Hydrogen Peroxide Sensing with Microstructured Optical Fibres

Fuel, Wine & Babies

by

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To Megan

I am among those who think that science has great beauty. A scientist in his laboratory is not only a technician: he is also a child placed before natural phenomena which impress him like a fairy tale.

— Marie Curie

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ACRONYMS

AR Amplex Red

ARD Amplex Red Derivative

AUR Amplex Ultrared

CE Coupling Efficiency

EDC 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide

F2/F2HT Lead silicate soft glasses

FCF Fluorescence capture fraction

FMOC Fluorenylmethyloxycarbonyl chloride

FOM Figure of Merit

FWHM Full Width Half Maximum

HRP Horseradish Peroxidase

IR Infra-red

IVF In Vitro Fertilisation

MCVD Modified Chemical Vapour Deposition

MOF Microstructured Optical Fibre

NA Numerical Aperture

NHS N-Hydroxysuccinimide

OD Outer Diameter

OSA Optical Spectrum Analyser

PBGF Photonic Band Gap Fibre

PBS Phosphate Buffered Saline

PCF Photonic Crystal Fibre

PF Power Fraction

PMT Photomultiplier Tube

Qdot Quantum Dot

SEM Scanning Electron Microscope

TEM Transmission Electron Microscope

TLC Thin Layer Chromatography

WW(F) Wagon-Wheel (Fibre)

PUBLICATIONS

The material in this thesis is based largely on the following publications

Journal Papers

- Erik P. Schartner , Heike Ebendorff-Heidepriem , Stephen C. Warren-Smith , Richard T. White and Tanya M. Monro, 'Driving down the Detection Limit in Microstructured Fiber-Based Chemical Dip Sensors,' Sensors, **11**(3), 2961-2971, 2011
- Tanya M. Monro, Stephen Warren-Smith, Erik P. Schartner, Alexandre François, Sabrina Heng, Heike Ebendorff-Heidepriem, Shahraam Afshar V., 'Sensing with suspended-core optical fibers,' Optical Fiber Technology, **16**, 343-356, 2010

Additionally, the original work on Quantum dot detection in fibres was work done for my honours project. The main achievements of this work are contained within

- Yinlan Ruan, Erik P. Schartner, Heike Ebendorff-Heidepriem, Peter Hoffmann, and Tanya M. Monro, 'Detection of quantum-dot labelled proteins using soft glass microstructured optical fibers,' Optics Express, **15**(26), 17819-17826 (2007)

Conference papers

- Erik P. Schartner, Heike Ebendorff-Heiepriem, Tanya M. Monro, Markus Pietsch, Chris Hulston and Claire Davis, 'Fuel Degradation Sensing Using Small-Cored Microstructured Optical Fibres,' AIP congress, Adelaide, Australia 2008.
- Erik P. Schartner, Tanya M. Monro, Heike Ebendorff-Heiepriem, Markus Pietsch, Chris Hulston and Claire Davis,' Fuel degradation sensing using microstructured optical fibres,' Structural Health Monitoring Workshop, Melbourne, Australia 2008.
- Erik P. Schartner, Heike Ebendorff-Heiepriem, Markus Pietsch and Tanya M. Monro, 'A hydrogen peroxide fibre optic dip sensor for aqueous solutions,' ACOLS/ACOFT, Adelaide, Australia, 2009.
- Erik P. Schartner, Richard T. White, Stephen C. Warren-Smith and Tanya M. Monro, 'Practical sensitive fluorescence sensing with microstructured fibres,' Optical Fibre Sensors, Edinburgh, UK, 2009

- Florian V. Englich, Erik P. Schartner, Dominic F. Murphy, Heike Ebendorff-Heidepriem, and Tanya M. Monro, 'Fusion Splicing Soft-Glass Suspended Core Fibers to Solid Silica Fibers for Optical Fiber Sensing,' ACOFT, Melbourne, Australia, 2010
- Erik P. Schartner, Heike Ebendorff-Heidepriem and Tanya M. Monro, 'Sensitive fluorescence detection with microstructured optical fibers,' SPIE Defense, Security & Sensing, Orlando, USA, 2011
- Erik P. Schartner, Dominic F. Murphy, Heike Ebendorff-Heidepriem & Tanya M. Monro, 'A low-volume microstructured optical fiber hydrogen peroxide sensor,' SPIE Defense, Security & Sensing, Orlando, USA, 2011
- Erik P Schartner, Heike Ebendorff-Heidepriem and Tanya M Monro, 'Driving down the detection limit in microstructured fiber-based chemical dip sensors,' Optical Fiber Sensors, Ottawa, Canada, 2011
- Erik P Schartner, Dayong Jin, Heike Ebendorff-Heidepriem, Jim A. Piper, Tanya M Monro, 'Lanthanide upconversion nanocrystals within microstructured optical fibres; a sensitive platform for biosensing and a new tool for nanocrystal characterisation,' Asia Pacific Optical Sensors, Sydney, 2012 (In press)

ABSTRACT

The capacity to measure the concentration of hydrogen peroxide in solution is critical for many disparate application areas, including wine quality sensing, aviation fuel monitoring and embryology. This thesis covers work related to the development of a low-volume hydrogen peroxide sensor, utilising microstructured optical fibres to perform measurements on small (<20 µL) sample volumes.

This work has used the interaction between the guided light and fluorescent molecules within the holes of microstructured optical fibres to perform detection. This interaction has been used firstly to optimise the sensing architecture, using photostable Quantum dots as a characterisation tool. This work also has potential biosensing applications, using the Quantum dots was fluorescent labels for antibody reactions. This thesis covers work related to lowering the effective detection limit using microstructured optical fibres to detect fluorescent molecules, utilising novel glasses and implementing a theoretical model to reduce the amount of background signal that is generated within the fibre. New candidates for fluorescent molecules in fibre are also examined, resulting in a further reduction of the minimum detectable concentration.

The second use of this interaction with the guided light involved the use of fluorophores that react with hydrogen peroxide to produce an increase in fluorescence. This increase in fluorescence can then be observed by monitoring the signal from either end of the fibre. By establishing a calibration curve that gives an expected fluorescence signal for a given hydrogen peroxide concentration it is then possible to correlate the observed fluorescence with the concentration of hydrogen peroxide present within the sample.

Additionally this thesis presents practical improvements to microstructured fibre dip sensors, including splicing the sensing fibres to commercial optical fibres as well as methods for mixing low volumes of liquids to enable rapid detection of target molecules.

DECLARATION

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 Erik Schartner 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.

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Adelaide, April 2012

Erik Peter Schartner

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I love deadlines. I like the whooshing sound they make as they fly by.

— Douglas Adams

SUMMARY

This thesis covers work related to the development of a low-volume hydrogen peroxide sensor. This work has used the interaction between the guided light and fluorescent molecules within the holes of microstructured optical fibres to perform detection. This has been used firstly for potential biosensing applications, by detecting Quantum dots which can be used as fluorescent labels for antibody reactions. The second application involves a fluorophore that reacts with hydrogen peroxide or hydroperoxides to produce an increase in fluorescence. This increase in fluorescence can then be observed by monitoring the fluorescence from either end of the fibre. By establishing a calibration curve that gives an expected fluorescence signal for a given hydrogen peroxide concentration it is then possible to correlate the observed fluorescence with the concentration of hydrogen peroxide present within the sample.

Chapter 1 reviews the literature on optical fibre based sensing methods, exploring both unstructured core-clad fibres, as well as microstructured fibres with transverse holes through their cross-sections. The main focus of this chapter is on fluorescent techniques, but alternative methods are also examined.

Chapter 2 documents progress during this PhD project towards lowering the effective detection limit using microstructured optical fibres to detect fluorescent molecules. This work begins with sensing using small, nanoscale core fibres, using quantum dots as the fluorophore for detection. Here, some basic theoretical models are also established to gain an understanding about how the parameters of the fibre geometry affect the sensing performance. This chapter proceeds with a detailed examination of the autofluorescence from different soft glasses, culminating in the fabrication of a microstructured optical fibre from the glass showing the lowest fluoresence signal. This work then moves on to utilising doped nanoparticles for detection, using an infra-red source and upconversion fluorescence signals to perform detection. Several types of nanoparticles are examined, including particles doped with both Erbium and Thulium. An extension of this work is included in Appendix A, looking at the fabrication of a novel fibre geometry to attempt to reduce the effects of glass fluorescence in these types of sensors.

Chapter 3 examines practical improvements to the currently used methods, that would act to improve the usability of these types of sensors in real world scenarios. This is an attempt to move these systems out of the laboratory, and develop them to a point at which they could potentially be deployed in the field. This covers work to splice

these to conventional silica fibres, including both practical results for splicing as well as a basic theoretical model to explore what would be required to improve the efficiency of these splices. This work also develops a novel temperature sensor, which is integrated with the fluorescent sensors discussed earlier.

Chapter 4 explores work on the use of microfluidic mixing techniques to attempt to circumvent the requirements for surface attachment, while preserving the low-volume characteristics that are inherent in sensing using these microstructured fibres. This allows easier changes to new fluorophores, as commercially available molecules can be used without the requirement of modifications to attach them to the surface. This includes work on relatively large scale microfluidic chips, moving on to development of a cost-effective mixing system utilising in-house made capillaries and a simple micro-T mixing chamber.

Chapter 5 delves into work on fabricating microstructured optical fibres from a new type of soft glass with an improved UV transmission. The motivation behind this work is to open up new possibilities for fluorescent molecules by increasing the transmission window of these fibres into a range which is suitable for more of these molecules. This chapter investigates work on extruding these types of preforms, and the subsequent fibre fabrication and characterisation.

Chapter 6 investigates work towards practical fuel degradation sensing, specifically looking for hydroperoxides, again using a fluorescent method which a literature survey shows to be the method most suitable for use in a microstructured fibre. The motivation for this work is the desire to fabricate a quick, effective sensor that can give an immediate indication as to the degradation state of a sample of aviation fuel. This chapter primarily looks at characterisation of fluorophores synthesised at the University of Adelaide to determine their viability for use in the optical fibres.

Chapter 7 looks at an extension to this work, where the focus has shifted from sensing in fuel to work on detection of hydroperoxides in aqueous solutions. This initially begins with wine sensing as the application, but it becomes apparent that the ideal application for this type of low-volume sensor is in the detection of hydrogen peroxide around embryos in In vitro fertilisation (IVF). This chapter again primarily focuses on fluorophore characterisation, looking both at the performance of the fluorophore in cuvette as well as in fibre. This covers both commercially available fluorophores, as well as characterisation of several fluorophores synthesised at Adelaide.

This chapter culminates with work on the functionalisation of one of these synthesised fluorophores on the internal surfaces of the microstructured fibres. This exploress progress towards developing a new method for functionalisation in the fibres, as well as characteri-

sation and progressive development of the performance of the fluorophore itself.