Single walled carbon nanotube photovoltaics



Thesis submitted to the School of Chemical and Physical Sciences Faculty of Science and Engineering The Flinders University of South Australia in fulfilment of the requirements for the degree of Doctor of Philosophy July 2013

Daniel D. Tune

Supervisor: Prof. Joseph G. Shapter Co-supervisors: Assoc. Prof. Jamie S. Quinton & Prof. Amanda V. Ellis

Copyright © Daniel Tune, 2013. All rights reserved.

Reproduction or translation of any part of this work beyond that permitted by the Copyright Act 1968 or the Copyright Amendment Act 2006 without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to The Flinders University of South Australia Library.

Boldface is used for vectors and hat notation for unit vectors. Numbering begins with the title page for compatibility with electronic document conventions.

For my beloved family

Preface

Energy has been a challenge for us since the dawn of time and we continue to invent even more clever ways of capturing and harnessing it. However, only recently have we become so numerous, and the waste from our industrial scale energy generation so great, that getting our energy in the wrong ways now poses a real, existential threat to us all. Fortunately, there is more than one form of energy and many technologies are available to us to capture, store and use it without generating much waste. Unfortunately, the ability of many economies, including Australia's, to respond effectively to our changing energy needs is constrained by the preponderance of established infrastructure investment and the watering down or outright capture of government and regulatory bodies. In short, we already have the technological solutions we need to solve our current energy challenges, but due to the pervasive influence of those who continue to profit from fossil fuels at everyone else's expense, renewable technologies are at a disadvantage. The large-scale deployment of green energy quickly becomes the most profitable investment on any mid to long term scale when tax payer handouts to the fossil fuel industry are taken out of the equation. That is, the energy problem is no longer a scientific or engineering one, but one of public policy in our choice of industrial subsidies.

Thus, the need is great for disruptive new technologies or advances in current systems or processes that, through performance or cost improvements, render untenable any attempts to thwart or delay further our requirement for technologies that enable a sustainable energy future. It is the sincere hope of the Author that the use of single walled carbon nanotubes in photovoltaics will become such a technology.

Table of Contents

Prefac	ce	5
Table	of Contents	7
Abstra	act	11
Declar	ration	13
Ackno	owledgements	15
Conte	extual statement	17
Public	cations	19
Chapt	ter 1 Introduction	21
1.1	The energy challenge	23
1.2	Solar energy	27
1.3	Carbon nanotubes	
1.4	Carbon nanotube-silicon solar cells	
1.5	Other carbon nanotube solar cells	
1.6	Summary	55
1.7	References	56

Chapter 2 SWCNT working electrodes for

dye sensitised solar cells65		
	Introduction	2.1
	Method	2.2
	Results and Discussion	2.3
	Summary	2.4
	References	2.5

Chapter 3 SWCNT front electrodes for

silicon solar cells		
3.1	Introduction	
3.2	Method	
3.3	The effect of front electrode thickness	
3.4	The back junction	
3.5	SWCNT film thickness	
3.6	Summary	
3.7	References	

Chapter 4 The role of nanotubes in SWCNT – silicon

solar cells10		109	
	4.1	Introduction	
	4.2	Method	
	4.3	Results and discussion	
	4.4	Summary	
	4.5	References	123

Chapter 5 The effect of film metallicity on

SWCNT-silicon solar cells		
5.1	Introduction	
5.2	Method	
5.3	Results and discussion	
5.4	Summary	
5.5	References	

Chapter 6 SWCNT - polyaniline - silicon solar cells 147

6.2	Introduction149
6.3	Method149
6.4	Results and discussion150
6.5	Summary158
6.6	References158

Chapter 7 The potential sunlight harvesting efficiency

of SWO	CNT solar cells	161
7.1	Introduction	
7.2	Method	165
7.3	Results and discussion	168
7.4	Summary	174
7.5	References	176

Chapter 8 Conclusion 179

Glossary		187
----------	--	-----

Appendix 1 Summary of SWCNT-silicon solar cell
literature reports191
Appendix 2 Custom Labview [™] virtual instrument
for solar cell testing197
Appendix 3 Light and dark JV curves underlying
the data presented in Chapter 3 209
Appendix 4 Simulation of s-SWCNT absorption
properties

Abstract

The environmental and climatic drivers for massively increased use of photovoltaics for energy generation can hardly be understated. Due to the high cost of energy from the current generation of silicon-based photovoltaics relative to that from highly subsidised fossil fuels, there is great interest in finding alternative materials and device architectures for light harvesting applications. Single walled carbon nanotubes are an allotrope of carbon with some unique electrical and optical properties which make them promising as various elements of photovoltaic systems. Exploring and developing methods of harnessing their properties is thus desirable and much work has already been done in this emerging field. Before the work presented in this thesis began in 2009, carbon nanotubes had been employed in various roles in different types of solar cells including as transparent electrodes, as additives to improve charge dissociation and transport in organic bulk heterojunctions and the titania of dye sensitised solar cells, and as contributing or scaffolding elements of donor-acceptor type photoelectrochemical systems with porphyrins, quantum dots and more.

Throughout this thesis, the results of new experimental and theoretical investigations into some further applications of single walled carbon nanotubes in photovoltaics will be presented, with particular focus on carbon nanotube-silicon solar cells.

Declaration

I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

P.P.T-

Acknowledgements

In acknowledging the input of others in the production of this work I must start with the most important of all - my wife Melissa. Without her almost sole-parenting our girls for the last six months, and much more over the years, I could never have done any of this and indeed, without her inspiration, I wouldn't have even tried. I would also like to sincerely thank my supervisor Joe Shapter for his steadfast guidance and ever helpful advice throughout the PhD process and for his untiring support, and my co-supervisors Jamie Quinton and Amanda Ellis for all their input over the years. My doctoral studies were made easier by having friends and colleagues in the same field, in particular Benjamin Flavel, with whom I have also shared many a collaboration, and Katherine Moore, as well as Adam Blanch and Chris Gibson, Mark Bissett, Cameron Shearer and Ashley Slattery, not to mention the understanding and backing of old mates. I could not have become the first Doctoral student in my family without the solid and continuing foundation of love and support from my parents, Karen and Richard, and my inspirational sister, Luanne. I wish to extend my thanks also to Ralph Krupke for hosting my research stay at Karlsruhe Institute of Technology and for ongoing collaborations, The Flinders University of South Australia for providing a supportive environment in which I could pursue and develop my research, as well as for my undergraduate degree, the Australian Microscopy and Microanalysis Research Facility for many of the instruments I have relied upon and the Australian Nanotechnology Network for so many helpful conferences and workshops. Lastly, for good measure, I will thank my wife again.

Contextual statement

Each chapter in this thesis is either a complete published work, or a complete published work with additional data, analysis and discussion expanding upon that which can be found in the literature. The work in this thesis follows the Author's interest in exploring the use of single walled carbon nanotubes in photovoltaics, partly with a view to determining solar cell architectures which exploit the ability of single walled carbon nanotubes to absorb sunlight energy. Chapter 1 introduces the issues, states the case for using carbon nanotubes in solar cell applications and reviews some of the important background theory and literature, focussing particularly on carbon nanotube-silicon solar cells which form the bulk of this thesis. Chapter 2 reports the fabrication and characterisation of dye sensitised solar cells in which the titanium dioxide working electrode is replaced with nanotubes. Chapter 3 comprises a device structure analysis of carbon nanotube-silicon solar cells whilst Chapter 4 delves into the role that the nanotubes play in them. Chapter 5 compares devices with either semiconducting or metallic nanotubes and investigates the effect of nanotube film metallicity on solar cell output. In Chapter 6, the conductive polymer, polyaniline, is used in conjunction with the nanotubes with a synergistic effect on performance. Lastly, the modelling presented in Chapter 7 explores the use of single walled carbon nanotubes as the primary light absorbing elements of tandem solar cells and highlights the great potential of them for this purpose. All chapters have been edited for consistency however there may still remain some minor repetition and formatting differences.

Publications

The following is a list of the original publications arising from the Author's Doctor of Philosophy studies where this thesis incorporates all except publications 3 and 5.

- Tune, D.D., Flavel, B.S., Quinton, J.S., Ellis, A.V., and Shapter, J.G., Single walled carbon nanotube network electrodes for dye solar cells. Solar Energy Materials and Solar Cells, 2010. 94(10): p. 1665-1672. DOI: 10.1016/j.solmat.2010.05.026
- [2] Tune, D.D., Gibson, C.T., Quinton, J.S., Ellis, A.V., and Shapter, J.G. Single walled carbon nanotube array as working electrode for dye solar cells. in ICONN2010: International Conference on Nanoscience and Nanotechnology. 2010. Sydney, Australia. DOI: 10.1109/iconn.2010.6045232
- [3] Vogt, A.P., Gibson, C.T., Tune, D.D., Bissett, M.A., Voelcker, N.H., Shapter, J.G., and Ellis, A.V., *High-order graphene oxide nanoarchitectures*. Nanoscale, 2011. 3(8), pp.3076-3079. DOI: 10.1039/c1nr10406c
- [4] Tune, D.D., Flavel, B.S., Krupke, R., and Shapter, J.G., Carbon nanotubesilicon solar cells. Advanced Energy Materials, 2012. 2(9): p. 1043-1055. DOI: 10.1002/aenm.201200249
- [5] Larsen, L.J., Tune, D.D., Kemppinen, P., Winzenberg, K.N., Watkins, S.E., and Shapter, J.G., *Increased performance of single walled carbon nanotube photovoltaic cells through the addition of dibenzo[b,def]chrysene derivative.* Journal of Photochemistry and Photobiology A: Chemistry, 2012. 235(0): p. 72-76. DOI: 10.1016/j.jphotochem.2012.03.001

- [6] Tune, D.D., Flavel, B.S., Hennrich, F., Krupke, R., and Shapter, J.G. The role of nanotubes in carbon nanotube-silicon heterojunction solar cells. in ICONN2012: International Conference on Nanoscience and Nanotechnology. 2012. Perth, Western Australia.
- [7] Tune, D.D. and Shapter, J.G. Comparison by chirality of the sunlight absorption efficiency of carbon nanotube solar cells. in IWCN12: 3rd ISESCO International Workshop and Conference on Nanotechnology. 2012. Bangi, Malaysia.
- [8] Tune, D.D., Flavel, B.S., Quinton, J.S., Ellis, A.V., and Shapter, J.G., Single walled carbon nanotube/polyaniline/n-silicon heterojunction solar cells: fabrication, characterisation and performance measurements. ChemSusChem, 2013. 6(2): p. 320-327. DOI: 10.1002/cssc.201200600
- [9] Tune, D.D., Hennrich, F., Dehm, S., Klein, M.F.G., Colsmann, A., Shapter, J.G., Lemmer, U., Kappes, M., Krupke, R., and Flavel, B.S., *The role of nanotubes in carbon nanotube-silicon solar cells*. Advanced Energy Materials, 2013. 3(8): p. 1091-1097. DOI: 10.1002/aenm.201200949
- [10] Tune, D.D. and Shapter, J.G., *The potential sunlight harvesting efficiency of single walled carbon nanotube solar cells*. Energy & Environmental Science, 2013. 6(9): p. 2572-2577. DOI: 10.1039/c3ee41731
- [11] Tune, D.D. and Shapter, J.G., The potential sunlight harvesting efficiency of single walled carbon nanotube solar cells. in NT13: The Fourteenth International Conference on the Science and Application of Nanotubes. 2013. Helsinki, Finland.
- [12] **Tune, D.D.,** and Shapter, J.G., *Single walled carbon nanotube front electrodes for silicon heterojunction solar cells.* In preparation, 2013.
- [13] **Tune, D.D.,** Blanch, A.J., Flavel, B.S., Krupke, and Shapter, J.G., *The effect* of nanotube film metallicity on single walled carbon nanotube-silicon heterojunction solar cells. In preparation, 2013.