Carbon Nanotubes for Photovoltaic Devices

Flinders UNIVERSITY

smart surface structures

Thesis submitted to the School of Chemical and Physical Sciences, Faculty of Science and Engineering, Flinders University in fulfilment of the requirements for the degree of Doctor of Philosophy

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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.

Mark Alexander Bissett

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Publications From This Thesis

Journal Publications

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2. **Bissett, M. A**.; Shapter, J. G., Electrochemistry and Photocurrent Response from Vertically-Aligned Chemically-Functionalized Single-Walled Carbon Nanotube Arrays. *J. Electrochem. Soc.* 2011**,** *158* (3), K53-K57, DOI: 10.1149/1.3527057

3. **Bissett, M. A.**, Köper, I., Quinton, J. S., Shapter, J. G., Dendron Growth from Vertically Aligned Single-Walled Carbon Nanotube Thin Layer Arrays for Photovoltaic Devices. *Phys. Chem. Chem. Phys. 2011, 13, 6059-606,* DOI: 10.1039/C0CP02740E.

4. **Bissett, M. A.**, Barlow, A. J., Shapter, J. G., Quinton, J. S., Transition from single to multi-walled carbon nanotubes grown by inductively coupled plasma enhanced chemical vapor deposition. *J. Appl. Phys.* 2011, 110 (13), 34301-34306, DOI:10.1063/1.3615945

5. **Bissett, M. A.**, Köper, I., Quinton, J. S., Shapter, J. G., Dye Functionalisation of PAMAM-type Dendrons Grown from Vertically Aligned Single-Walled Carbon Nanotube Arrays for Light Harvesting Antennae. *J. Mater. Chem.* 2011, DOI: 10.1039/C1JM13957F

6. **Bissett, M. A.**, Barlow, A. J., Shearer, C., Quinton, J. S., Shapter, J. G., Carbon Nanotube Modified Electrodes for Photovoltaic Devices. *Carbon,* In Press

Published Conference Proceedings

1. **Bissett, M. A.**, Köper, I.; Shapter, J.G., Photocurrent Response from Vertically Aligned Single-walled Carbon Nanotube Arrays. *Proceedings of the International Conference on Nanoscience and Nanotechnology* (ICONN2010)

2. Shapter, J.G., **Bissett, M. A**.; Photocurrent Response from Vertically-Aligned Chemically-Functionalised Single-walled Carbon Nanotube Arrays. *Proceedings of the International Conference on Nanotechnology: Fundamentals and Applications* (ICNFA2010)

3. **Bissett, M. A.**, Barlow, A. J., Shapter, J. G, Quinton, J. S.; Raman Characterisation of Carbon Nanotubes Grown by Plasma Enhanced Chemical Vapour Deposition. *Proceedings of the Fifth International Conference on Advanced Materials and Nanotechnology* (AMN-5)

Conference Presentations

1. *"Photocurrent Response from Vertically Aligned Single-walled Carbon Nanotube Arrays",* International Conference on Nanoscience and Nanotechnology 2010 (ICONN2010), Sydney, NSW, Australia

2. *"Electrochemical Impedance Spectroscopy of Chemically Modified Single-Walled Carbon Nanotube Arrays",* ARNAM/ARCNN 2010 Joint Workshop, Adelaide, SA, Australia

3. "Dendrimer Functionalisation of Single Walled Carbon Nanotube Arrays", 23rd International Microprocesses and Nanotechnology Conference (MNC 2010), Kokura, Fukuoka, Japan

4. *"Plasma Enhanced Chemical Vapour Deposition Growth of Single-Walled Carbon Nanotubes"*, Fifth International Conference on Advanced Materials and Nanotechnology (AMN-5), 2011, Wellington, New Zealand

Abstract

The aim of this work was to investigate how carbon nanotubes can be applied in the development of novel photovoltaic devices. This has been done by taking an existing system of vertically aligning single-walled carbon nanotubes on oxide surfaces and adapting it to solar cell design. Once the ability to construct solar cells from CNT functionalised electrodes was demonstrated, work then focused on improving the performance of these cells. Initially arrays of vertically aligned SWCNT were used as the working electrode in a DSSC type cell architecture. These CNT solar cells were then characterised by photovoltaic testing. The arrays themselves were investigated using electrochemistry and Raman spectroscopy. It was found that the vertically aligned single walled carbon nanotube arrays were capable of producing a prompt, response times less than 200ms, and stable photocurrent of ~13µA.cm^{-2} and a voltage of 42mV when exposed to 100mW.cm^{-2} of light. This photoresponse changed with the number of nanotubes attached to the surface and the treatment time used to process the CNTs before attachment. Multi-walled carbon nanotube arrays were also created and analysed and found to be inferior to the SWCNT arrays due to their metallic band structure.

To improve upon the response of the SWCNT arrays they were then chemically modified to increase the cell's performance. This will be done firstly by further functionalising the CNT arrays with chromophores such N3 dye and ruthenium tetraphenyl porphyrin molecules. Attachment of these redox active molecules was verified by electrochemistry and the surface concentration and electron transfer rates compared to literature and found to be in good agreement. Photovoltaic testing indicated that N3 dye attachment lead to an increased photocurrent density (~17µA.cm^{-2}) but a reduced voltage (26mV) when compared to the unmodified array, in agreement with similar work in the

literature. This response could also be modified by altering the attachment of nanotubes to the surface thus altering the resultant dye concentration, with 2 hours of CNT attachment found to produce the maximum dye concentration. Functionalisation was then progressed from simple molecules to PAMAM-type dendrons that were grown from the SWCNT array acting as a core. These dendrons were analysed using electrochemistry, Raman spectroscopy and photovoltaic testing and found to be able to increase performance over the unmodified array by ~70% for the 2^{nd} generation dendron. The two methods of chemical modification were then combined with the dendrons being grown from the SWCNT array and then N3 dye attached to the amine terminated chains. This produced an increased performance over the unmodified dendron with a current density of ~15μA.cm^{-2} whilst maintaining a voltage of 45mV.

To further increase the density of carbon nanotubes on the surface growth of CNTs was undertaken using chemical vapour deposition and then the resultant performance compared to the chemically attached arrays. Growth of nanotubes was undertaken using both thermal and plasma-enhanced procedures. Thermal CVD was found to produce predominantly MWCNT whilst PECVD was able to produce SWCNT. It was found upon comparison of the CVD growth procedure to the covalent attachment that the chemical attachment provided for superior electron transfer kinetics despite lower nanotube coverage. This equated into a superior photoresponse. It was also found that the grown SWCNT were superior to the grown MWCNT, in agreement with previous results which suggested that SWCNT are needed to produce photocurrent due to their semi-conducting nature.

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Abbreviations

4-Aminopyridine	4-AP
Air Mass	AM
Acetylene	C_2H_2
Counter Electrode	CE
Methane	CH_4
Carbon Nanotube	CNT
Constant Phase Element	CPE
Cyclic Voltammetry	CV
Chemical Vapour Deposition	CVD
Disorder Raman Band	D-Band
N,N'-Dicyclohexylcarbodiimide	DCC
Dichloromethane	DCM
De-Ionised	DI
4-Dimethylaminopyridine	DMAP
N,N-Dimethylformamide	DMF
Dimethyl Sulfoxide	DMSO
Density of States	DOS
Differential Pulse Voltammetry	DPV
Dye Sensitised Solar Cell	DSSC
Ethylenediamine	EDA
Energy Dispersive X-ray Analysis	EDX
Electrochemical Impedance Spectroscopy	EIS
Peak Potential	E_p
Fill Factor	*ff*
Fluorine Doped Tin Oxide	FTO
Full Width Half Maximum	FWHM
Graphitic Raman Band	G-Band
Hydrogen Peroxide	H_2O_2
Sulphuric Acid	H_2SO_4
Nitric Acid	HNO_3
Iodide/Tri-iodide	I^-/I_3^-

Inductively Coupled Plasma	ICP
Incident Photon to Current Efficiency	IPCE
Indium Tin Oxide (In_2O_3 90% - SnO_2 10%)	ITO
Current-Voltage	I-V
Short Circuit Current Density	J_{sc}
Current Density-Voltage	J-V
Electron Transfer Co-efficient	k_s
Multi-Walled Carbon Nanotube	MWCNT
cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)	N3
Poly(amidoamine)	PAMAM
P-Phenylenediamine	PDA
Plasma Enhanced Chemical Vapour Deposition	PECVD
Radial Breathing Mode	RBM
Reference Electrode	RE
Ruthenium Tetraphenyl Porphyrin	RuTPP
Standard Cubic Centimetres per Minute	SCCM
Scanning Electron Microscopy	SEM
Single-Walled Carbon Nanotube	SWCNT
Tetrabutylammonium Hexafluorophosphate	$TBAPF_6$
Thermal Chemical Vapour Deposition	tCVD
Transmission Electron Microscopy	TEM
Titanium Dioxide, Titania	TiO_2
Ultra-Violet-Visible Light Spectroscopy	UV-Vis
Open Circuit Voltage	V_{oc}
Working Electrode	WE
X-ray Photoelectron Spectroscopy	XPS
Real Component of Impedance	Z’
Imaginary Component of Impedance	Z”
Global Efficiency	η
Scan Rate	*v*
Raman Frequency	ω