Hollow-core optical fibres as optofluidic microreactors

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Motivation

We use hollow waveguides to enhance light-matter interactions in: microscale chemistry, biosensing, optical manipulation

Photonic crystal fibre is ideal because:
- well-defined optical modes
- tightly confined light
- long interaction lengths
- small sample volumes (nL/cm)
Outline

- photonic crystal fibre
- optofluidic microreactors
- (photo)catalysis in PCF
- HC-PCF Raman probes
- higher-order modes

https://www.np.phy.cam.ac.uk/research-themes/optofluidics  te287@cam.ac.uk
photonic crystal fibre
light guided by total internal reflection: “perfect mirror”

typical diameter 125 μm
How to guide light in a hollow core?

hollow glass capillary ⇒ light leaks out

extremely high losses for small diameter capillaries: >1000 dB/m for a bore radius of 10 µm

We need a mirror to keep the light trapped!
Inspiration from nature: photonic crystal mirrors

“crystal”: ordered dielectric composite
refractive index $n$
varying spatially
⇒ light is scattered

“photonic”: $d \approx \lambda$
⇒ scattered light interferes,
  Bragg diffraction

Condition: $m\lambda = 2d \sin \theta$
Hollow-core photonic crystal fibre (PCF)

- typical diameter: 100-200 µm
- periodic array of air channels
- central defect
- light trapped in hollow core

Bragg condition:

\[ m\lambda = 2d \sin \theta \]


Stack-and-draw process

- silica capillary (1mm)
- low index defect
- fabrication
- 20 mm
- ≈ 2000 °C
- 0.1 mm
Hollow-core photonic crystal fibre

HC bandgap PCF
- small core: ~12 µm
- low losses (~0.1 dB/m)
- narrow transmission window

Kagome HC-PCF
- large core: ~23 µm
- higher loss (~1 dB/m)
- broadband guiding
optofluidic HC-PCF microreactors
Conventional photochemical reactors

- large sample volumes (100s of ml)
- high power excitation required (>100 Watts)
- offline detection only => very slow optimization processes
Liquid-filled photonic bandgap fibre

only core filled

- total internal reflection
- highly multimode

core and cladding holes filled

- bandgap guidance
- single-mode

Optofluidic photonic bandgap fibre

low loss of 5dB/m (1064 nm) and 90% launch efficiency

well-defined guided mode in the liquid core ($D_2O$)

excellent optofluidic waveguide!

Optofluidic kagomé hollow-core PCF

- broadband guiding
  (water-filled: 450-700 nm)
- fundamental mode guidance
- low loss: 5-10 dB/m
High-index soft glass HC-PCF

- single-ring hollow core fibres [1,2], based on anti-resonant reflection [3]
- high-index SF6 soft glass (n=1.8): => can use high-index solvents
- well-defined modes in toluene (n= 1.49 at 600 nm) [4]
- monitored photochemical CO-dissociation

Why use HC-PCF as microreactors?

<table>
<thead>
<tr>
<th></th>
<th>Cuvette</th>
<th>Fiber</th>
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</thead>
<tbody>
<tr>
<td><strong>Length</strong></td>
<td>1-10 cm</td>
<td>10 cm-1 m</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>3 mL/cm</td>
<td>4 nL/cm</td>
</tr>
<tr>
<td><strong>Intensity</strong></td>
<td>1 W/cm²</td>
<td>3.5×10⁵ W/cm²</td>
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Photocatalysis in optofluidic HC-PCF
Early photochemistry work in PCF

• 100,000 x enhanced photolysis
• photoswitching of azodyes
• heterogeneous catalysis in PCF
• microfluidic flow reactor for rapid screening of photo drugs

mostly proof-of-principle studies
can we also do new chemistry?

Enhanced photolysis,

Sub-picomole photo-switching,
Williams, Lab Chip. (2012).

Rh heterogeneous catalysis,

Microfluidic integration

overall goal: **sustainable** catalysts for **solar fuel** generation

- carbon nanodot (CND) light absorbers: non-toxic, cheap, scalable
- Ni- or Co-based molecular catalysts (avoid Pt, Rh)

**Key issue:**
limited mechanistic understanding due to a lack of *in situ* measurements
electron-transfer process between CNDs and catalysts is rate-limiting

=> we study this process using a methyl viologen (MV) redox dye
Photocatalysis in HC-PCF microreactors

- Catalyst screening using very small sample volumes (<40 nL)
- Observed unknown CND activation process
- Compare UV-Vis absorption time-traces with kinetics modelling

Monitoring Cobaloxime photocatalysts

• cobaloxime intermediates involved in H₂ generation via H⁺ reduction detected in fibre
  • Ru(bpy)₃²⁺ was used in lieu of CNDs.

• long pathlength in HC-PCF enables detection of weak absorption peaks
  • transient and steady-state observed and assigned with DFT

• measure fluorescence to understand photocatalytic pathways?
Micro Stern Volmer analysis in hollow-core fibre

- collection of fluorescence through fibre modes
- obtain quenching coefficients using sub-µL catalyst samples
- demonstrated here with a 4CzIPN photocatalyst

with Alex Cresswell (Bath), Erwin Reisner (Cambridge)

A. S. Gentleman and T. Lawson et al., Chem. Science (2022)
https://doi.org/10.1039/D2CC03996F
In-situ Raman sensing in photocatalysis

- CND driven reduction of $\text{MV}^{2+}$ to $\text{MV}^{•+}$
- observed clear changes in Raman peaks
- excellent agreement with DFT calculations

A. S. Gentleman, E. Miele et al., CLEO PR 2020 paper SM4M.8
Outlook photocatalysis

• optimize reaction conditions for catalysis (CND / electron donor / pH)

• further studies with novel catalysts (CoP, enzymes)

• combine with microfluidic mixing chips for rapid catalyst screening

• monitor with in fibre Raman spectroscopy

T. Lawson et al. (ACS Catal., accepted)

S. Unterkofler et al. (Opt. Lett. (2014).)
Raman probes for Li:ion battery chemistry
Motivation: understanding battery degradation

Faraday Institution: UK-wide project to study degradation mechanisms in next-generation Li-ion batteries

We develop background-free **operando** fibre-coupled **Raman** probes to track changes in the **electrolyte** chemistry.

**THE FARADAY INSTITUTION**

with Clare Grey, Michael de Volder, Jeremy Baumberg

Michael Frosz (Erlangen)
Embedding hollow-core fibre probes in batteries
Setup for operando Raman sensing in batteries

E. Miele et al., Nature Comms 12, 1651 (2022). https://doi.org/10.1038/s41467-022-29330-4
Setup for operando Raman sensing in batteries

- single-ring anti-resonant hollow-core fibre
- sample volume ca 1 µL **LP57** electrolyte: 1.0 M LiPF$_6$ in 3:7 ethylene carbonate (EC): ethyl methyl carbonate (EMC) + 1% vinylene carbonate (VC) additive

Raman spectra during electrochemical cycle

track Raman lines of electrolyte components during electrochemical cycle:

- ethylene carbonate (EC)
- vinylene carbonate (VC)

Raman spectra during electrochemical cycle

key observations:

- increase in EC mode (SEI formation / Li$^+$ intercalation?)
- bubble formation (SEI / singlet oxygen formation?)
- increase in vinylene mode (cathode electrolyte oxidation?)

- first operando Raman detection in a full-cell battery
- observed creation of vinylene species
Outlook: battery Raman probes

Electrolyte studies

- study degradation mechanism with ‘spiked’ cells (acid, H₂O ...)

Localized sensing

- embedded high-index glass microlens
- monitor electrode surfaces during cycling

Hollow-core fibre with high-NA micro lens

(M. Groom and E. Miele, in preparation)

microlens method similar to: Lombardini et al. Light: Sc. & Appl. 7, 10 (2018)
Higher-order modes in optofluidic HC-PCF
1. probe in **core** and **surface** regions with:
   - **(A)** fundamental mode
   - **(B)** higher-order mode

2. excite reaction in **fundamental mode**

3. measure diffusion of reaction products

   how to controllably excite higher-order modes?

Spatial light modulation

- SLM surface imaged onto fibre end face
- control both phase- and amplitude profile

Setup for higher-order mode excitation

- tunable light source (filtered supercontinuum)
Mode quality in optofluidic kagomé fibre

LP_{31} mode: good agreement between simulation and experiment
Modes in optofluidic kagomé PCF

- excited modes up to LP$_{33}$ across visible range

Transmission matrix measurements

Holographic excitation of input mode

Measured output modes

Interferometric analysis of output modes

Transmission Matrix

with George Gordon (Nottingham), Tim Wilkinson (Cam)

Efficient excitation of high-purity modes

- calculate mode by FDFD
- generate hologram
- measure field by off-axis holography

Can obtain pure modes with high launch efficiency

Outlook: mode-based ‘tomography’

- study catalytic surfaces under reaction conditions
- probe radial concentration profile with higher-order modes
- measure transverse diffusion times

PCF flow reactor, Pt nanoparticles within HC-PCF.
Outlook: functionalize HC-PCF with flavins: enzyme-mimic photocatalysts

- immobilise Flavins on inner HC-PCF walls
- surface-selective probing with higher-order modes
- study enzyme-functionalized carbon nanodots

Conclusions

• optofluidic PCF microreactors allow in-situ monitoring of (photo)catalytic processes

• Raman fibre probes can monitor electrolyte chemistry in Li:ion batteries

• higher-order modes enable spatially-resolved sensing
Thank you for your attention!

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Thank you for your attention!

- **photonic crystal fibre**
- **optofluidic microreactors**
- **(photo)catalysis in PCF**
- **HC-PCF Raman probes**
- **higher-order modes**

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