Metal octacarboxyphthalocyanines/ Multi-walled carbon nanotubes hybrid for development of dye solar cells

Kanyane Nonhlanhla Mphahlele
OUTLINE

Background and Introduction

Experimental Procedure

Characterization

Electrochemical Evaluation

Conclusions

Acknowledgements
Dye solar cells (DSCs) have become one of the attractive devices as an alternative energy resources for the conversion of solar irradiation into electricity:

- Low cost
- Easy to fabricate
- Non toxic
- Light weight and semitransparent

First reported in 1991, by O’Regan and Gratzel with a solar power conversion of 11%.

This device was achieved by using high surface area nanocrystalline TiO₂ coated with an adsorbed dye molecule in order to maximise light harvesting.
DSCs

Three main components in DSCs

Working electrode, Counter electrode and Electrolyte (iodide/triiodide redox couple)

**Major research areas**

- Investigate an alternative photosensitiser to enhance the performance and efficiency of DSCs.

**Requirements for Sensitisers**

- Sensitisers should be panchromatic.
- Contain functional groups such as Carboxylic group.
- It should have suitable ground and excited state for redox properties.
- The energy level of the excited dye molecule should be well matched to the lower bound of the conduction band.
- Stable to sustain about $10^8$ turnover cycles for about 20 years when exposed to light.
- Thermal and photochemical stability.

Alternative Photosensitiser

Metal octacarboxyphthalocyanines

The use of MPc in DSCs is rarely reported
**Background of Phthalocyanines**

- Aromatic planar complex
- Tetraazoporphyrins – four isondole unit
- Braun and Teherniac – 1907
- Pcs have been used: Pigments and dyestuff for over 70 years

![Graph showing absorbance vs wavelength with B-band and Q-band peaks]

- Two isolated absorption band
- Modifying MPC with MWCNT
- CNT – efficient catalyst and conductive species

Approach:

• Synthesise various metal octacarboxyphthalocyanine (M = Ga, Zn, Si);
• Modification with multiwalled carbon nanotubes;
• Investigate the spectroscopic, microscopic; determine the electrochemical behaviour of metal octacarboxyphthalocyanines supported on carbon nanotubes
• Incorporate in DSC
Synthesis of Metal Octacarboxyphthalocyanines

Urea, metal salt, DBU
Reflux for 30mins

20% $\text{H}_2\text{SO}_4$
Reflux for 3days

$[\text{MOCPC (} M = \text{Zn, (OH)}_2\text{Si & (OH)Ga)}]$

[Diagram of the synthesis process with chemical structures and reaction conditions]
Synthesis route for the MOCPc - MWCNT

(i) Acid functionalization
(ii) Thionyl chloride
(iii) Ethylenediamine / DCC

DMF / ultrasonication
Fabrication of DSCs using MOCPc-MWCNT hybrid

Complete DSCs

- ITO glass substrate
- TiO$_2$ substrate
- Pt catalyst substrate
- MPc adsorbed on TiO$_2$

Solar tester
Autolab system

Graphs (a) and (b) show the current density ($j$) vs. voltage ($V$) for different conjugated polymers: ZnOCPC, (OH)2SiOCPC, (OH)GaOCPC, ZnOCPC-MWCNT, (OH)2SiOCPC-MWCNT, and (OH)GaOCPC-MWCNT.
Electronic spectra of MOCPc and MOCPc-MWCNTs in DMF. Upon integration with MWCNT, Q band red shifted.
XRD & EDX

- Raw MWCNT
- a-MWCNT
- MWCNT-NH2
- SiOCPc-MWCNT

C (002)
C (100)

Counts/μ

0.15 1.15 2.15
KeV 2.15

(OH)GaOCPc-MWCNT
(OH)2SiOCPc-MWCNT
ZnOCPc-MWCNT

C
O
Si
Ga
Cl
Zn
Si
Cl
Clearly showing the attachment of ZnOCPc molecules on the walls and edge-plane sites of the MWCNTs.
Both the MPc and MPc-MWCNT hybrids on the ITO substrate show photocurrent response under visible light illumination, a reversible rise/decay of the photocurrent in response to the on/off illumination. The measurements show an almost rectangular photoresponse when switching on and off the illumination.
CHRONOAMPEROMETRY

![Graph showing chronopotentiometry measurements with labels (OH)GaOCPc-MWCNT and (OH)GaOCPc-ON OFF.](image)
Nyquist plots of DSCs fabricated with a) TiO$_2$/ZnOCPc, b) TiO$_2$/((OH)$_2$SiOCPc and their corresponding MWCNT-integrated hybrids.

Investigate the electron transport and recombination mechanism of DSCs.
Nyquist plots of DSCs fabricated with c) TiO\textsubscript{2}/OHGaOCPc and their corresponding MWCNT-integrated hybrids.

Vogit circuit comprising three RC elements in series to fit the circuit.
MOCPc (M = Ga, Si, Zn) complexes were successfully synthesised. As confirmed by FTIR, UV/Vis and electrochemistry characterisation. Amine functionalised multi-walled carbon nanotubes were successfully incorporated with MOCPc to produce MOCPc - MWCNTs hybrid and satisfactory characterisations were obtained. The incorporation of MWCNTs improved the photocurrent response of MOCPc. Therefore, ZnOCPc - MWCNT showed high photocurrent response than (OH)$_2$SiOCPc - MWCNT and (OH)GaOCPc - MWCNT.
• **Prof. Kenneth Ozoemena:** Research group leader

• **Dr Lukas Le Roux:** Senior researcher at CSIR

• **Dr Leskey Cele:** Senior Lecture at TUT

• **Dr Mkhulu Mathe:** Competence area manager

• **Tohoku university = Japan**
Thank You

www.tut.ac.za