THE UNIVERSITY OF ADELAIDE
AUSTRALIA

Fluorescence-Based Chemical Sensing Using Suspended-Core Microstructured Optical Fibres

by

Stephen Christopher Warren-Smith

A thesis submitted for the degree of
Doctor of Philosophy

in the

Faculty of Science
School of Chemistry & Physics

October 2010

To Anna, Joey, Emily, Aaron, Ellie, Declan, Orlando, Noah, and Ruby

Choose your road.
Ride it well.

Alastair Humphreys

Contents

Errata

Stephen Warren-Smith

December 2010

Chapter 1, Section 1.2, Page 6: For a scale reference, the optical fibre outer diameters in Fig. 1.1 are 160 μm.

Chapter 2, Section 2.5.4, Page 32: "Fibre Bragg Gratings" should be "Long Period Gratings", in relation to Ref. [87].

Chapter 2, Section 2.5.4, Page 36, Line 4 from below: "Fig. 2.15(b, c))" and "Fig. 2.15(d, e))" should be swapped.

Chapter 3, Section 3.6.1, Page 112, Lines 5-6: The statement "that this was the first experimental example of internal surface functionalisation with fluorophores and the technique has since evolved, such as that used in Chapter 5" is incorrect as this has previously been achieved in Refs. [87, 152].

Chapter 5, Section 5.2.3, Page 192: The smallest y-axis tick should be "1" instead of "0".

Appendix B, Section B.3, Pages 246-248: In Eqs. B.29 to B.39 there should be a prime above the electric and magnetic fields on the right hand side of the equations to separate them from fields on the left hand side as these fields are in two different waveguides. That is, there should be a prime above fields that have a ν subscript.

Response to general examiner remarks

1. The soft glass fibres fabricated and used in this project were generally not coated. While fragility was an issue, it was still possible to re-spool and handle the fibres. Note that the fibres were lead-silicate glass, which is less fragile than most other soft glasses. Practical applications would require the fibre to be coated.

2. For most of the exposed-core fibres in this project air holes had formed between the cane and jacket during drawing, such as seen in Fig. 5.11. This resulted from an imperfect fit between the cane and jacket, and the inability to apply a vacuum to the wedged jacket during drawing for the exposed-core fibre. However, the presence of these holes had no detrimental effect on the performance of the fibre as they are sufficiently far from the guided modes of the core.

3. Photobleaching is recognised as a significant problem for organic fluorophore-based sensing. As shown in [P1], the effect of photobleaching is to reduce the fluorescence intensity by an order of magnitude over several minutes. Note that a major contributing factor is the small volume used, and thus the small number of molecules that are located within the optical fibre. For the experiment on page 163 a larger volume size was used and thus photobleaching was not a significant problem for the time frames used.

THE UNIVERSITY OF ADELAIDE

Abstract

Faculty of Science
School of Chemistry & Physics

Doctor of Philosophy

by Stephen Christopher Warren-Smith

This thesis contains a study on the fluorescence based chemical sensing properties of microstructured optical fibres. Specifically, suspended core optical micro/nano-wires, including those with the core partially exposed along their length, are studied both theoretically and experimentally. Comparisons are made between these exposed-core and enclosed-core optical fibres in terms of their fluorescence sensing performance, fabrication, and function. The application of corrosion sensing of aluminium alloys was the primary motivator for this project and methods for achieving this are presented. However, the findings presented in this thesis could be extended to many other biological and chemical applications.

Chapter 1 outlines the motivation of the work and the structure of the thesis. Chapter 2 reviews the state of the art for optical fibre chemical sensing. In Chapter 3 a theoretical model is derived and used to predict the fluorescence capture of high index contrast small-core fibres using vectorial solutions to Maxwell's equations. This model is subsequently used to compare exposed-core and enclosed-core fibres, where distinct advantages are found for liquid-immersed exposed-core fibres due to their asymmetric refractive index profile. In Chapter 4 the fabrication of both enclosed and exposed suspended-core fibres are demonstrated using the extrusion technique for soft-glass preform development. It is then confirmed experimentally that advantages of using exposed-core fibres include the ability to perform real time and distributed fluorescence based sensing. In Chapter 5 two methods of sensitising these fibres for corrosion sensing of aluminium alloys are investigated. Both methods use a fluorescence based indicator molecule for aluminium ions, which is either embedded into a porous polymer coating or chemically attached via polyelectrolytes.

Declaration

I confirm 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 to Stephen Warren-Smith and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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 (listed on pages xiv and xv) 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, the Australasian Digital Theses Program (ADTP) and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

Signed: ____________________________________

Date: ____________________________________

Acknowledgements

I have many people to acknowledge for their contribution and support throughout my PhD experience both professionally and personally. Due to the collaborative nature of this project it is impossible to acknowledge everyone who contributed in some way to this thesis. I hope the following does some justice to the efforts of those who supported me and that those who are not specifically acknowledged are already aware of my appreciation.

First acknowledgements must go to my supervisors, Tanya Monro, Heike Ebendorff-Heidepriem, and Shahraam Afshar. The results of this thesis would not have been possible without their support and guidance. Tanya's enthusiasm and ability to find solutions to all aspects of physics research make her a fantastic supervisor and a great role model for a young scientist. Heike's approach to science is to be envied, she has an understanding of the fibre fabrication process that is inspiring, making her an excellent supervisor for a project such as this. I thank Shahraam for sharing the fluorescence sensing theory journey with me. Indeed, Shahraam's enthusiam and skills in theoretical physics have constantly been pivotal in producing the final results that appear in this thesis.

I would like to acknowledge the optics and photonics research group as a whole. In particular, those associated with the soft-glass optical fibre fabrication. It is not possible for an individual PhD student to work on a project such as this without significant infrastructure and personnel already in place. Tanya's original decision to start a soft-glass optical fibre group at the University of Adelaide has been greatly beneficial to me personally, as was the support of others who encouraged her to come here such as the Defence Science and Technology Organisation (DSTO). I also thank the many people who have been involved in starting and running this group such as Heike Ebendorff-Heideprie and Roger Moore.

I would like to acknowledge the many other people at the University of Adelaide who also contributed to this project in one way or another. I would like to thank Roger Moore for drawing the fibres that are presented in this thesis. I have been privileged to have a technician with over 20 years experience drawing my fibres that, due to their unique design, were not a simple task. I thank the other technical staff that were always willing to assist with practical aspects of this project. This includes Adrian Selby, Alastair Dowler, Trevor Waterhouse, and Blair Middlemiss. I thank Herbert Foo for helping me with hydrofluoric acid (HF) etching experiments, FTIR-ATR measurements, and general discussions on the chemical aspects of this project. Kevin Kuan for general support in chemistry. Markus Pietsch for starting work on the chemical synthesis of a derivative of lumogallion that was used in this project, Sabrina Heng for continuing and finishing this work, and Andrew Abell for encouraging this work to be done in his lab. Alexandre Francois for instruction on the use of polyelectrolytes for surface funtionalisation. Erik Schartner for many useful and critical discussions on my project, and the sharing of ideas and work due to our closely related projects. Dominic Murphy and Florian Englich for purchasing some of the optical equipment used in the later experiments of this project. John Terlet and other staff at Adelaide Micrscopy who made it possible to perform scanning electron microscope (SEM) imaging of optical fibres at their very convenient on-campus location. Peter Hoffman who collaborated in the biosensing project that resulted in one of the publications in this thesis. Olivia Towers and Sara Boffa who constantly helped to take the pain out of university administration and beaurocracy.

One of the strengths and most enjoyable aspects of this PhD has been the collaboration with not only many different people but also organisations. This has allowed many things to be achieved that otherwise could not have been possible had I been working in isolation.

I would like to thank Claire Davis, Silvia Tejedor, and Grant McAdam from DSTO for providing funding for this project, their many useful conversations on my work, and allowing me to perform experiments in their labs. In particular, I acknowledge the DSTO Corporate Initiative on Smart Materials and Structures for sponsorship of this program of research. I would like to thank Elena Sinchenko and Paul Stoddart from Swinburne University with whom I performed distributed sensing measurements using my fibres, which lead to a publication contained within this thesis. I acknowledge Christopher Gibson from Flinders University for assisting me with atomic force microscopy images that appear in this thesis. Also, Milena Ginic-Markovic from Flinders University for assisting Herbert Foo and myself with fourier-transform infra-red (FTIR) spectroscopy: attenuated total reflectance (ATR) measurements that unfortunately do not appear in this thesis.

On the personal side, there are many people, both friends and family, who I would like to thank for their continued friendship and support over the last few years. There are too many to name everyone here, but particular thanks to my friends since childhood, Richard Harvey, Brett Thredgold, Tristan Williamson, Michael Sawyer, Adam Hennessy, and Cathryn Matto. Thanks to the many other friends I have made over recent years, in particular, Adam Kilpatrick, Michael Oermann, Jeffrey Newman, Katrina Newman, Michael Woodward, Hannah Laven, Erik Schartner, Herbert Foo, and Faisal Amir.

Special thanks to Mum and Dad for their love, support, and encouragement not just during my PhD but for the last 25 years. Thanks to my step-mum, Suzanne. Thanks to my grandpa. Thanks to my brothers and sisters, Anna, Joey, Emily, Aaron, Ellie, and

Declan, and to my nephews and niece, Orlando, Noah, and Ruby. I sincerely wish the best for you all.

Publications Contained Within Thesis

P1. S. Afshar V., S. C. Warren-Smith, and T. M. Monro, "Enhancement of fluorescence-based sensing using microstructured optical fibres," *Optics Express* **15**, 17891-17901 (2007).

P2. S. Afshar V., Y. Ruan, S. C. Warren-Smith, and T. M. Monro, "Enhanced fluorescence sensing using microstructured optical fibers; a comparison of forward and backward collection modes," *Optics Letters* **33**, 1473-1475 (2008).

P3. S. C. Warren-Smith, S. Afshar V., and T.M. Monro, "Theoretical study of liquid-immersed exposed-core microstructured optical fibres for sensing," *Optics Express* **16**, 9034-9045 (2008).

P4. S. C. Warren-Smith, S. Afshar V., and T.M. Monro, "Fluorescence-based sensing with optical nanowires: a generalized model and experimental validation," *Optics Express* **18**, 9474-9485 (2010).

P5. Y. Ruan, T. C. Foo, S. C. Warren-Smith, P. Hoffmann, R. C. Moore, H. Ebendorff-Heidepriem, and T. M. Monro, "Antibody immobilization within glass microstructured fibers: a route to sensitive and selective biosensors," *Optics Express* **16**, 18514-18523 (2008).

P6. H. Ebendorff-Heidepriem, S. C. Warren-Smith, and T. M. Monro, "Suspended nanowires: fabrication, design and characterization of fibers with nanoscale cores," *Optics Express* **17**, 2646-2657 (2009).

P7. S. C. Warren-Smith, H. Ebendorff-Heidepriem, T. C. Foo, R. Moore, C. Davis, and T. M. Monro, "Exposed-core microstructured optical fibers for real-time fluorescence sensing," *Optics Express* **17**, 18533-18542 (2009).

P8. S. C. Warren-Smith, E. Sinchenko, P. R. Stoddart, and T. M. Monro, "Distributed fluorescence sensing using exposed-core microstructured optical fiber," *Photonics Technology Letters* **22**, 1385-1387 (2010).

These publications are included within the main body of this thesis. When referred to in the text the reference number is prefixed by a 'P'. For example, the first publication in this list is referred to as [P1].

Other Publications

The following paper was prepared after Chapter 5 was drafted and thus is included in Appendix D.

1. S. C. Warren-Smith, S. Heng, H. Ebendorff-Heidepriem, A. D. Abell, T. M. Monro, "Fluorescence-based aluminum ion sensing using a surface functionalized microstructured optical fiber," to be submitted to the *Journal of the American Chemical Society*.

The following papers, which are not included in this thesis, have been submitted for publication.

2. T. M. Monro, S. C. Warren-Smith, E. P. Schartner, A. Franois, S. Heng, H. Ebendorff-Heidepriem, S. Afshar V., "Sensing with suspended-core optical fibers," accepted for publication in *Optical Fiber Technology*.

3. T. Palmisano, F. Prudenzano, S. C. Warren-Smith, T. M. Monro, "Design of exposed-core fiber for methadone monitoring in biological fluids," submitted to the *Journal of Non-Crystalline Solids*.

Conference Presentations During Candidature

1. S. C. Warren-Smith, S. Afshar V., and T. M. Monro, "Highly-efficient fluorescence sensing using microstructured optical fibres; side-access and thin-layer configurations," *19th International Conference on Optical Fibre Sensing (OFS)*, Perth, Australia (April 2008).

2. S. Afshar V., Y. Ruan, S. C. Warren-Smith, H. Ebendorff-Heidepriem, and T. M. Monro, "Highly-efficient fluorescence sensing using microstructured optical fibres; general model and experiment," *19th International Conference on Optical Fibre Sensing (OFS)*, Perth, Australia (April 2008).

3. S. C. Warren-Smith, H. Ebendorff-Heidepriem, S. Afshar V., G. McAdam, C. Davis, and T. M. Monro, "Corrosion sensing of aluminium alloys using exposed-core microstructured optical fibres," *2nd Asia-Pacific Workshop on Structural Health Monitoring*, Melbourne, Australia (December 2008).

4. S. C. Warren-Smith, H. Ebendorff-Heidepriem, and T. M. Monro, "Suspended optical nanowires for sensing applications," *18th Australian Institute of Physics (AIP) Congress*, Adelaide, Australia (December 2008).

5. H. Ebendorff-Heidepriem, S. C. Warren-Smith, and T. M. Monro, "Fabrication of suspended nanowire optical fibres," *18th Australian Institute of Physics (AIP) Congress*, Adelaide, Australia (December 2008).

6. S. C. Warren-Smith, H. Ebendorff-Heidepriem, T. C. Foo, R. C. Moore and C. E. Davis, and T. M. Monro, "Exposed-core microstructured fibres for real-time fluorescence sensing," *20th International Conference on Optical Fibre Sensors (OFS)*, Edinburgh, United Kingdom (October 2009).

7. E. P. Schartner, R. T. White, S. C. Warren-Smith, and T. M. Monro, "Practical sensitive fluorescence sensing with microstructured fibres," *20th International Conference on Optical Fibre Sensors (OFS)*, Edinburgh, United Kingdom (October 2009).

8. Y. Ruan, H. Ebendorff-Heidepriem, S. Afshar V., S. C. Warren-Smith, and T. M. Monro, "Advances in chemical and biological sensing using emerging soft glass optical fibers," *Frontiers in Optics*, San Jose, United States of America (October 2009).

9. S. C. Warren-Smith, E. Sinchenko, P. R. Stoddart, C. E. Davis and T. M. Monro, "Distributed fluorescence sensing with exposed-core microstructured optical fibres," *34th Australian Conference on Optical Fibre Technology (ACOFT)*, Adelaide, Australia (December 2009).

10. H. Ebendorff-Heidepriem, S. Afshar V., S. C. Warren-Smith, W. Q. Zhang, Y. Ruan, S. Atakaramians and T. M. Monro, "Fibres with subwavelength features: fabrication and novel guidance properties," 34th *Australian Conference on Optical Fibre Technology (ACOFT)*, Adelaide, Australia (December 2009).

List of Figures

Abbreviations

8-HQ	8-**H**ydroxy**q**uinoline
AFM	**A**tomic **F**orce **M**icroscopy
BF	**B**are **F**ibre
CCD	**C**harge **C**oupled **D**evice
CE	**C**oupling **E**fficiency
CL	**C**onfinement **L**oss
CW	**C**onitinuous **W**ave
DMSO	**D**i**m**ethyl **S**ulf**o**xide
DNA	**D**eoxyribo**n**ucleic **A**cid
EDC	1-**E**thyl-3-(3-**D**imethylaminopropyl)**C**arbodiimide
ELISA	**E**nzyme **L**inked **I**mmuno**s**orbent **A**ssay
F2	Lead-Silicate Glass ($n \approx 1.62$)
FBG	**F**ibre **B**ragg **G**rating
FCF	**F**luorescence **C**apture **F**raction
FEM	**F**inite **E**lement **M**odelling
GMBS	N-γ-Maleimidobutyryloxy Succinimide Ester
HF	**H**ydro**f**luoric acid
ID	**I**nner **D**iameter
IR	**I**nfra **R**ed
JASR	**J**acketed **A**ir **S**uspended **R**od
LIT	**L**iquid **I**nterface **T**ransmission
LLF1	Lead-Silicate Glass ($n \approx 1.55$)
LLJ	**L**ong **L**ap **J**oint
LP	**L**ong **P**ass
LPG	**L**ong **P**eriod **G**rating

MDS	**M**ercaptomethyl**d**imethylethoxy**s**ilane
MMF	**M**ulti **M**ode **F**ibre
MOF	**M**icrostructured **O**ptical **F**ibre
MTS	3-**M**ercaptopropyl**t**rimethoxy**s**ilane
Nd:YAG	**N**eo**d**ymium-doped **Y**ttrium **A**luminium **G**arnet
NHS	**N**-**H**ydroxy**s**uccinimide
NOI	**N**ormalised **O**verlap **I**ntegral
OD	**O**uter **D**iameter
OSA	**O**ptical **S**pectrum **A**nalyser
OTDR	**O**ptical **T**ime **D**omain **R**eflectometry
PAH	**P**oly(**A**llylamine **H**ydrochloride)
PBG	**P**hotonic **B**and**g**ap
PF	**P**ower **F**raction
PML	**P**erfectly **M**atched **L**ayer
PMMA	**P**oly(**m**ethyl **m**eth**a**crylate)
PMT	**P**hoto **M**ultiplier **T**ube
PU	**P**oly **U**rethane
PVA	**P**oly**v**inyl**a**lcohol
SEM	**S**canning **E**lectron **M**icroscope
SERS	**S**urface **E**nhanced **R**aman **S**pectroscopy
SF57	Lead-Silicate Glass ($n \approx 1.85$)
SLJ	**S**hort **L**ap **J**oint
SMF	**S**ingle **M**ode **F**ibre
SPR	**S**urface **P**lasmon **R**esonance
UV	**U**ltra **V**iolet
WW	**W**agon **W**heel Fibre (Enclosed suspended-core MOF)