Carbon Nanotube Composites: Advanced Properties for Emerging Applications

A thesis submitted in fulfillment of
the requirements for the degree of

Doctor of Philosophy
Engineering (Nanotechnology)

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January 2014

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Abstract

Carbon nanotubes (CNTs) have been considered as an outstanding nanomaterial, envisaged for developing a new generation of membranes for advanced molecular separation as a result of their unique transport properties and ability to mimic biological protein channels. Nevertheless, the excellent physical and chemical properties of CNTs make this material attractive for other potential applications. For example, free-standing or liberated CNTs are nanostructures with excellent properties to develop smart nanocarriers for targeted and localized drug delivery. Before these applications become feasible, however, the fabrication process of CNTs must be entirely understood in order to produce nanostructures with totally controlled dimensions and properties. So far, some approaches have been used to synthesise CNTs, the most representative of which are arc discharge, laser ablation and catalytic chemical vapor deposition (C-CVD). However, these fabrication methods present many fundamental disadvantages (e.g. expensive equipment, high temperature of synthesis, use of toxic and hazardous materials, impurities/contaminations, etc.). Therefore, the physical and chemical properties of the resulting CNTs rely both on fabrication method and manufacturer, thus preventing the production of standardized CNTs.

In this scenario, this thesis puts forward a catalyst-free CVD approach for fabricating CNTs with totally controlled properties (e.g. geometry, shape, chemical composition, surface chemistry, etc.) by using nanoporous templates with well-defined chemistry and geometry. As a result of its simplicity, versatility, scalability and cost-competitive fabrication process, this approach is envisaged for producing CNTs featuring standardized properties, which are required for a broad range of applications (e.g. separations, drug delivery, etc.). To develop this CVD approach, the optimal conditions for the fabrication of catalyst-free CNTs were determined by varying such parameters as temperature, reaction path length, absence or

presence of catalyst, type of nanoporous template (i.e. nanoporous anodic alumina (NAA) or titania nanotubes (TNTs)) and type of carbon source. The most relevant aspects of this study were:

1 – Carbon Source: Two unconventional carbon sources were explored: namely, a mixed solution of toluene and ethanol and non-degradable grocery plastic bags.

2 – Nanoporous Template: To understand the mechanism of this catalyst-free CVD approach using nanoporous templates, a set of experiments comparing the growth of CNTs inside NAA and TNTs were performed. This made it possible to understand the role of the nanoporous template in the growth of CNTs as well as to establish of the mechanism of growth of CNTs inside these nanoporous templates.

3 – Geometry and Shape: CNTs with different geometries and shapes (e.g. periodically modulated diameters) were fabricated by using NAA templates featuring different geometries and shapes. This confirmed the capability of the proposed CVD approach to synthesise CNTs with desired shapes and geometries, offering new opportunities to develop innovative nanostructures for emerging applications.

4 – Chemical Composition: The presence of heteroatoms has a direct impact over the synthesis of CNTs. To throw light on this question, the effect of such heteroatoms as nitrogen (N), sulfur (S), phosphorus (P) and co-doped sulfur/phosphorus (S/P) on the quality of the resulting CNTs was investigated.

5 – Surface Chemistry Functionalization: Chemical modification of the inner surface of CNTs was achieved through gas-phase and solvent-free functionalization with different functional

compounds (i.e. 1-octadecylamine (ODA), 1,8-diaminooctane (DO) and polyethyleneimine (PEI)).

6 – Applications: Finally, CNT membranes and free-standing CNTs obtained by the above-mentioned CVD approach were used in two significant applications:

- Sophisticated separation nanodevices (separation): To demonstrate the capability of these membranes to selectively tune molecular transport as a function of the interaction between molecules and inner surface of CNTs, the transport performance of these membranes was analyzed when transporting several dye molecules with positive, negative and neutral charge.

- Smart nano-carriers for delivering chemotherapeutic drugs (drug delivery): Free standing CNTs with hydrophilic core were used as nanocontainers for delivering anti-cancer drug. These CNTs were loaded with doxorubicin (Dox) and its external surface was chemically functionalized with a biodegradable polymer (chitosan) by anchoring its polymeric chains to functional groups on the external surface of CNTs.

The presented results are expected to be the starting point of the development of new nanodevices based on innovative CNTs featuring totally controlled properties (i.e. standardized product), which could be used in a broad range of research fields and commercial applications.

List of Contributions

Journal Papers Published:

1. **T. Altalhi**, T. Kumeria, A. Santos, D. Losic, Synthesis of well-organised carbon nanotube membranes from non-degradable plastic bags with tuneable molecular transport: Towards smart nanotechnological recycling, *Carbon*, 2013, **63**, 423-433.

2. T. Kumeria, M. Bariana, **T. Altalhi**, M. Kurkuri, C. T. Gibson, W. Yang, D. Losic, Graphene oxide decorated diatom silica particles as a new nano-hybrid: toward smart natural drug carriers, *Journal of Materials Chemistry B*, 2013, **1**, 6302-6311.

3. **T. Altalhi**, M. Ginic-Markovic, N. Han, S. Clarke, D. Losic, Synthesis of Carbon Nanotube (CNT) Composite Membranes, *Membranes*, 2010, **1**, 37-47.

Journal Papers (in preparations):

4. M. Alsawat, **T. Altalhi**,, J. Shapter, D. Losic, Influence of dimensions, inter-distance and crystallinity of titania nanotubes (TNTs) on their photocatalytic activity, Catalysis Science and Technology (RSC), 2014 (under review)

5. **T. Altalhi**, T. Kumeria, A. Santos, D. Losic: Fabrication of CNTs with periodically shaped nanostructure and characterisation of their properties, *Advanced Functional Materials*, 2014 (in final preparation, to be submitted).

6. **T. Altalhi**, A. Santos, T. Kumeria, D. Losic, Doping carbon nanotubes for improved biocompatibility and degradation properties, *Biomaterials*, 2014 (in preparation, study of degradation properties in progress)

7. **T. Altalhi**, E. V. Basiuk, J. Rizo, V. A. Basiuk, M. A. T. Kumeria, A. Santos, D, Losic, Functionalization of innerwals of crabon nanotubes with long-chain amines, *Journal of Materials Chemistry*, 2014 (in final preparation).

8. **T. Altalhi**, R. Bhavesh, T. Kumeria, A. Santos, D. Losic, Synthesis of catalyst free-biocompatible carbon nanotubes from grocery plastic, as intracellular drug delivery vehicle for enhanced mitochondrial dysfunction and cell death in breast cancer, *Journal of Materials Chemistry*, 2013 (in final prep).

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1. **T. Altalhi**, E.V. Basiuk, J. Rizo, V. A. Basiuk, M. Ginic-Markovic, S. Clarke, D. Losic, Chemical Functionalization of inner walls of carbon nanotubes with long chain amine, *Chemeca 2012*, Proceedings, paper 0132 (23-26 Sept. Wellington, New Zealand).

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Conference Presentations (Abstracts)

1. R. Bhavesh, **T. Altalhi**, A. Santos, S. Hay, A. Evdokiou, D. Losic, Synthesis of catalyst free-biocompatible nanocapsules as intracellular drug delivery vehicle for enhanced mitochondrial dysfunction and cell death in breast cancer, (poster presentation), 22nd *Annual Conference of the Australasian Society for Biomaterials and Tissue Engineering (ASBTE)* 2-5 April 2013 Barossa Valley, Adelaide, Australia

2. T. Kumeria, **T. Altalhi**, M. Bariana, S. Chen, M. Kurkuri, W. Yang, D. Losic, Graphene modifications of diatom silica particles, (poster presentation). *Oz Carbon* 1-3 July 2013, Adelaide, Australia

3. K. Gulati, **T. Altalhi**, D. Findlay, D. Losic, Advanced drug releasing implants for bone therapies composed of carbon nanotubes and titania nanotube arrays, (poster presentation). *Oz Carbon* 1-3 July 2013, Adelaide, Australia

4. **T. Altalhi,** M. Ginic-Markovic, S. Clarke, D. Losic, Carbon nanotube membranes for advanced molecular separations, (poster presentation)**.** *Thirteenth International Conference on the Science and Application of Nanotube*s, 24-29 June 2012, Brisbane Convention & Exhibition Centre, Brisbane, Australia

5. **T. Altalhi,** E.V. Basiuk, J. Rizo, V.A. Basiuk, D. Losic, Carbon nanotube membranas with chemically functionalized inner walls with long chain aliphatic amines, (poster presentation). *Thirteenth International Conference on the Science and Application of Nanotubes*, 24-29 June 2012, Brisbane Convention & Exhibition Centre, Brisbane, Australia

6. **T. Altalhi**, H. Han, M. Ginic-Markovic, S. Clark, D. Losic, Synthesis of Multi-Walled Carbon Nanotube Framework Membranes for Emerging Applications (poster presentation) *ARNAM/ARCNN Joint Workshop*, Flinders University, 19-23 July 2010, Adelaide, Australia

7. M. Ginic-Markovic, **T. Altalhi**, N. Han, S. Clarke, D. Losic, Synthesis of Multi-Walled Carbon Nanotube (MWCNT) Composite Membranes (poster presentation) *AMS6/IMSTEC10, 6th conference of the Asian Membrane Society and the 7th International Membrane Science and Technology Conference*, 22-26 Nov. 2010, Sydney, Australia (Selected for journal publications)

Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due. In addition, I certify that no part of this work will, in the future, be used in a submission for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree. I give consent to this copy of my thesis when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968. The author acknowledges that copyright of published works contained within this thesis resides with the copyright holder(s) of those works. I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library catalogue and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

TARIQ ALTALHI

Acknowledgements

This thesis is not only a result of my passion for science but also of the help and support from many people, without their influential support and guidance this thesis would have never been accomplished.

I would like to thank my supervisors prof. Dusan Losic and Dr. Abel Santos for their support throughout. Prof. Losic, who gave me his priceless trust and total freedom to explore the exciting world of nanotechnology under his guidance. I will never forget Dr. Santos' words of support during the final stage of my PhD study about Chemistry. He is a brilliant scientist and a continuous source of scientific inspiration for me.

I would like to thank my brother and colleague Mohammed Alsawat, who I have known throughout my life. He is a great man with a very generous and kind heart and has always supported me during the hard times of this PhD study (اخي وصديقي الي الابد باذن الله عز وجل). For this PhD work, I would like to extend my gratitude to: Dr. Benjamin Wade and Dr. Ken Neubauer who taught me to operate the TEM, SEM. I have always received great support from all the Losic group's member of the Nanomaterials team including Dr. Mahaveer D. Kurkuri, Shervin Kabiri, Karan Gulati, and Krishna Kant in particular. Also Special thanks to Riju Bhavesh who taught me about the drug delivery, which helped in further extending the application of my material (CNTs) to this research field. Thanks to my friend and sister Manpreet Bariana for all her funny jokes and sense of humornaife. Also, I would like to thanks all my brothers and sisters.. Help from S. Hay from Queen Elizabeth Hospital for cell studies are greatly acknowledged. Help and support from my great teacher christopher Price for build CVD reactor in generosity collaboration from Flinders university workshop is greatly appreciated and acknowledged.

I want to extend a special acknowledgement to Tushar Kumeria for his support and friendship without his help I will never ever be able to succeed and I want to tell him how much your brotherhood meant to me (ستظل اخي وسندي الي الابد باذن الله عز وجل).

Finally I would like to acknowledge my great wife for her support through all the rough moments of my life in the Australia. She is one in a billion. Special thanks to my daughter for cheering me up all the time. And last but not least, I thank my family, *Dalal, Basmmah ,Afrah, Raghad, Rana, Lubna, Mlak, Maria, Rima, Rose, Abdul Rahman and above all my dearest parents.* Lastly, I want to thank *Allah* for maintaining his grace upon me at all times.

(الي امي يأغلى من سكن قلبي اليك كل الحب والتقدير)

I dedicate this painstakingly written thesis to these very special people in my life:

My parents

My lovely wife, Hajer Alharbi

My daughters, Hala and Rosa.

My brothers, Maher, Mohammed, Talal, Bader, Abdullah, Hemid Alshreef.

And both my uncle and dearest friend, Saleh Marzooq & Aidah Alshreef, who have been & still are, most sorely missed.

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