**Declaration**


I declare that this thesis titled "**Fly ash catalysed synthesis of CNFs for use in a photocatalytic CNF-$TiO_2$ hybrid"** is my own, unaided work.

It is being submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg,

in fulfilment of the requirements for the degree of Master of Science

(2015)

**Dedication**

This small voyage into the nanoworld of materials is only a small endeavour of hearing God's language and laws set in inanimate objects- "For by Him were all things created, that are in heaven, and that are upon earth, visible and invisible, whether thrones, or dominions, or principalities, or powers: all things were created by Him, and for Him: And He is before all things, and by Him all things consist…"

This work is an attempt to understand His splendour, creativity and fecundity through scientific enquiry. And it is in nature that we see His glory and are without excuse.

To my family, friends and fellow inquisitive beings made in His image!

## Acknowledgements

***Yahweh***

I would like to acknowledge my God and Lord, Jesus, for being with me as He promised and the Father, who in times of need has constantly fed me with His Spirit, the Holy Spirit. God decided that all the people who will surround me will be the ones who will carry me through His will and I cannot express, enough, the gratitude I have for them.

*Dr Shane Durbach*

Thanks to him for taking the task of being my supervisor, seeing potential in me and keeping to his promise. I am grateful for all the scientific insight, the prayers, the freeness he allowed me to have with regard to the work set before me. I am forever grateful for his steadfastness in being directed by God in all things pertaining to me. May his life be darted with more of the work he does through the power of God.

*Dr Paul Franklyn*

Thanks to him for co-supervising me and giving me the freedom to look into matters creatively. His scientific foresight helped me view my work in perspective. He opened up my understanding to more than I had imagined. I pray that God, my God, may increase His grace to him and his family.

*Mbali Mkhabela (Ba'e)*

To my Love, who has been my chief editor and tireless cheer-leader. God grant us many more years of joy, peace and love. His name above all be glorified in all our dealings. Thank you.

*Family and friends*

To my family & friends (Sello especially) who showed interest in my work & have great hopes for me. For being with me in Spirit through their prayers & supplications for my success in all I do. May my Lord show more grace & mercy as He did on Calvary for our sins. Amen.

Thanks to everyone whose help I may not have acknowledged, those who will assess this work and the Catommat group along with the School of Chemistry of the University of the Witwatersrand.

## Presentations

- NYRS presentation 2013: "***One pot synthesis of a CNF-$TiO_2$ composite for possible applications in photocatalysis***", 2nd prize
- Oral presentation at the Board meeting of the DST-NRF Centre of Excellence in Strong Materials, 2014 entitled: "***From waste to carbon nanofibres: why and how?***"

## Publications

The following manuscripts have been prepared for publication and will be submitted shortly:

1) The synthesis of CNFs from fly ash: monitoring the growth mechanism using laser Raman spectroscopy and transmission electron microscopy-EDS
2) The optimisation studies of a simple hydrothermal synthesis of a CNF-$TiO_2$ hybrid
3) C-$TiO_2$ hybrids: A review

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## Abstract

This study has explored the CVD synthesis of carbon nanofibres (CNFs) using Eskom's waste coal fly ash as a catalyst with acetylene and hydrogen as the carbon source and carrier gas, respectively. In the process, a possible growth mechanism for these carbon nanofibres was sought. CNFs were successfully synthesised from fly ash and were found to have an average diameter of 22±7 nm.

The growth mechanism of these CNFs was studied using EDS, TEM and laser Raman spectroscopy. It was observed that CNFs grew via root growth on spherical particles of fly ash and by tip growth on irregular-shaped metal oxide agglomerates. Both of these were found, through EDS analysis, to be Fe-rich.

CNFs were functionalised between 2-12 h under reflux at 110 °C using a 3:1 (v/v) combination of $HNO_3$ and $H_2SO_4$ in order to introduce functional groups onto their surfaces to act as anchors for hydrophilic reactants. The functionalisation of these CNFs was studied using TEM, laser Raman spectroscopy, ATR-FTIR spectroscopy, PXRD, BET, XRF and TGA. ATR-FTIR spectroscopy showed that some carbonyl functional groups were present on the surfaces of these CNFs after functionalisation.

The functionalised CNFs (fCNFs) were then treated using a simple hydrothermal method to deposit 10% (m/m) of $TiO_2$ nanoparticles onto their surface. This hydrothermal method employed the drop-wise addition of $TiCl_4$ to a cold water-fCNFs mixture, which was then refluxed at 115 °C for 2-12 h. Laser Raman spectroscopy confirmed the presence of both $TiO_2$ (phase pure anatase) and CNFs. ATR-FTIR spectroscopy provisionally revealed the presence of covalent Ti-O-C bonds.

Studies where the duration of exposure to $TiCl_4$ and the functionalisation time of CNFs were examined showed that the particle size and agglomeration of the $TiO_2$ nanoparticles did not affect the surface area of the CNF-$TiO_2$ hybrids significantly. However, CNF-$TiO_2$ hybrids which were shown by TGA to have high fly ash content were observed to have low surface areas. fCNFs functionalised at 2 h had the highest surface area, at all fixed durations of exposure to $TiCl_4$ by comparison with fCNFs which had been functionalised for longer periods.

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## List of Abbreviations

CVD- Chemical vapour deposition

CNFs- Carbon nanofibres

ATR-FTIR- Attenuated total reflection Fourier Transform Infrared spectroscopy

fCNFs- Functionalised carbon nanofibres

SEM- Scanning electron microscopy

ASTMs- American Society for Testing Materials

REE- Rare earth elements

CNT/s- Carbon nanotube/s

PECVD- Plasma enhanced chemical vapour deposition

NHE- Normal hydrogen electrode

UV- Ultraviolet

EDS- Energy dispersive X-ray spectrometry

TGA- Thermogravimetric analysis

PXRD- Powder X-ray diffraction

XRF- X-ray fluorescence spectrometry

BET- Brunauer-Emmett-Teller

FIB/SEM- Focused ion beam scanning electron microscopy

TEM- Transmission electron microscopy

HRTEM- High resolution transmission electron microscopy

VTPXRD- Variable temperature powder X-ray diffraction

SPM- Scanning probe microscopy

AFM- Atomic force microscopy

UHR-STEM- ultra high resolution scanning transmission electron microscopy