SYNTHESIS AND STUDY OF CARBON NANOTUBES AND CARBON SPHERES

Sabelo Dalton Mhlanga

(Student number: 0405600Y)

Degree of Doctor of Philosophy in Chemistry

A thesis submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the Degree of Doctor of Philosophy.

February 2009

DECLARATION

I declare that the work presented in this thesis was carried out by myself under the supervision of Professor Neil. J. Coville. It is being submitted for the degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg, and has not been submitted before for any degree or examination at any other university.

_____

Sabelo Dalton Mhlanga

On this _____ day of _____ 2009

Dedicated to

My beautiful wife Phindile Thembelihle Zwane,

my mother Margaret Makoti Masuku, *my grandmother Mirriam Estel Masuku,*

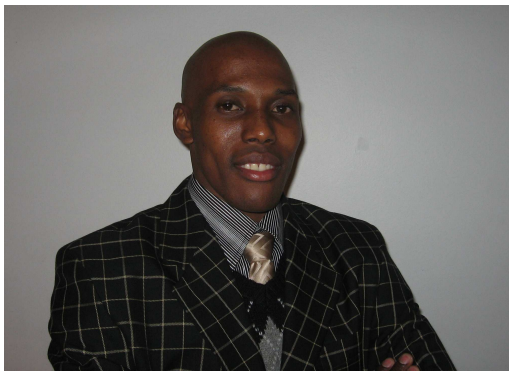
my sisters and brothers

and

to the memory of my father Daniel July Mhlanga.

"The love that I have for you cannot be measured. May God bless you all."

ACKNOWLEDGEMENT



I cannot adequately thank everyone who has contributed to my successes (of any kind). Indeed "*i'm in need of a thousand tongues"* to express my sincere gratitude to the following people:

- My supervisor and mentor **Professor Neil. John Coville** for being such an inspiration to my life. Prof. has not only been a supervisor but a true father and a role model to me. I could write a whole book about my encounters with him in the past three years that I spent with him. He has impacted positively in my life academically and personally. He has instilled confidence in me and for that I have achieved many honours and awards during my stay at wits.

- My friends and colleagues in our research group, the **catalysis-materials-organometallics** (CATOMAT) group in the school of chemistry, headed by Prof. Neil Coville and Prof. Mike Scurrell. "You guys were awesome to hang around with. I would like to acknowledge all of you for honouring my wedding ceremony on the 13th December 2008, and for being such a friendly and sociable group. Keep up the good work in the group and leave a good mark. *I will miss all the moments of laughter and sharing of jokes."*

- The **electron microscopy and microanalysis unit** personel: Professor Michael Witcomb, Abe Seema and Caroline Lalkhan. Thank you for your assistance and patience with me. "Those TEM images were put to good use".

- The **Molecular Sciences Institute, School of Chemistry** for giving me the grounds to conduct my research. I appreciate all those members of staff, chemical stores, and cleaning departments who became friends to me.

- The various **postdoctoral fellows** who helped me at the beginning to my studies, especially Dr Kartick Mondal and Dr Robin Carter. I also thank Dr Vincent Nyamori and Dr Amit Deshmukh for inviting me to write reviews with them.

- The various **honours students:** Nerona, Ahmed and Itumeleng whom I co-supervised in their honours' projects. The work done with them contributed a small part of this thesis.

- Mr **Edward Nxumalo, Ketulo Salipira** and **Ahmed Shaikjee** for proof reading this thesis. Ed and Ketulo have been a part of my life since our studies at M-Tech level. "I leave you guys to inspire other students within the research group."

- Mr **Basil Chassoulas** for all the technical assistance he rendered in the laboratory, such as the installation of gas lines and fixing the furnaces and reactors. Without him I may have taken longer to achieve some of my goals.

- Mr **Rudolf M. Erasmus** for doing the Raman analysis of my carbon nanotube and carbon sphere samples.

- The glassblowers, **Steve and Barry** for providing me with the quartz boats and reactors that were required by me to conduct experiments in the laboratory.

- Funding from the Wits Postgraduate Merit Award, the Mellon Postgraduate Mentoring Programme and the Council for Scientific and Industrial Research (CSIR) for funding my studies at Wits. I truly acknowledge and appreciated all the financial support.

- My internal and external examiners for taking their valuable time to examine this 'long' thesis.

- My wife, family and friends for believing in me and giving me support throughout the duration of my studies.

- *Above all and everyone I thank **God** for directing my footstep. With God nothing could be impossible for me. He's my father. To Him be all glory and honour.*

LIST OF PUBLICATIONS

The following publications emanated from different parts the work presented in this thesis.

1. Sabelo D. Mhlanga and Neil J. Coville, Iron-cobalt catalysts synthesized by a reverse micelle impregnation method for controlled growth of carbon nanotubes, *Diam. Rel. Mater*. **17** (2008) 1489.

2. Vincent O. Nyamori, Sabelo D. Mhlanga, Neil J. Coville. The use of organometallic transition metal complexes in the synthesis of shaped carbon nanomaterials, *J. Organometal. Chem.* **693** (2008) 2205.

3. Sabelo D. Mhlanga, Kartick C. Mondal, Nerona Naidoo, Nikiwe Kunjuzwa, Mike J. Witcomb, Neil J. Coville, Carbon microsphere supported cobalt catalysts, *S. Afr. J. Scie*, accepted, 2008.

4. Sabelo D. Mhlanga, Kartick C. Mondal, Robin Carter, Michael J. Witcomb and Neil J. Coville, The effect of synthesis parameters on the catalytic synthesis of multiwalled carbon nanotubes using Fe-Co/$CaCO_3$ catalysts, , *S. Afr. J. Chem.* **62** (2009) 67.

5. Kartick C Mondal, André Strydom, Zikhona Tetana, Sabelo D. Mhlanga, Mike J. Witcomb, Josef Havel, Rudolph Erasmus, Neil J. Coville, Boron Doped Carbon Microspheres: A New Generation Electronic Material, *Mater. Chem. Phys.* **114** (2009) 973.

6. Sabelo D. Mhlanga, Michael J. Witcomb, Rudolf M. Erasmus, Neil J. Coville, A novel $Ca_3(PO_4)_2$-$CaCO_3$ support mixture for the CVD synthesis of roughened multiwalled carbon nanotubes, *Mater. Chem. Phys.*, submitted, 2009.

7. Sabelo D. Mhlanga, Neil J. Coville, The effect of reagent residues on the stability and structure of CVD carbon nanotubes, *J. Nanoscie. Nanotechnol*, submitted revision, 2009.

8. Sabelo D. Mhlanga, Neil J. Coville, Sunny E. Iyuke, Ayo S. Afolabi, Saka A. Abdulkareem, Nikiwe Kunjuzwa, Controlled syntheses of carbon spheres in a swirled floating catalytic chemical vapour deposition (SFCCVD) vertical reactor, *to be submitted.*

9. U.M. Graham, A. Dozier, R.A. Khatri, M.C. Bahome, L.L. Jewel, S.D. Mhlanga, N.J. Coville, B.H. Davies, *Catal. Lett.* **129** (2009) 39.

PRESENTATION AT CONFERENCES AND SEMINARS

Date	Name and Place	Type of presentation
October 2006	CATOMAT seminar, Room C509 Humphrey Raikes Building, Wits University.	Oral
December 2006	SACI conference, UKZN, Durban	Poster
February 2007	DST/NRF Centre of Excellence in Strong Materials' Seminar, Room C6 Humphrey Raikes Building, Wits University.	Oral
July 2007	ICMR Conference at University of Zululand, Richards Bay, KwaZulu Natal.	Poster
September 2007	CATOMAT seminar, Room C509 Humphrey Raikes Building, Wits University.	Oral
September 2007	18th Diamond and Related Materials Conference, Berlin, Germany.	Poster
January 2008	South African Nanotechnology Initiative (SANi) stakeholder meeting, Physics Department, UCT.	Poster
February 2008	Centre of Excellence in Strong Materials' Seminar, Room C312 Humphrey Raikes Building, Wits University.	Oral
March 2008	DST/NRF Centre of Excellence in Strong Materials Research Showcase, Richard Ward Building, School of Chemical Engineering, Wits University.	Oral
July 2008	CATOMAT seminar, Room C509 Humphrey Raikes Building, Wits University.	Oral
October 2008	SACI Young Chemists Symposium – Gauteng Region, Room C6 Humphrey Raikes Building, Wits University	Oral
February 2009	3rd Nanoafrica 2009 conference, CSIR convention centre, Pretoria.	Oral
February 2009	School of Chemistry departmental seminar, PhD thesis - final, Room C6 Humphrey Raikes Building, Wits University.	Oral

Note: CATOMAT = catalysis-organometallics-materials research group

HONOURS AND AWARDS

1. November 2007: Obtained ***3rd position*** in the ***Wits Enterprise-National Innovation Competition*** with a business plan based on the making and selling of carbon nanotubes at a commercial scale. This business plan competition was open to all students of the University of the Witwatersrand and its emphasis was to promote entrepreneurship through innovation.

2. January 2008: Member of the ***South African Nanotechnology Initiative (SANi)*** executive committee as a student representative.

3. January 2008: Awarded ***best (1st place) student poster*** presentation at the SANi stakeholder workshop held at the University of Cape Town.

4. October 2008: Awarded ***1st place PhD oral presentation*** at the SACI Young Chemists' Symposium by the SACI and the Royal Society of Chemistry at Wits University.

5. October 2008: Awarded the distinguished ***Sasol Post-graduate Medal*** of the South African Chemical Institute. This medal is awarded to students engaged in research towards a MSc or PhD degree at a University, or a M-Tech or D-Tech degree at a University or Institute of Technology. The award of the medal is limited to one per institution.

6. November 2008: Awarded for ***outstanding research*** by the DST/NRF Centre of Excellence in Strong Materials at the University of the Witwatersrand in 2008.

7. November 2008: ***Interim chairperson*** of the ***SANi student chapter***.

8. December 2008: Announced ***winner of the Penny Huddle Memorial Award*** for 2nd and 3rd year chemistry in 2008. This award is given to a postgraduate student who has shown exceptional ability as a tutor and demonstrator. Candidates are nominated by their peers or members of staff and selected by a selection committee of representatives of the academic staff, the technical staff and the postgraduate students.

9. January 2009: Awarded ***best (1st place) student oral presentation*** at the International Conference on Nanoscience and Nanotechnology (Nanoafrica 2009) by the SANi.

ABSTRACT

The synthesis of multi-walled carbon nanotubes (MWCNTs) and carbon spheres (CSs) was achieved using catalytic and non-catalytic chemical vapour deposition processes (CVD) respectively. Fe-Co bimetallic catalysts supported on $CaCO_3$ were prepared by a wet impregnation (IMP), a deposition-precipitation (DP) and a reverse micelle method (RM). The sizes of the Fe and Co particles were not affected by the Fe and Co sources (nitrate, acetate) when the wet impregnation and deposition-precipitation methods were used. High quality 'clean' multi-walled carbon nanotubes (MWCNTs) were obtained from all three Fe-Co synthesis procedures under optimized reaction conditions. The CNTs produced gave yields ranging from 623% - 1215% in 1 h under the optimum conditions, with similar outer diameters (o.d.) of 20 - 30 nm and inner diameters (i.d.) ~ 10 nm. The Fe-Co catalyst formed in the wet impregnation method revealed that the *yield, outer diameter* and *purity* of the CNTs were influenced by C_2H_2/N_2 *ratios, time* and *temperature*. All the methods gave high quality CNTs after short reaction times but the quality deteriorated as the synthesis time was increased from 5 - 360 min. Indeed, the influential parameter in controlling CNT purity, length and outer diameter was found to be the synthesis time.

In order to control the i.d. of the CNTs, the three methods of catalyst preparation were employed with the aim of controlling the Fe-Co catalyst particle sizes. It was observed that the IMP and DP methods were less effective in controlling the size of the metal particles. A reverse micelle process was used to synthesize Fe-Co nanoparticles that were highly crystalline and uniform in size. The reverse micelle technique displayed the ability to prepare nanoparticles of controlled size (3, 6 and 13 nm) obtained by varying the concentrations of Fe and Co in the micelle. By using the RM method, smaller diameter CNTs could be obtained compared with the IMP and DP methods. The CNT i.d. was found to correlate with the size of the catalyst particle used.

The effect of synthesis time on *CNT widths* was investigated for the first time. In this study the issue of carbon build up on the CNTs as a function of time was investigated. It was observed that both the CNT yield and the outer diameters increased with time. With increase in synthesis time, the tubes *broke* into small *fragments*. The use of

excess C_2H_2 resulted in the deposition of carbon on the already formed CNTs and it is this deposited carbon that caused tube fragmentation.

MWCNTs with unusual rough surfaces (including pits) were synthesized by the CVD of acetylene using a novel $Ca_3(PO_4)_2$-$CaCO_3$ support mixture. Mixtures of $Ca_3(PO_4)_2$-$CaCO_3$ (0/100 to 100/0) yielded tubes with *very rough surfaces* and the CNT yield increased as the amount of $CaCO_3$ in the support mixture was increased. The inner walls of the CNTs possessed a regular orientation of crystalline graphite sheets (3 - 5 nm) while the outer surface of the CNTs had a thick, rough, compact layer (~ 30 nm) of carbon with a random orientation of graphite sheets.

The production of pure carbon spheres (CSs) was achieved in the absence of a catalyst through the direct pyrolysis of acetylene and ethylene in a horizontal CVD reactor. The detailed experiments conducted with acetylene as a precursor indicated that the diameters of the CSs could be controlled by varying the pyrolysis conditions (e.g. temperature and synthesis time) and that the process could readily be scaled up for commercial production. This process thus provides a variant of the carbon black synthesis procedure. The effect of using oxygenates (alcohol C:O ratio dependence) on the CS morphology was also investigated.

CSs were also synthesized in a vertical swirled floating catalytic chemical vapour deposition (SFCCVD) reactor for the first time. This process allowed for continuous and large scale production of these materials. The CSs were obtained by the direct pyrolysis of acetylene in an inert atmosphere without the use of a catalyst. The effect of pyrolysis temperatures and the flow rate of argon carrier gas on the size, quality and quantity of the synthesized carbon spheres were investigated. TEM analysis of the carbon materials revealed graphitic spheres with a smooth surface and uniform diameter that could be controlled by varying reaction conditions (size: 50 - 250 nm). The materials were spongy and very light. It was established that under controlled experimental parameters, sphere size is also regulated by the structural and bonding properties of a hydrocarbon source such as *carbon/hydrogen (C:H) content, hybridization* and *isomerism*.

CONTENTS

Chapter 3: Carbon nanotubes from supported catalysts: a literature review

---

Chapter 4: The use of organometallic transition metal complexes in the synthesis of shaped carbon nanomaterials: a review

---

Chapter 5: Catalytic CVD synthesis of multiwalled carbon nanotubes using Fe, Co, and Fe-Co/$CaCO_3$ catalysts

---

Chapter 6: Iron-Cobalt catalysts synthesized by a reverse micelle impregnation method for controlled growth of carbon nanotubes

---

Chapter 7: A novel $Ca_3(PO_4)_2$-$CaCO_3$ support mixture for the CVD synthesis of roughened multiwalled carbon nanotubes

---

Chapter 8: The effect of reagent residues on the stability and structure of CVD carbon nanotubes

---

Chapter 9: Carbon spheres: a literature review

Chapter 10: Synthesis and study of carbon microspheres for use as catalyst support for cobalt

LIST OF ABBREVIATIONS

Al_2O_3	aluminium oxide
Ar	argon
BET	Brunauer-Emmett-Teller
C %	carbon deposit percentage
C_2H_2	acetylene
C_2H_4	ethylene
$Ca_3(PO_4)_2$	calcium pyrophosphate
$CaCO_3$	calcium carbonate
CaO	calcium oxide
CCVD	catalytic chemical vapour deposition
CNT(s)	carbon nanotube(s)
Co	cobalt
CO_2	carbon dioxide
CS(s)	carbon sphere(s)
CVD	chemical vapour deposition
DP	deposition-precipitation
DWCNT(s)	double walled carbon nanotube(s)
EDS	energy dispersive X-ray spectroscopy
EM	electron micscopy
FcH	ferrocene
Fe	iron
FID	flame ionization detector
GHSV	gas hourly space velocity
h	hour
HNO_3	nitric acid
HRSTEM	high resolution scanning tunnelling electron microscopy
HRTEM	high resolution transmission electron microscopy
i.d.	inner diameter
ICP-AES	Inductively coupled plasma-atomic emission spectroscopy
IMP	wet impregnation
IR	infrared spectroscopy
MCMBs	mesoporous carbon microbeads

ml/min	millilitre per minute
MVOCC	mixed valence oxide catalysts
MWCNT(s)	multi walled carbon nanotubes(s)
N_2	nitrogen
nm	nanometre
μm	micrometre
o.d.	outer diameter
PXRD	powder X-ray diffraction spectroscopy
RM	reverse micelle
sccm	standard cubic centimetres per minute
SCNM(s)	shaped carbon nanomaterial(s)
SEM	scanning electron microscopy
SFCCVD	swirled floating catalytic chemical vapour deposition
SiO_2	silicon dioxide
SWCNT(s)	single walled carbon nanotubes(s)
t	time
T	temperature
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
TiO_2	titanium dioxide
VLS	vapour-liquid-solid
wt%	weight percentage
XPS	X-ray photoelectron spectroscopy

LIST OF TABLES

LIST OF FIGURES AND SCHEMES