Optical Fibre Sensors with Surface-immobilised Fluoroionophores

By

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A thesis submitted for the fulfilment of the degree of Doctor of Philosophy

in the

Faculty of Science

School of Chemistry and Physics

July 2014

Declaration of Authorship

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Abstract

Regular monitoring of the concentration of ionic nutrients such as Nitrate (N), Phosphate (P) and Potassium (K) ions in soils is necessary for agricultural management. Optical fibre dip sensors provide sensing platforms that have the potential to be small and flexible that can reach the root zone. This thesis contains studies towards the development of novel optical fibre soil nutrient sensors using suspended core fibres (SCFs) and Photoinduced Electron Transfer (PET) based fluoroionophores. SCFs provide long interaction path length that potentially increase the sensitivity and lower the detection limit. Furthermore it requires only nanoliters for analysis. PET fluoroionophores using 4-amino-1,8-naphthalimide as the common fluorophore can be integrated within a SCF to become optical fibre sensors in two ways. The first approach is to pre-mix the fluoroionophore with the analyte to be sensed; the second approach is to immobilise the fluoroionophore on the internal surface of SCF. Chapter 2 and 5 of this thesis has demonstrated both potential operating scenarios are feasible for cation sensing. Furthermore, both cation and anion sensing are feasible using the first approach.

Surface immobilisations of the fluoroionophores on the glass materials are critical for the development of the practical SCF sensors (second approach). In order to achieve this, it is first necessary to develop techniques for the characterisation of the functionalised surfaces. Chapter 3 and 4 of this thesis has demonstrated a versatile approach of using different glass model systems and surface analysis techniques such as X-ray photoelectron spectroscopy, Time of flight secondary ion mass spectrometry (ToF-SIMS), fluorescence imaging, spectroscopic ellipsometry, atomic force microscopy for measuring parameters such as the surface density of amine groups and sensor molecules, coating coverage, surface roughness and coating thickness that represent the surface chemistry of SCF. In addition, ToF-SIMS imaging is demonstrated to reveal that the lead ions distribution could be used as a marker of surface coverage of the coating. The application of using ToF-SIMS for relative coating thickness measurement on is also demonstrated in this thesis.

Publications during candidature

<u>Journal publications:</u>

Englich, F. V.; Foo, T. C.; Richardson, A. C.; Ebendorff-Heidepriem, H.; Sumby, C. J.; Monro, T. M., Photoinduced Electron Transfer Based Ion Sensing within an Optical Fiber. *Sensors-Basel,* **2011,** *11* (10), 9560-9572

Foo, H. T. C.; Ebendorff-Heidepriem, H.; Sumby, C. J.; Monro, T., Towards microstructured optical fibre sensors: surface analysis of silanised lead silicate glass. *Journal of Materials Chemistry C* **2013,** *1*, 6782-6789.

<u>Conference papers:</u>

Foo, T. C.; François, A.; Ebendorff-Heidepriem, H.; Sumby, C. J.; Monro, T. M., Comparison of Surface Functionalization Techniques on Silica and Soft Glasses for Optical Fibre Sensing Applications. In *Australian Conference on Optical Fibre Technology (ACOFT)*, Adelaide, Australia, 2009 (Accepted for oral presentation)

Englich, F. V.; Foo, T. C.; Ebendorff-Heidepriem, H.; Sumby, C. J.; Monro, T. In *Towards a microstructured optical fibre fluorescence sensor based on photoinduced electron transfer photobleaching*, Proceedings of the Australian Conference on Optics, Lasers and Spectroscopy and Australian Conference on Optical Fibre Technology in association with the International Workshop on Dissipative Solutions, Adelaide, Adelaide, 2009; pp 105-106 (Accepted for oral presentation)

Richardson, A. C; Foo, T. C; Englich, F. V; Ebendorff-Heidepriem, H; Sumby, C. J; Monro, T. M. *A microstructured optical fiber sensor for ion-sensing based on the photoinduced electron transfer effect*, Proceedings of the 3rd Asia Pacific Optical Sensors Conference (APOS 2012), 2012

<u>Note that I officially changed my name from Tze Cheung Foo to Herbert Tze Cheung Foo in October 2013</u>

Acknowledgements

This was certainly an enjoyable transdisciplinary research journey, where I have had the chance to work with and learn from scientists from various discipline areas such as glass chemistry, surface chemistry, organic chemistry, physical chemistry, optics and photonics. It is my pleasure to acknowledge everyone for their support and assistance to me throughout my degree of Doctor of Philosophy (PhD).

First of all, I would like to thank my supervisors Heike Ebendorff-Heidepriem, Chris Sumby and Tanya Monro. This is a great team with a glass scientist, a chemist and a physicist. Without their guidance and support, it would have been impossible to accomplish the research presented in this thesis. Thanks to all supervisors for editing this thesis.

I would like to acknowledge my collaborators Mai-Chi Nguyen, Andrew Richardson, Florian Englich and Alexandre François in the Institute of Photonics and Advanced Sensing (IPAS) for their important contributions to this research project.

I acknowledge the support from some of the surface scientists at Flinders University; they are Natalya Schmerl and Günther Andersson. A lot of the data presented in this thesis were measured by the well-maintained MIES-XPS instrument at Flinders University. They are acknowledged also for many useful discussions regarding surface analyses.

I also acknowledge the support from John Denman from Ian Wark Research Institute, who runs the ToF-SIMS instrument. John is also acknowledged for discussions regarding the complicated Tof-SIMS data analyses.

I would like to thank the technical support from Roger Moore, Peter Henry, Kevin Kuan and Alastair Dowler for fabricating all fibres and capillaries used in this research project.

To Stephen Warren-Smith, Erik Schartner and Matthew Henderson, thanks for many academic and non-academic discussions and advices, which helped me enormously throughout my PhD. Thanks to them also for help with proof-reading this thesis.

To all my friends in the chemistry department and the Institute for Photonics and Advanced Sensing (IPAS), thanks for the support over years. It is certainly enjoyable to work with you guys.

I acknowledge the financial support from Micormet Pty Ltd and specifically to Jim Townsend, Terry Crawn and Paul Dalby, who provided their professional support and opinions throughout the whole research project.

On the personal side, I would like to thank my housemates Raymond, Edward and Yaying for making our home such a wonderful place to live. Finally and most importantly, I would like give a special thank to my sister Fiona, my mum Yin Fui and my dad Pit Yue for their love, support and encouragement to me over years. This thesis was accomplished during a personally difficult time. Without the support from friends and family, I could not imagine that I can complete this thesis.

Contributions

This transdisciplinary research project was supported by the Australian Research Council Linkage Grant Scheme and our industry partner, Micromet Pty Ltd, who sought to develop a solar-powered soil ionic nutrient probe that could be inserted within the root zone to continuously monitor concentrations of phosphate, nitrate and potassium (P, N, K) ions. The National Collaborative Research Infrastructure Strategy (NCRIS) has provided equipment used regularly in this project.

This research project was supervised by Heike Ebendorff-Heidepriem, Chris Sumby and Tanya Monro. I was responsible to the development of sensor molecules and surface functionalisation procedures for the suspended core fibres (SCFs); the Physics Research Fellows employed on the project were responsible for the development of the optical set-ups. The Physics Research Fellows were Florian Englich (2009 to 2011) and Andrew Richardson (2011 to 2012). Research assistant Mai-Chi Nguyen joined the project team in 2012 to perform additional optics experiments for this project.

The development of the project was regularly discussed with Paul Dalby, Jim Townsend and Terry Crawn from Micromet Pty Ltd. All academic aspects of this project related to this thesis were discussed at regular meetings with my supervisors Heike Ebendorff-Heidepriem, Chris Sumby and Tanya Monro.

Most of the experiments reported in this thesis were performed collaboratively. The following sections describe the specific contributions by me and my collaborators in each experiment reported in this thesis.

Organic synthesis of model fluorophores and fluoroionophores

I performed the synthesis and characterisation of model fluorophores and PET fluoroionophores for sodium and fluoride ions sensing. I also perform synthesis of the surface attachable fluorophores and fluoroionophores. Furthermore, I worked to synthesise a novel potassium-selective fluoroionophore. The attempted synthesis of a previously reported potassium-selective fluoroionophore (**He.2**) was performed by Peter Valente.

Characterisation of model fluoroionophores and fluorophores in SCFs and cuvette using the different optic setups

The optical set-up for the cuvette and SCFs measurements was developed initially by Florian Englich and subsequently byAndrew Richardson. Ion sensing experiments using a diode laser were performed collaboratively by Mai-Chi Nguyen, Andrew Richardson and Florian V. Englich, with my assistance for sample preparation. Codes for analysing the fluorescence spectra were written by Andrew Richardson, Mai-Chi Nguyen and modified by me using MATLAB (R2008a, The MathWorks, Natick, Massachusetts).

Glass Preform and slides fabrication

Glass perform and slides were fabricated by Heike Ebendorff-Heidepriem.

Suspended core fibres (SCFs) fabrication

Lead silicate (F2) SCFs and silica SCFs were fabricated by Roger Moore, Alastair Dowler and Erik Schartner.

Surface functionalisation experiment using capillary

I performed the surface functionalisation experiments using capillaries in collaboration with Alexandre Francois. The tellurite and ZBLAN glass were fabricated by Kevin Kuan. The lead silicate (F2), bismuth and tellurite glass capillaries were fabricated by Heike Ebendorff-Heidepriem and Roger Moore.

Surface characterisation of bare glass and functionalised glass slides

I performed the surface functionalisation experiments using silane reagents and surface attachable fluoroionophores.

I performed the XPS measurements with training and assistance from Natalya Schmerl and Günther Andersson, The Flinders University of South Australia. I performed the XPS data analyses.

The ToF-SIMS measurements were performed by John Denman from the Ian Wark Research Institute, the University of South Australia. I performed the Tof-SIMS data analyses.

Characterisation of the ion sensing function of SCFs functionalised with fluoroionophores

Functionalisation experiments on the silica SCFs for loss and fluorescence measurements were performed collaboratively by Ms Mai-Chi Nguyen and me. The sodium ions sensing experiments were performed primarily by Ms Mai-Chi Nguyen with my assistance in the solution preparation. The SEM images were captured by Erik Schartner. The functionalised SCF loss measurements were performed by Ms Mai-Chi Nguyen. The losses of uncoated silica SCFs were measured by Erik Schartner.

Experiments to identify methods for normalisation

The planning and the results of the normalisation experiments were discussed with Stephen Warren-Smith, Erik Schartner and Mai-Chi Nguyen. The optics experiments were performed predominantly by Mai-Chi Nguyen with my assistance for the solution preparation

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Abbreviations

AFM	**A**tomic **f**orce **m**icroscopy
APTES	3-**A**mino**p**ropyl**t**ri**e**thoxy**s**ilane
ATR-FTIR	**A**ttenuated **T**otal **R**eflectance- **F**ourier **T**ransform **I**nfra**r**ed
AUTES	11-**A**mino**u**ndecyl**t**ri**e**thoxy**s**ilane
CCD	**C**harge **C**oupled **D**evice
CDI	1,1-**C**arbonyl**d**iim**i**dazole
DBU	1,8-**D**iaza**b**icyclo[5.4.0]-**u**ndec-7-ene
DIPEA	N,N-**Di**iso**p**ropyl**e**thyl**a**mine
DMF	**Dim**ethyl**f**ormamide
EDC	1-**E**thyl-3-(3-**d**imethylaminopropyl) **c**arbodiimide
EDX	**E**nergy-**D**ispersive **X-**ray
FE	**F**luorescence **E**nhancement
F2	Lead silicate glass
HR	**H**igh **R**esolution
HRMS	**H**igh **R**esolution **M**ass **S**pectrometry
HRXPS	**H**igh **R**esolution **X**-ray **P**hotoelectron **S**pectroscopy
NMR	**N**uclear **M**agnetic **R**esonance
PC	**P**rinciple **C**omponent
PCA	**P**rinciple **C**omponent **A**nalysis
PCT	**P**hotoinduced **C**harge **T**ransfer
PET	**P**hotoinduced **E**lectron **T**ransfer

PMT	**P**hoto**m**ultiplier **T**ube
SCFs	**S**uspended-**C**ore **F**ibres
SE	**S**pectroscopic **E**llipsometry
SEM	**S**canning **E**lectron **M**icroscopy
THF	**T**etra**h**ydro**f**uran
TLC	**T**hin **L**ayer **C**hromatography
Tof-SIMS	**T**ime **O**f **F**light **S**econdary **I**on **M**ass **S**pectroscopy
NMP	**N**-**M**ethyl-2-**P**yrrolidone
NHS	**N-h**ydroxy**s**uccinimide
XPS	**X**-ray **P**hotoelectron **S**pectroscopy
+SIMS	Positive **S**econdary **I**on **M**ass **S**pectroscopy
-SIMS	Negative **S**econdary **I**on **M**ass **S**pectroscopy