

Single Walled Carbon Nanotube Array as Working Electrode for Dye Solar Cells

Daniel D. Tune, Christopher T. Gibson, Jamie S. Quinton, Amanda V. Ellis, and Joseph G. Shapter

Centre for Nanoscale Science and Technology

School of Chemical and Physical Sciences, Flinders University, Bedford Park, South Australia

Abstract - A new working electrode for dye solar cells has been fabricated incorporating an array of dye sensitised single walled carbon nanotubes on an indium tin oxide coated glass substrate as a replacement for the titania used in conventional dye solar cells.

Keywords - SWCNT, indium tin oxide, N3 dye, AFM, UV-Vis

I. INTRODUCTION

Since they were first reported by Iijima and co-workers in 1991 [1] carbon nanotubes have attracted interest across a diverse range of fields including, but not limited to, microelectronics [2], medicine [3], energetic materials [4], polymers [5], energy storage [6] and recently, light harvesting [7-10]. Single-walled carbon nanotubes (SWCNTs) display excellent electrical conductivity in the longitudinal direction but conduct poorly through their sidewalls.

Coupled with their very large surface area to volume ratio this makes them good candidates as scaffold material for the photoactive sensitizer in dye solar cells (DSCs) based on the O'Regan/Grätzel architecture [11]. Furthermore, it is suggested that a nanoporous network of SWCNTs has the potential to provide a greater surface area for dye attachment than the mesoporous titania currently employed as the scaffold in DSCs.

II. RESULTS AND DISCUSSION

The cell electrodes use SWCNTs functionalised with carboxyl groups using a well established technique [12]. The carboxylated SWCNTs are covalently bound by ester bonds to previously hydroxylated indium tin oxide (ITO) in the presence of dicyclohexylcarbodiimide (DCC) coupling agent to produce ITO-SWCNT. The SWCNT functionalised substrate is then sensitised with the 'N3' ruthenium dye [13] [*cis*- bis(4,4' -dicarboxy -2,2' -bipyridine) dithiocyanato ruthenium(II)] via an ethylenediamine linker to produce ITO-SWCNT-N3 as shown in Fig. 1. The amidic addition of ethylenediamine to the SWCNTs and subsequent attachment of the ruthenium dye to the resultant free amine is catalysed by both DCC and dimethylaminopyridine (DMAP).

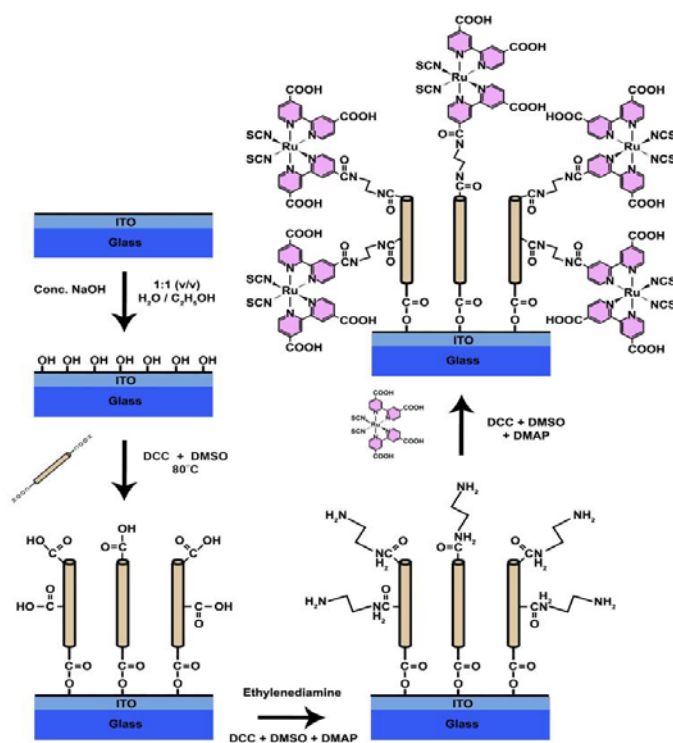


Figure 1: Reaction pathway beginning with ITO coated glass (upper left) which is hydroxylated (middle left) and carbon nanotubes are added (lower left). To these are attached an ethylenediamine linker (lower right) which facilitates the attachment of the dye sensitizer (upper right).

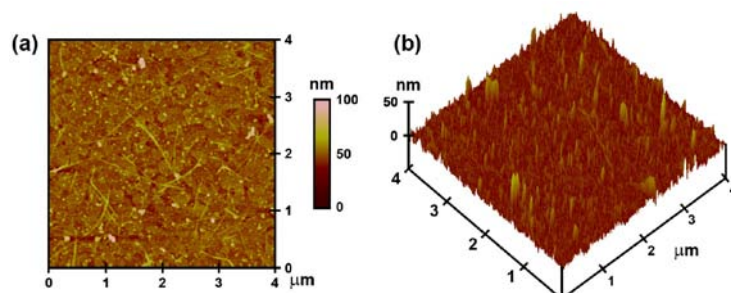


Figure 2: (a) Tapping mode AFM image of single-walled carbon nanotubes on an indium tin oxide coated glass substrate. (b) 3D representation of the image shown in (a).

AFM images of the electrode surface (Fig. 2) show that the SWCNTs are present on the surface predominantly in the vertical orientation, although some horizontally aligned SWCNTs are evident. Vertical orientation of SWCNTs greatly increases the surface area available for dye attachment. The preference for electron transfer down a SWCNT rather than through its sidewall also means that

electron conduction between the dye and the ITO is favoured over reduction of the electrolyte at the SWCNT surface. In DSCs employing titania, reduction of the electrolyte via photo-generated electrons at the titania/electrolyte interface is one of the most significant drawbacks and it is suggested that using SWCNTs instead may reduce the likelihood of this type of back reaction occurring.

The attachment of the dye to the diamine functionalised SWCNT electrode is verified UV-Visible spectroscopy (Fig. 3). Peaks observed at 380 nm and 505 nm are characteristic of the two types of metal to ligand charge transfer (MLCT) between the ruthenium complex centre and its dual bipyridine and thiocyanate ligands. Due to the very small quantity of SWCNTs on the electrode surface the amount of ruthenium dye present is correspondingly small hence the observation of c.a. 1% absorbance peak height in Fig. 3(a). The position of the MLCT bands at 380 nm and 505 nm in Fig. 3(a) is shifted slightly from those at 405 nm and 525 nm in Fig. 3(b). This is due to the effect of the dimethylsulphoxide (DMSO) solvent used to obtain the absorption spectrum of the ruthenium dye compared to the dye sensitised electrode for which the absorption spectrum was obtained in air.

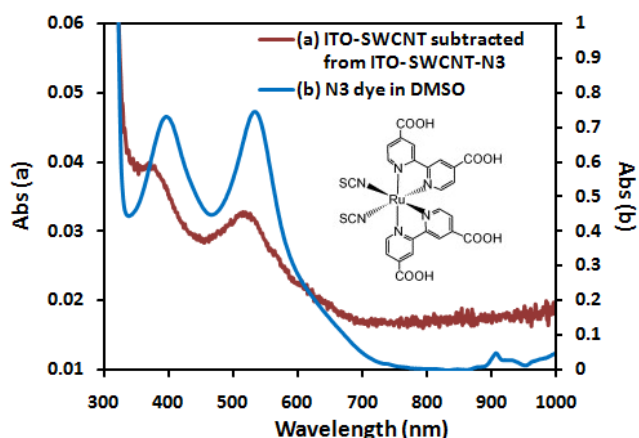


Figure 3: Comparison of UV-Vis difference spectrum produced by subtracting the spectrum of ITO-SWCNT from that of ITO-SWCNT-N3 with the UV-Vis spectrum of the N3 ruthenium dye showing characteristic MLCT bands.

The new working electrodes were incorporated into complete DSCs employing a platinum coated fluorine tin oxide (FTO) counter electrode (Fig. 4). The electrolyte used was a solution of 3-methoxypropionitrile containing 1-propyl 3-methylimidazolium iodide, iodine and benzimidazole, also known as 'robust' electrolyte. The iodide/triiodide redox couple allows for the refilling of photo-generated holes at the working electrode whilst the addition of benzimidazole has been shown to increase photovoltaic performance in titania-based DSCs [14].

Cells incorporating the new SWCNT-based working electrode produce an appreciable photoresponse under illumination with simulated sunlight. The light used was a quartz arc lamp producing 25 mW cm^{-2} at the cell surface and light entered the cell through the working electrode. Tests were performed at $25 \text{ }^\circ\text{C}$ and since light was channelled to the cell via a fibre optic cable, no heating of the cell was observed during the course of experiments.

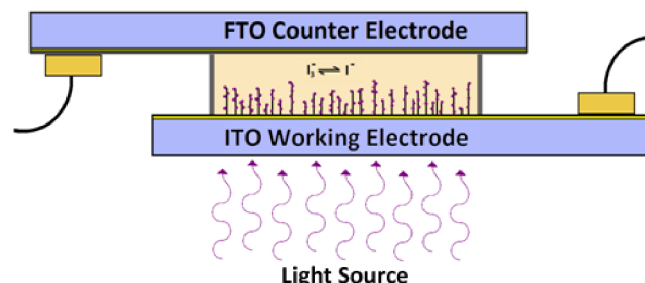


Figure 4: Schematic of DSC incorporating dye-sensitised SWCNT working electrode.

Current-voltage data was collected on a Keithley 236 Source Measure Unit and recorded using a custom Digital Instruments' LabView virtual instrument. The dye sensitised SWCNT cells produced an open circuit photovoltage (V_{OC}) of 43 mV, a short circuit current density (J_{SC}) of $2.8 \text{ } \mu\text{A cm}^{-2}$ and the fill factor of the J/V curve was 0.28. This modest photoresponse, coupled with the minimal fill factor indicate (a) considerable electron hole recombination within the cell and/or (b) a significant mismatch between the energy levels of the various cell components, upon which the performance of DSCs is highly dependent. Of course, the quantity of photoactive material on the surface is miniscule compared to that in conventional DSCs so it was not expected that the power generated would be comparable. Further work will involve developing strategies for increasing the number of SWCNTs on the surface to allow for the attachment of more dye.

Importantly, in contrast to DCSs using a titania scaffold for dye adsorption, the observed photocurrent of the SWCNT-based DSC flows in the reverse direction. In titania-based cells the excited dye injects photo-generated electrons into the conduction band of the titania with the resultant holes in the dye being filled by oxidation of triiodide to iodide. In these SWCNT-based cells, photo-generated electrons must reduce the iodide to triiodide with resultant holes being refilled by electrons returning from the external circuit via the ITO and SWCNTs. This reversal of the direction of photocurrent is certainly a result of a substantial difference in the potential of SWCNTs conduction band(s) compared to that of titania and suggests a markedly different mechanism of electron transfer within and between the components of the DSC. This effect and the electronic basis for it are currently being investigated.

Another noteworthy observation is that cells fabricated from working electrodes containing only SWCNTs produce a significant photoresponse without any sensitisation by photoactive dye. In fact, the SWCNT-only cells produce a V_{OC} of 47 mV, a J_{SC} of $2.0 \mu A cm^{-2}$ and a fill factor of 0.28. This means that photo-generated charge separation is occurring within the SWCNTs and that iodide is being reduced to triiodide at the surface or, more likely the open ends, of the SWCNTs. The generation of excitons within SWCNTs when illuminated by light is one of 'the unique electrical and optical properties of SWCNTs' so often mentioned in the introductions of SWCNT-related publications but these excitons are very tightly bound and usually decay rapidly via phonon emission long before they can be exploited. The fact that the observed photocurrent of the SWCNT-only cell is $\sim 71\%$ of that produced by the dye sensitised cell shows that whilst dye sensitisation does increase photoresponse it is the action of the SWCNTs that accounts for most of the power generated. Furthermore, the reduction of V_{OC} from 47 mV to 43 mV upon dye sensitisation implies (a) a reduced ability of the cell to maintain charge separation (likely due an increased back reaction of electrons from triiodide to SWCNT and/or ITO – effectively a short circuit) and/or (b) the dye introducing an electronic state between the SWCNT and the iodide/triiodide thus reducing the maximum obtainable voltage.

III. CONCLUSION

Solar cells based on the O'Regan/Grätzel architecture were fabricated from working electrodes incorporating an array of dye sensitised SWCNTs as a replacement for the conventional mesoporous titania scaffold. The morphology of the electrode was shown to consist of SWCNTs aligned predominately in the vertical orientation with respect to the surface. Dye sensitisation via an ethylenediamine linker was confirmed by UV-Visible spectroscopy. The photovoltaic performance of cells containing the new working electrode was measured showing an appreciable, though modest, photoresponse. The source of the low power generated compared to conventional titania-based DSCs is largely due to far less photoactive material being present on the electrode surface. Additionally, a markedly reduced fill factor indicates substantial electron hole recombination the cells. Nevertheless, the observation of a photocurrent in both the dye sensitised and SWCNT-only cells reported in this work is promising for future low cost, minimal material use solar cell applications if the underlying mechanism of action is further understood and improved.

IV. ACKNOWLEDGMENTS

This work is supported by the Australian Microscopy and Microanalysis Research Facility (AMMRF).

REFERENCES

- [1] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, pp. 56-58, 1991.
- [2] K. Ryu, et al., "CMOS-Analogous Wafer-Scale Nanotube-on-Insulator Approach for Submicrometer Devices and Integrated Circuits Using Aligned Nanotubes," *Nano Letters*, vol. 9, pp. 189-197, 2008.
- [3] K. Bin, et al., "Cancer-Cell Targeting and Photoacoustic Therapy Using Carbon Nanotubes as 'Bomb' Agents," *Small*, vol. 5, pp. 1292-1301, 2009.
- [4] S. H. Tseng, et al., "Ignition of carbon nanotubes using a photoflash," *Carbon*, vol. 45, pp. 958-964, 2007.
- [5] J. Zhang, et al., "Conductive carbon nanoparticles hybrid PEO/P(VDF-HFP)/SiO₂ nanocomposite polymer electrolyte type dye sensitized solar cells," *Solid State Ionics*, vol. 178, pp. 1595-1601, 2007.
- [6] M. Hirscher, et al., "Hydrogen Absorption in Carbon Nanotubes: A Critical Review," in *Encyclopedia of Materials: Science and Technology* Oxford: Elsevier, 2006, pp. 1-4.
- [7] Z. Li, et al., "Light-Harvesting Using High Density p-type Single Wall Carbon Nanotube/n-type Silicon Heterojunctions," *ACS Nano*, vol. 3, pp. 1407-1414, 2009.
- [8] J. Yu, et al., "Ruthenium Porphyrin Functionalized Single-Walled Carbon Nanotube Arrays - A Step Toward Light Harvesting Antenna and Multibit Information Storage," *Journal of the American Chemical Society*, vol. 130, pp. 8788-8796, 2008.
- [9] R. Ulbricht, et al., "Transparent carbon nanotube sheets as 3-D charge collectors in organic solar cells," *Solar Energy Materials and Solar Cells*, vol. 91, pp. 416-419, 2007.
- [10] T. Y. Lee, et al., "Fabrication of dye sensitized solar cell using TiO₂ coated carbon nanotubes," *Thin Solid Films*, vol. 515, pp. 5131-5135, 2007.
- [11] B. O'Regan, et al., "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films," *Nature*, vol. 353, pp. 737-740, 1991.
- [12] M. W. Marshall, et al., "Measurement of functionalised carbon nanotube carboxylic acid groups using a simple chemical process," *Carbon*, vol. 44, pp. 1137-1141, 2006.
- [13] M. K. Nazeeruddin, et al., "Conversion of light to electricity by cis-bis (2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium(II) charge-transfer sensitizers (X = Cl-, Br-, I-, CN-, and SCN-) on nanocrystalline titanium dioxide electrodes," *Journal of the American Chemical Society*, vol. 115, pp. 6382-6390, 1993.
- [14] H. Kusama, et al., "Influence of benzimidazole additives in electrolytic solution on dye-sensitized solar cell performance," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 162, pp. 441-448, 2004.