2135-& (1965).
- 53. Kim, H.S. Electrostatic Gibbs free energy and solvation number of tetraalkylammonium ions in pyridine at 25 degrees C obtained using conductance of corresponding ion. *Bulletin of the Korean Chemical Society* 19, 1347-1350 (1998).

- Varela, H., Torresi, R.M. & Buttry, D.A. Mixed cation and anion transport during redox cycling of a self-doped polyaniline derivative in nonaqueous media. J Electrochem Soc 147, 4217-4223 (2000).
- 55. Varghese, O.K., Gong, D.W., Paulose, M., Grimes, C.A. & Dickey, E.C. Crystallization and high-temperature structural stability of titanium oxide nanotube arrays. *J. Mater. Res.* 18, 156-165 (2003).
- Marcus, Y. Solvent Mixtures : Properties and Selective Solvation. (Marcel Dekker, Inc, New York; 2002).
- 57. McCoubrey, J.C. The Acid Strength of the Hydrogen Halides. *Transactions of the Faraday Society* **51**, 743-747 (1955).
- Pletnev, M.A., Shirobokov, I.B., Ovechkina, O.E. & Reshetnikov, S.M. Effect of Tetraalkylammonium Salts on the Cathodic Evolution of Hydrogen in Concentrated Acidic Bromide Solutions. *Protection of Metals* 31, 317-320 (1995).
- 59. Oguzie, E.E., Okolue, B.N., Ebenso, E.E., Onuoha, G.N. & Onuchukwu, A.I. Evaluation of the inhibitory effect of methylene blue dye on the corrosion of aluminium in hydrochloric acid. *Mater Chem Phys* 87, 394-401 (2004).
- Tsuchiya, H., Macak, J.M., Ghicov, A., Taveira, L. & Schmuki, P. Self-organized porous TiO2 and ZrO2 produced by anodization. *Corrosion Science* 47, 3324-3335 (2005).
- Choi, J.S. et al. Porous niobium oxide films prepared by anodization in HF/H3PO4. *Electrochimica Acta* 51, 5502-5507 (2006).
- Hoar, T.P. & Mott, N.F. A Mechanism for the Formation of Porous Anodic Oxide Films on Aluminium. *J Phys Chem Solids* 9, 97-99 (1959).

- Thompson, G.E., Furneaux, R.C., Wood, G.C., Richardson, J.A. & Goode, J.S.
 Nucleation and Growth of Porous Anodic Films on Aluminum. *Nature* 272, 433-435 (1978).
- 64. Osulliva.Jp & Wood, G.C. Morphology and Mechanism of Formation of Porous Anodic Films on Aluminium. *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences* **317**, 511-& (1970).
- 65. Jessensky, O., Muller, F. & Gosele, U. Self-organized formation of hexagonal pore arrays in anodic alumina. *Applied Physics Letters* **72**, 1173-1175 (1998).
- 66. Li, A.P., Muller, F., Birner, A., Nielsch, K. & Gosele, U. Hexagonal pore arrays with a 50-420 nm interpore distance formed by self-organization in anodic alumina. *Journal of Applied Physics* 84, 6023-6026 (1998).
- Sharma, G. in Materials Science and Engineering, Vol. Ph.D. (The Pennsylvania State University, 2005).
- Osullivan, J.P. & Wood, G.C. Morphology and Mechanism of Formation of Porous Anodic Films on Aluminium. *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences* 317, 511-& (1970).
- Mor, G.K., Varghese, O.K., Paulose, M., Shankar, K. & Grimes, C.A. A review on highly ordered, vertically oriented TiO2 nanotube arrays: Fabrication, material properties, and solar energy applications. *Solar Energy Materials and Solar Cells* 90, 2011-2075 (2006).
- 70. Macak, J.M., Tsuchiya, H. & Schmuki, P. High-aspect-ratio TiO2 nanotubes by anodization of titanium. *Angew. Chem.-Int. Edit.* **44**, 2100-2102 (2005).

- Taveira, L.V., Macak, J.M., Tsuchiya, H., Dick, L.F.P. & Schmuki, P. Initiation and growth of self-organized TiO2 nanotubes anodically formed in NH4F/(NH4)(2)SO4 electrolytes. *J Electrochem Soc* 152, B405-B410 (2005).
- 72. Zhu, K., Neale, N.R., Miedaner, A. & Frank, A.J. Enhanced charge-collection efficiencies and light scattering in dye-sensitized solar cells using oriented TiO2 nanotubes arrays. *Nano Letters* 7, 69-74 (2007).
- Tohrengel, M.M. Thin Anodic Oxide Layers on Aluminum and Other Valve
 Metals High-Field Regime. *Materials Science & Engineering R-Reports* 11, 243-294 (1993).
- Bard, A.J. & Faulkner, L.R. Electrochemical Methods : Fundamentals and Applications. (John Wiley & Sons, Inc., 2001).
- 75. Shankar, K., Mor, G.K., Fitzgerald, A. & Grimes, C.A. Cation Effect on the Electrochemical Formation of Very High Aspect Ratio TiO2 Nanotube Arrays in Formamide-Water Mixtures. J. Phys. Chem. C (2006).
- Cabrera, N. & Mott, N.F. Theory of the Oxidation of Metals. *Reports on Progress in Physics* 12, 163-184 (1948).
- 77. Guntherschulze, A. & Betz, H. Electrolytkondensatoren. (Hebert Cram, Stuttgart; 1952).
- 78. Verwey, E.J.W. Electrolytic conduction of a solid insulator at high fields The formation of the anodic oxide film on aluminium. *Physica* **2**, 1059-1063 (1935).
- Zhang, L., Macdonald, D.D., Sikora, E. & Sikora, J. On the kinetics of growth of anodic oxide firms. *J Electrochem Soc* 145, 898-905 (1998).

- Olsson, C.O.A., Verge, M.G. & Landolt, D. EQCM study of anodic film growth on valve metals. *J Electrochem Soc* 151, B652-B660 (2004).
- Omanovic, S. & Metikoshukovic, M. The Ionic Conductance of Barrier Anodic Oxide-Films on Indium. *Solid State Ionics* 78, 69-78 (1995).
- Patermarakis, G. & Moussoutzanis, K. Electrochemical Kinetic-Study on the Growth of Porous Anodic Oxide-Films on Aluminum. *Electrochimica Acta* 40, 699-708 (1995).
- Law, M., Greene, L.E., Johnson, J.C., Saykally, R. & Yang, P.D. Nanowire dyesensitized solar cells. *Nat Mater* 4, 455-459 (2005).
- Sbergveglieri, G. & Nelli, P. Nanostructured semiconducting thin films as gas sensors. (World Scientific Publishing Company, 1994).
- Comte, P., Nazeeruddin, M.K., Rotzinger, F.P., Frank, A.J. & Gratzel, M.
 Artificial Analogs of the Oxygen-Evolving Complex in Photosynthesis the Oxo-Bridged Ruthenium Dimer 2,2'-Bipyridyl-4,4'-Dicarboxylate-2(H2o)Ruiii-O-Ruiii(H2o)L2. *J Mol Catal* 52, 63-84 (1989).
- Tenne, R. & Rao, C.N.R. Inorganic nanotubes. *Philos T Roy Soc A* 362, 2099-2125 (2004).
- Gratzel, M. Conversion of sunlight to electric power by nanocrystalline dyesensitized solar cells (vol 164, pg 3, 2004). *Journal of Photochemistry and Photobiology a-Chemistry* 168, 235-235 (2004).

- 88. Adachi, M. et al. Highly efficient dye-sensitized solar cells with a titania thin-film electrode composed of a network structure of single-crystal-like TiO2 nanowires made by the "oriented attachment" mechanism. *Journal of the American Chemical Society* **126**, 14943-14949 (2004).
- Song, M.Y., Ahn, Y.R., Jo, S.M., Kim, D.Y. & Ahn, J.P. TiO2 single-crystalline nanorod electrode for quasi-solid-state dye-sensitized solar cells. *Applied Physics Letters* 87 (2005).
- 90. Varghese, C.K., Paulose, M., Shankar, K., Mor, G.K. & Grimes, C.A. Waterphotolysis properties of micron-length highly-ordered titania nanotube-arrays. *Journal of Nanoscience and Nanotechnology* 5, 1158-1165 (2005).
- Zaban, A.G., M. & Bisquert, J. Determination of the Electron Lifetime in Nanocrystalline Dye Solar Cells by Open-Circuit Voltage Decay Measurements. *ChemPhysChem* 4, 859-864 (2003).
- 92. Niinobe, D., Makari, Y., Kitamura, T., Wada, Y. & Yanagida, S. Origin of enhancement in open-circuit voltage by adding ZnO to nanocrystalline SnO2 in dye-sensitized solar cells. *Journal of Physical Chemistry B* 109, 17892-17900 (2005).
- 93. Fabregat-Santiago, F. et al. The origin of slow electron recombination processes in dye-sensitized solar cells with alumina barrier coatings. *Journal of Applied Physics* 96, 6903-6907 (2004).

- 94. van de Lagemaat, J., Park, N.G. & Frank, A.J. Influence of electrical potential distribution, charge transport, and recombination on the photopotential and photocurrent conversion efficiency of dye-sensitized nanocrystalline TiO2 solar cells: A study by electrical impedance and optical modulation techniques. *Journal of Physical Chemistry B* 104, 2044-2052 (2000).
- 95. Frank, A.J., Kopidakis, N. & van de Lagemaat, J. Electrons in nanostructured TiO2 solar cells: transport, recombination and photovoltaic properties. *Coordination Chemistry Reviews* 248, 1165-1179 (2004).
- 96. Vanmaekelbergh, D., Marin, F.I. & vandeLagemaat, J. Transport of photogenerated charge carriers through crystalline GaP networks investigated by intensity modulated photocurrent spectroscopy. *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics* 100, 616-626 (1996).
- 97. Schlichthorl, G., Huang, S.Y., Sprague, J. & Frank, A.J. Band edge movement and recombination kinetics in dye-sensitized nanocrystalline TiO2 solar cells: A study by intensity modulated photovoltage spectroscopy. *Journal of Physical Chemistry B* 101, 8141-8155 (1997).
- 98. Kopidakis, N., Schiff, E.A., Park, N.G., van de Lagemaat, J. & Frank, A.J.
 Ambipolar diffusion of photocarriers in electrolyte-filled, nanoporous TiO2. *Journal of Physical Chemistry B* 104, 3930-3936 (2000).
- 99. Solbrand, A. et al. Electron transport in the nanostructured TiO2-electrolyte system studied with time-resolved photocurrents. *Journal of Physical Chemistry B* 101, 2514-2518 (1997).

- 100. Tirosh, S., Dittrich, T., Ofir, A., Grinis, L. & Zaban, A. Influence of ordering in porous TiO2 layers on electron diffusion. *Journal of Physical Chemistry B* 110, 16165-16168 (2006).
- O'Regan, B.C. et al. Measuring charge transport from transient photovoltage rise times. A new tool to investigate electron transport in nanoparticle films. *Journal* of Physical Chemistry B 110, 17155-17160 (2006).
- Schlichthorl, G., Park, N.G. & Frank, A.J. Estimation of the charge-collection efficiency of dye-sensitized nanocrystalline TiO2 solar cells. *Z Phys Chem* 212, 45-50 (1999).
- Schlichthorl, G., Park, N.G. & Frank, A.J. Evaluation of the charge-collection efficiency of dye-sensitized nanocrystalline TiO2 solar cells. *Journal of Physical Chemistry B* 103, 782-791 (1999).
- 104. Law, M. et al. ZnO-Al2O3 and ZnO-TiO2 core-shell nanowire dye-sensitized solar cells. *Journal of Physical Chemistry B* **110**, 22652-22663 (2006).
- Greene, L.E., Yuhas, B.D., Law, M., Zitoun, D. & Yang, P.D. Solution-grown zinc oxide nanowires. *Inorganic Chemistry* 45, 7535-7543 (2006).
- 106. Nishimura, S. et al. Standing wave enhancement of red absorbance and photocurrent in dye-sensitized titanium dioxide photoelectrodes coupled to photonic crystals. *Journal of the American Chemical Society* **125**, 6306-6310 (2003).

- 107. Nazeeruddin, M.K. et al. Conversion of Light to Electricity by Cis-X2bis(2,2'-Bipyridyl-4,4'-Dicarboxylate)Ruthenium(Ii) Charge-Transfer Sensitizers (X = Cl-, Br-, I-, Cn-, and Scn-) on Nanocrystalline Tio2 Electrodes. *Journal of the American Chemical Society* 115, 6382-6390 (1993).
- Mor, G.K., Shankar, K., Paulose, M., Varghese, O.K. & Grimes, C.A. Use of highly-ordered TiO2 nanotube arrays in dye-sensitized solar cells. *Nano Letters* 6, 215-218 (2006).
- 109. Kroeze, J.E. et al. Parameters influencing charge separation in solid-state dye-sensitized solar cells using novel hole conductors. *Advanced Functional Materials* 16, 1832-1838 (2006).
- Schmidt-Mende, L., Zakeeruddin, S.M. & Gratzel, M. Efficiency improvement in solid-state-dye-sensitized photovoltaics with an amphiphilic Ruthenium-dye.
 Applied Physics Letters 86 (2005).
- 111. O'Regan, B., Lenzmann, F., Muis, R. & Wienke, J. A solid-state dye-sensitized solar cell fabricated with pressure-treated P25-TiO2 and CuSCN: Analysis of pore filling and IV characteristics. *Chemistry of Materials* 14, 5023-5029 (2002).
- 112. O'Regan, B.C. & Lenzmann, F. Charge transport and recombination in a nanoscale interpenetrating network of n-type and p-type semiconductors: Transient photocurrent and photovoltage studies of TiO2/Dye/CuSCN photovoltaic cells. *Journal of Physical Chemistry B* 108, 4342-4350 (2004).

- Perera, V.P.S., Senevirathna, M.K.I., Pitigala, P. & Tennakone, K. Doping CuSCN films for enhancement of conductivity: Application in dye-sensitized solid-state solar cells. *Solar Energy Materials and Solar Cells* 86, 443-450 (2005).
- 114. Pleskov, Y.V. Solar Energy Conversion : A Photoelectrochemical Approach. (Springer Verlag, 1990).
- 115. Khan, S.U.M., Al-Shahry, M. & Ingler, W.B. Efficient photochemical water splitting by a chemically modified n-TiO2 2. *Science* **297**, 2243-2245 (2002).
- 116. Oliva, F.Y., Avalle, L.B., Santos, E. & Camara, O.R. Photoelectrochemical characterization of nanocrystalline TiO2 films on titanium substrates. *Journal of Photochemistry and Photobiology a-Chemistry* **146**, 175-188 (2002).
- Pleskov, Y.V. & Krotova, M.D. Photosplitting of Water in a Photoelectrolyser with Solid Polymer Electrolyte. *Electrochimica Acta* 38, 107-109 (1993).
- Pleskov, Y.V., Sakharova, A.Y., Krotova, M.D., Bouilov, L.L. & Spitsyn, B.V.
 Photoelectrochemical Properties of Semiconductor Diamond. *Journal of Electroanalytical Chemistry* 228, 19-27 (1987).
- Sukamto, J.P.H., Mcmillan, C.S. & Smyrl, W. Photoelectrochemical Investigations of Thin Metal-Oxide Films - Tio2, Al2o3, and Hfo2 on the Parent Metals. *Electrochimica Acta* 38, 15-27 (1993).
- Sukamto, J.P.H., Smyrl, W.H., Mcmillan, C.S. & Kozlowski, M.R.
 Photoelectrochemical Measurements of Thin Oxide-Films Multiple Internal-Reflection Effects. *Journal of the Electrochemical Society* 139, 1033-1043 (1992).

- 121. vandeLagemaat, J., Plakman, M., Vanmaekelbergh, D. & Kelly, J.J. Enhancement of the light-to-current conversion efficiency in an n-SiC/solution diode by porous etching. *Applied Physics Letters* 69, 2246-2248 (1996).
- 122. Hamnett, A. Faraday Discussions of the Chemical Society 70, 127 (1980).
- Lubberhuizen, W.H., Vanmaekelbergh, D. & Van Faassen, E. Recombination of photogenerated charge carriers in nanoporous gallium phosphide. *J Porous Mat* 7, 147-152 (2000).
- 124. Ong, K.G., Varghese, O.K., Mor, G.K. & Grimes, C.A. Numerical simulation of light propagation through highly-ordered titania nanotube arrays: Dimension optimization for improved photoabsorption. *Journal of Nanoscience and Nanotechnology* 5, 1801-1808 (2005).
- Campbell, S.A. et al. Titanium dioxide (TiO2)-based gate insulators. *Ibm J Res Dev* 43, 383-392 (1999).
- Reddy, K.M., Manorama, S.V. & Reddy, A.R. Bandgap studies on anatase titanium dioxide nanoparticles. *Mater Chem Phys* 78, 239-245 (2003).
- 127. Shibata, T. et al. Comparison of photochemical properties of brookite and anatase TiO2 films. *Physical Chemistry Chemical Physics* 6, 1359-1362 (2004).
- 128. Gratzel, M. Applied physics Solar cells to dye for. *Nature* **421**, 586-587 (2003).
- Gratzel, M. Harvesting sunlight by photoelectrochemical energy conversion.
 Electrochemistry 70, 397-397 (2002).
- Dvoranova, D., Brezova, V., Mazur, M. & Malati, M.A. Investigations of metaldoped titanium dioxide photocatalysts. *Appl Catal B-Environ* 37, 91-105 (2002).

- 131. Wilke, K. & Breuer, H.D. The influence of transition metal doping on the physical and photocatalytic properties of titania. *Journal of Photochemistry and Photobiology a-Chemistry* **121**, 49-53 (1999).
- 132. Wilke, K. & Breuer, H.D. Transition metal doped titania: Physical properties and photocatalytic behaviour. *Zeitschrift Fur Physikalische Chemie-International Journal of Research in Physical Chemistry & Chemical Physics* 213, 135-140 (1999).
- 133. Choi, W.Y., Termin, A. & Hoffmann, M.R. The Role of Metal-Ion Dopants in Quantum-Sized Tio2 - Correlation between Photoreactivity and Charge-Carrier Recombination Dynamics. *Journal of Physical Chemistry* 98, 13669-13679 (1994).
- 134. Luo, Z.H. & Gao, Q.H. Decrease in the Photoactivity of Tio2 Pigment on Doping with Transition-Metals. *Journal of Photochemistry and Photobiology a-Chemistry* 63, 367-375 (1992).
- 135. Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K. & Taga, Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science* 293, 269-271 (2001).
- 136. Morikawa, T., Asahi, R., Ohwaki, T., Aoki, K. & Taga, Y. Band-gap narrowing of titanium dioxide by nitrogen doping. *Jpn J Appl Phys 2* **40**, L561-L563 (2001).
- Umebayashi, T., Yamaki, T., Itoh, H. & Asai, K. Band gap narrowing of titanium dioxide by sulfur doping. *Applied Physics Letters* 81, 454-456 (2002).
- Umebayashi, T. et al. Sulfur-doping of rutile-titanium dioxide by ion implantation: Photocurrent spectroscopy and first-principles band calculation studies. *Journal of Applied Physics* 93, 5156-5160 (2003).

- Batzill, M., Morales, E.H. & Diebold, U. Influence of nitrogen doping on the defect formation and surface properties of TiO2 rutile and anatase. *Phys Rev Lett* 96 (2006).
- 140. Di Valentin, C., Pacchioni, G., Selloni, A., Livraghi, S. & Giamello, E.
 Characterization of paramagnetic species in N-doped TiO2 powders by EPR
 spectroscopy and DFT calculations. *Journal of Physical Chemistry B* 109, 1141411419 (2005).
- 141. Lindgren, T. et al. Photo electrochemical study of sputtered nitrogen-doped titanium dioxide thin films in aqueous electrolyte. *Solar Energy Materials and Solar Cells* 84, 145-157 (2004).
- 142. Lindgren, T. et al. Photoelectrochemical and optical properties of nitrogen doped titanium dioxide films prepared by reactive DC magnetron sputtering. *Journal of Physical Chemistry B* 107, 5709-5716 (2003).
- 143. Torres, G.R., Lindgren, T., Lu, J., Granqvist, C.G. & Lindquist, S.E.
 Photoelectrochemical study of nitrogen-doped titanium dioxide for water oxidation. *Journal of Physical Chemistry B* 108, 5995-6003 (2004).
- 144. Ohno, T. et al. Preparation of S-doped TiO2 photocatalysts and their photocatalytic activities under visible light. *Applied Catalysis a-General* 265, 115-121 (2004).
- Umebayashi, T., Yamaki, T., Tanaka, S. & Asai, K. Visible light-induced degradation of methylene blue on S-doped TiO2. *Chem Lett* 32, 330-331 (2003).

- 146. Yamaki, T. et al. Fluorine-doping in titanium dioxide by ion implantation technique. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 206, 254-258 (2003).
- 147. Choi, Y., Umebayashi, T., Yamamoto, S. & Tanaka, S. Fabrication of TiO2 photocatalysts by oxidative annealing of TiC. *Journal of Materials Science Letters* 22, 1209-1211 (2003).
- Choi, Y., Umebayashi, T. & Yoshikawa, M. Fabrication and characterization of C-doped anatase TiO2 photocatalysts. *Journal of Materials Science* 39, 1837-1839 (2004).
- Serpone, N. Is the band gap of pristine TiO2 narrowed by anion- and cation-doping of titanium dioxide in second-generation photocatalysts? *Journal of Physical Chemistry B* 110, 24287-24293 (2006).
- 150. Chen, X.B., Lou, Y.B., Samia, A.C.S., Burda, C. & Gole, J.L. Formation of oxynitride as the photocatalytic enhancing site in nitrogen-doped titania nanocatalysts: Comparison to a commercial nanopowder. *Advanced Functional Materials* 15, 41-49 (2005).
- 151. Niu, L. et al. Corrosion inhibition of iron in acidic solutions by alkyl quaternary ammonium halides: Correlation between inhibition efficiency and molecular structure. *Appl Surf Sci* **252**, 1634-1642 (2005).
- 152. Suda, Y., Kawasaki, H., Ueda, T. & Ohshima, T. Preparation of nitrogen-doped titanium oxide thin film using a PLD method as parameters of target material and nitrogen concentration ratio in nitrogen/oxygen gas mixture. *Thin Solid Films* 475, 337-341 (2005).

- Sato, S., Nakamura, R. & Abe, S. Visible-light sensitization of TiO2 photocatalysts by wet-method N doping. *Applied Catalysis a-General* 284, 131-137 (2005).
- Zukalova, M. et al. Organized mesoporous TiO2 films exhibiting greatly enhanced performance in dye-sensitized solar cells. *Nano Lett.* 5, 1789-1792 (2005).
- Noworyta, K. & Augustynski, J. Spectral photoresponses of carbon-doped TiO2 film electrodes. *Electrochemical and Solid State Letters* 7, E31-E33 (2004).
- 156. Mor, G.K., Varghese, O.K., Paulose, M., Ong, K.G. & Grimes, C.A. Fabrication of hydrogen sensors with transparent titanium oxide nanotube-array thin films as sensing elements. *Thin Solid Films* **496**, 42-48 (2006).
- Chourasia, A.R. & Chopra, D.R. X-ray Photoelectron Study of TiN, Vol. 1. (American Vacuum Society, 1992).
- Chourasia, A.R. & Chopra, D.R. X-Ray Photoelectron Study of Tin/Sio2 and Tin/Si Interfaces. *Thin Solid Films* 266, 298-301 (1995).
- 159. Yakovleva, N.M. et al. Structural study of anodic films formed on aluminum in nitric acid electrolyte. *Thin Solid Films* **416**, 16-23 (2002).
- 160. Augustynski, J., Berthou, H. & Painot, J. XPS study of the interactions between aluminium metal and nitrate ions. *Chemical Physics Letters* **44**, 221-224 (1976).
- Parhutik, V.P., Makushok, I.E., Kudriavtsev, E., Sokol, V.A. & Khodan, A.N.
 Russian Journal of Electrochemistry 23, 1538 (1987).

VITA

Karthik Shankar

Education

Bachelor of Technology, Indian Institute of Technology-Madras, India, 2000 M.S. in Electrical Engineering, Pennsylvania State University, PA, USA 2002

Employment History

Oct 1998-Oct 1999 : Research Intern, The Materials Science Research Center, Indian Institute of Technology-Madras, India.

Aug 2000-Dec 2002 : Research Assistant, Center for Thin Film Devices, Department of Electrical Engineering, The Pennsylvania State University, PA. Jan 2003-Present : Research Assistant, The Materials Research Institute, Pennsylvania State University, PA.

Honors and Awards

- 2000 Governor's Gold Medal for Excellence, Indian Institute of Technology-Madras, India.
- 2003 Kodak Research Fellowship, Eastman Kodak Corporation, Rochester, NY.
- 2004 Individual gold medal in the Men's Blues Division at the United States Intercollegiate Racquetball Tournament organized by the United States Racquetball Association (USRA). Part of the Penn State racquetball team that finished fifth in the nation in 2005 among 60 competing schools.

Selected Publications

Shankar K, Mor GK, Fitzgerald A and Grimes CA, Cation effect on the electrochemical formation of very high aspect ratio TiO₂ nanotube arrays in formamide-water mixtures, *Journal of Physical Chemistry C* ASAP article published 12/14/2006

Shankar K, Tep, KC and Grimes CA, N-doped and N, F-codoped TiO₂ photoelectrodes : An electrochemical strategy to incorporate anionic dopants, *J. Phys. D: Appl. Phys* 39 2361-2366 2006

Shankar K, Paulose M, Mor GK, Varghese OK and Grimes CA, A study on the spectral photoresponse and photoelectrochemical properties of flame-annealed titania nanotube arrays, *J. Phys. D: Appl. Phys.* 38 3543-3549 2005

Shankar K and Jackson TN, Morphology and electrical transport in pentacene films on silylated oxide surfaces, *Journal of Materials Research* 19 2003-2007 2004

Mor GK, Shankar K, Paulose M, Varghese OK, Grimes CA, Use of highlyordered TiO₂ nanotube arrays in dye-sensitized solar cells, *Nanoletters* 39 2498-503 2006