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Hydrogel-based pH-sensors

Development and characterisation of optical and electrical pH-sensors based on stimuli-responsive hydrogels

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Sundsvall 2019-03-19

Outline

- Introduction
- Problem motivation and research question
- Theory and experimental results:
  - pH-sensors
  - Hydrogels
  - Optical sensors
  - Electric sensors
- Conclusions
- Future work

Introduction

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Scope of the thesis work

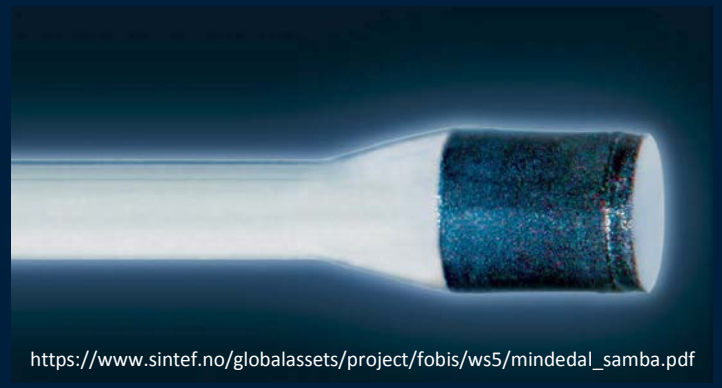
- Synthesis and characterization of pH-sensitive hydrogels not before used in sensor configurations
- The hydrogels have been evaluated in both optical and electrical sensor systems
- Conceptual verification of a multi parameter optical sensor

Introduction

Continuous monitoring patients at Intensive Care Units (ICU)

- Stress-induced hyperglycemia is common in ICU patients and is associated with poor outcome
- Blood glucose concentrations should be carefully continuously controlled in ICU
- Glucose sensors susceptible to pH changes

Introduction



https://www.sintef.no/globalassets/project/fobis/ws5/mindedal_samba.pdf

Optical pressure sensor

https://www.sintef.no/globalassets/project/fobis/ws5/mindedal_samba.pdf

Introduction

Waste water treatment

Industry processes

Food industry

Health care

DOI:10.1097/PRS.0b013e318186ca8a

DOI: 10.1126/sciadv.1601314

Concreate constructions

Research question

There is a need for new pH sensitive materials that can be used in new and improved sensor designs.

Problem formulation

- Identify suitable pH-sensitive hydrogels that can be coated on flexible substrates and optical fibers (article I, III)
- Characterization and evaluation of these hydrogels in optical (article I, V) and electrical (article IV) sensor configurations
- Dual-parameter sensing (article II)

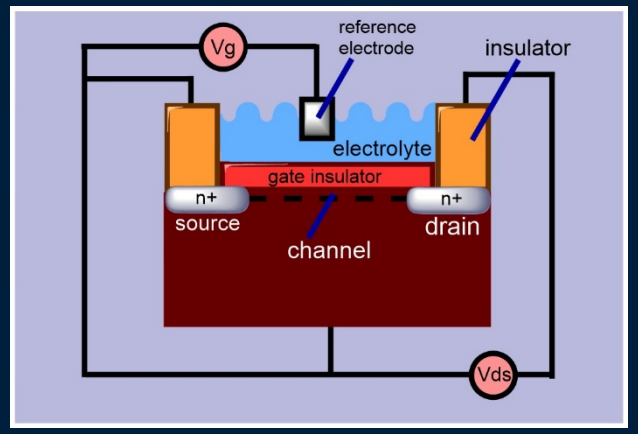
Theory
pH-sensors

Glass electrode

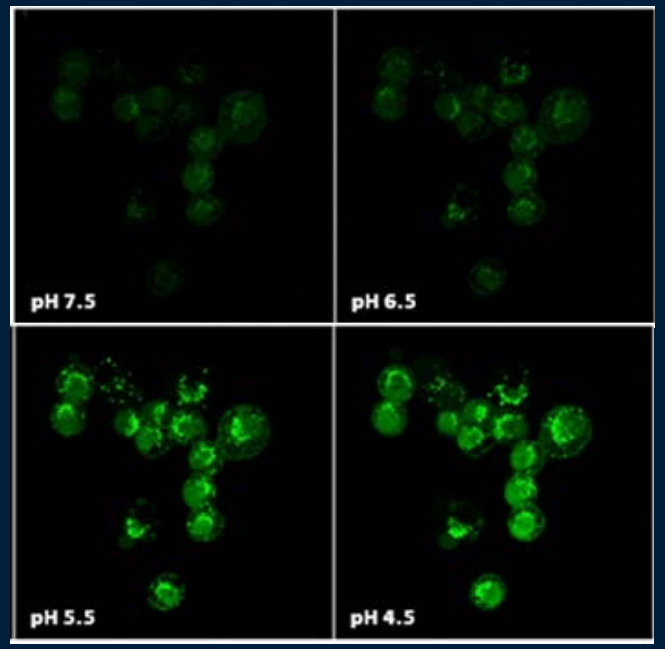
pH paper sticks

Theory
pH-sensors

Ion-sensitive field-effect transistor (ISFET)



Fluorescent pH sensors



https://www.thermofisher.com/se

Imaging pH sensors

https://www.presens.de/fileadmin/user_upload/brochures/180516_char_VisiSens_Broschuere_2018_dv1_web_2.pdf

Theory
pH sensitive hydrogels

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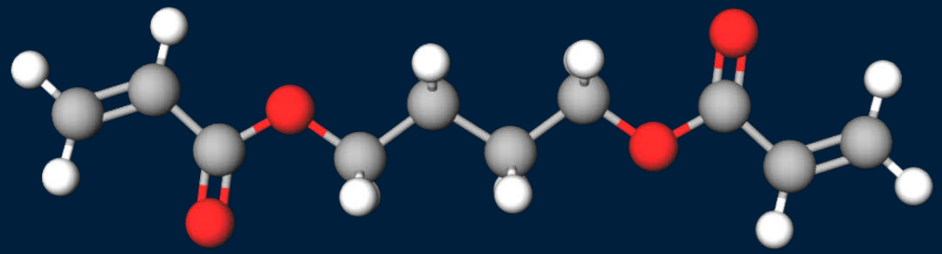
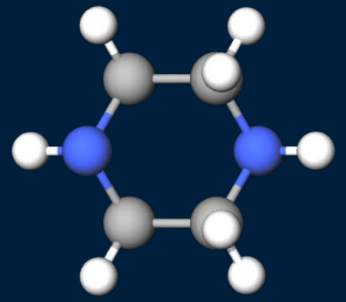
1,4-butanediol diacrylate



Piperazine



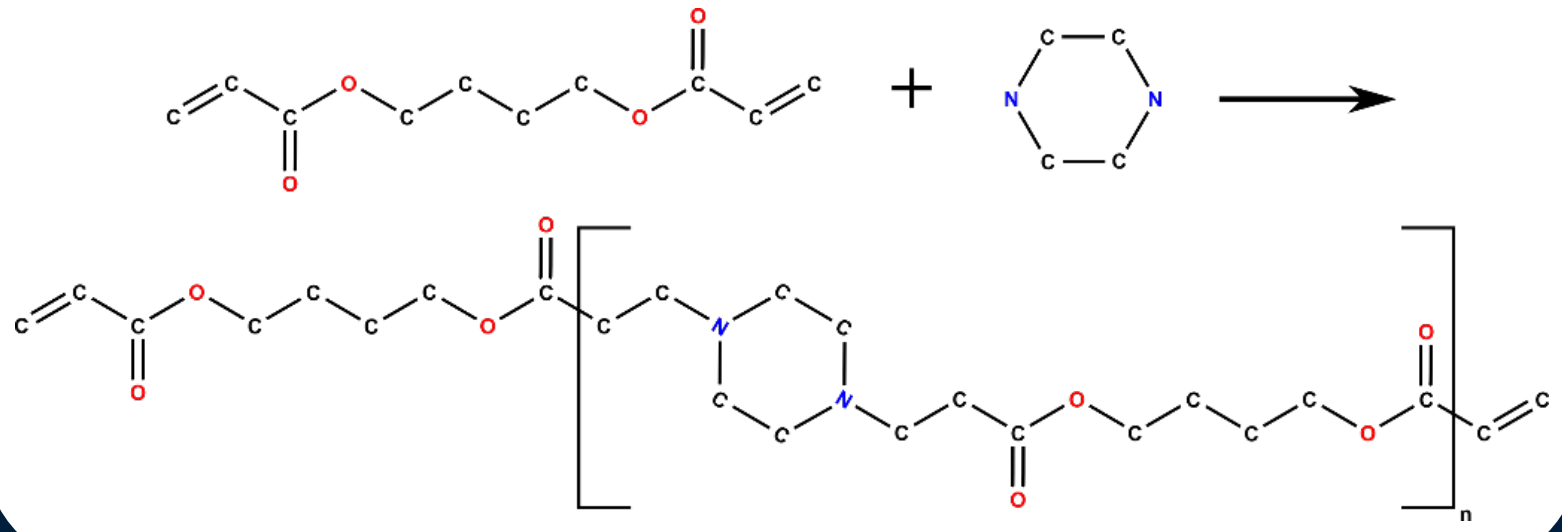
Hydrogen
Carbon
Oxygen
Nitrogen

Theory

Synthesizing a polymer

1,4-butanediol diacrylate

Piperazine



Theory

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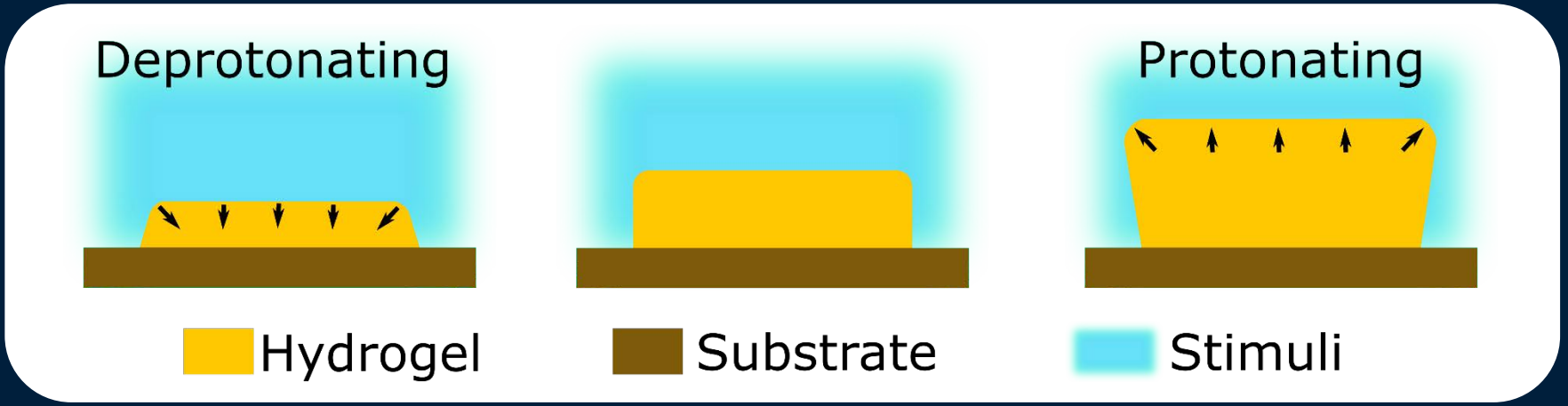
pH sensitive polymer



Theory

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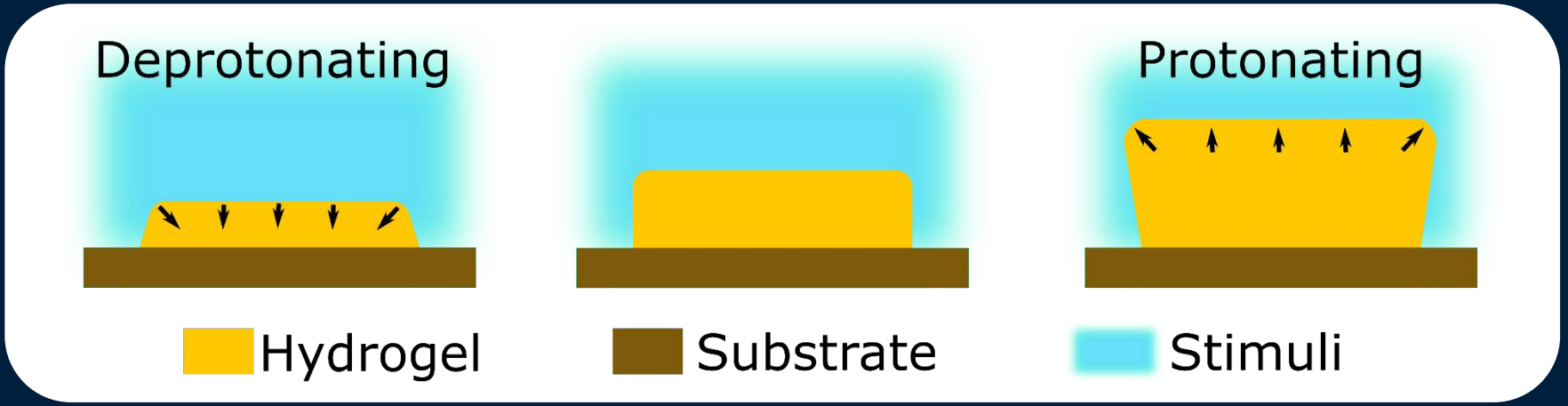
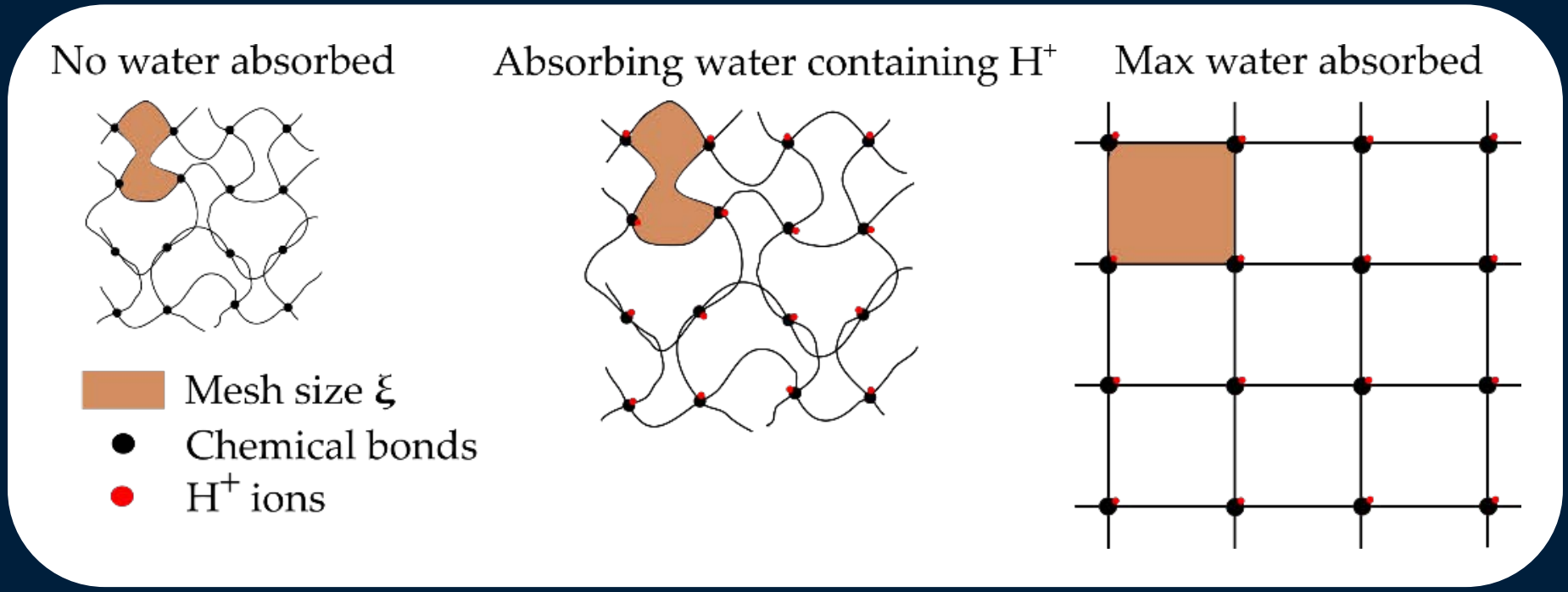
pH sensitive polymer



Water content changes within the hydrogel, alters the effective refractive index and permittivity of the hydrogel

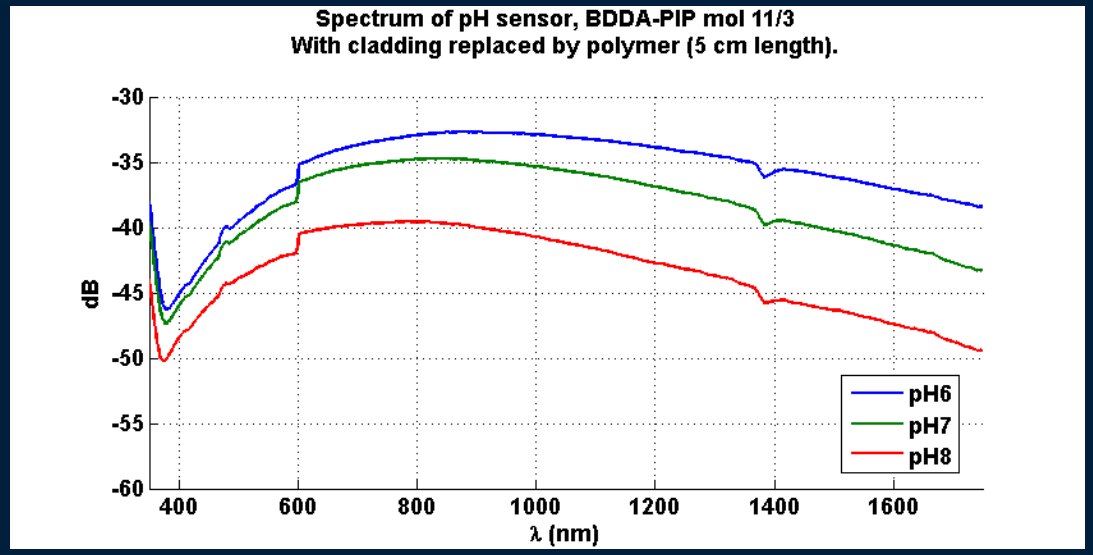
Theory

Cationic hydrogel

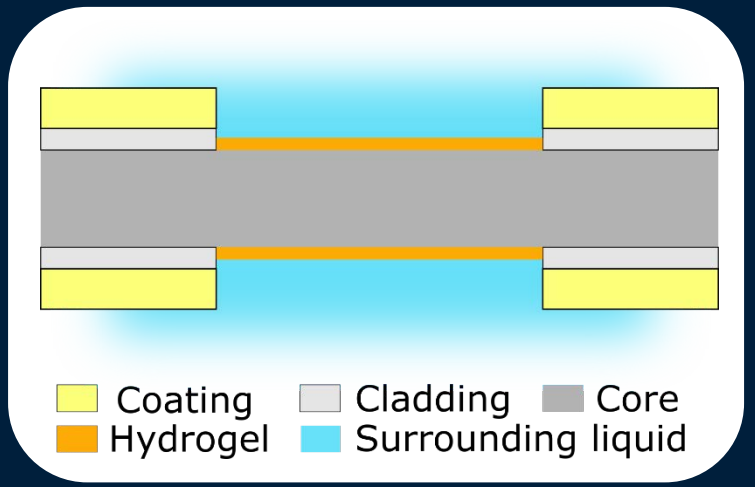


Experimental results

Amplitude sensor



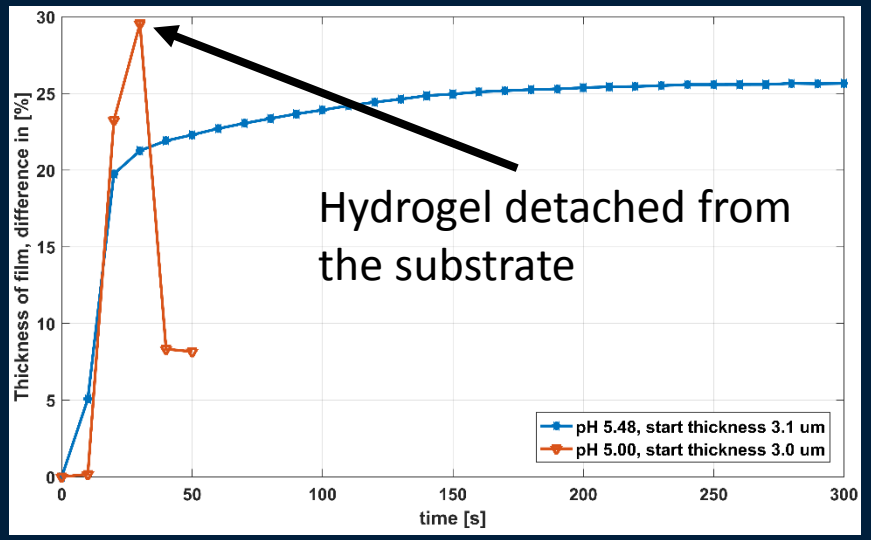
Visible — Near infrared (NIR)



- Strip the fiber
- Etch away the cladding
- Coat the core with pH-sensitive hydrogel

Challenges due to large parameter space

- Hydrogel preparation
  - Adhesion
  - Viscosity
  - Wetting
  - Crystallization at room temperature
  - Hydrogel expansion with pH
  - Curing of hydrogel
- Sensor configuration
  - Flexible substrates (bending)
  - pH responsivity
  - pH range
  - Repeatability
  - Optical fiber cleave angles and length



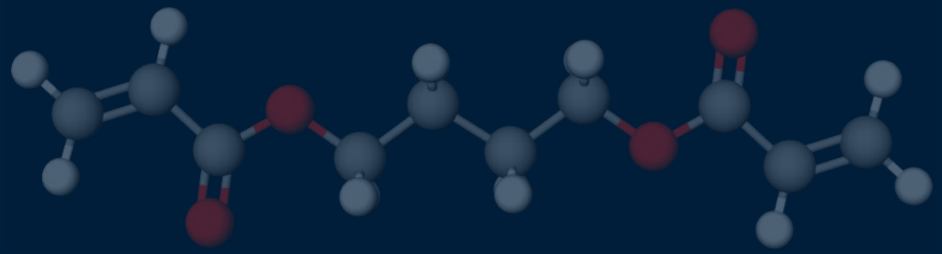
Adhesion problem on a wafer

Adhesion problem on an optical fiber

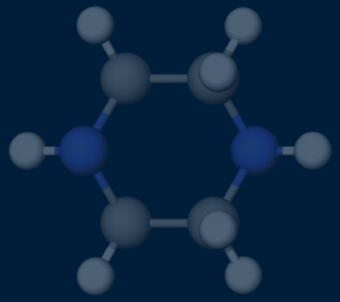
Theory
Hydrogels

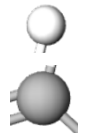
Symmetrical molecules

1,4-butanediol diacrylate



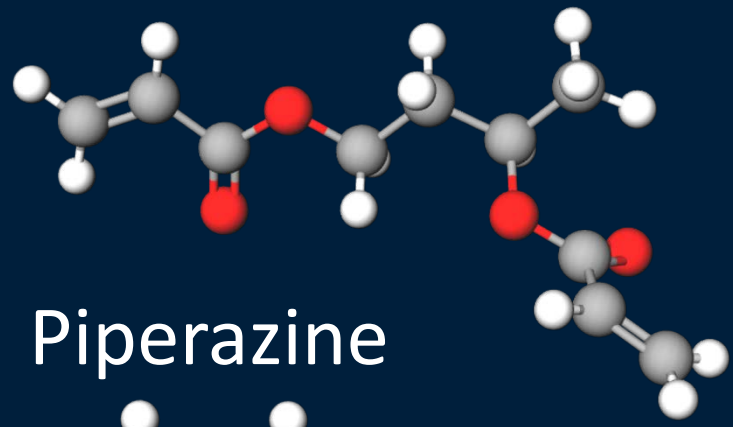
Piperazine



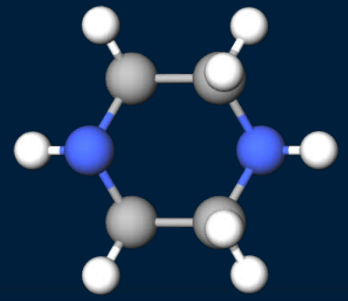


Unsymmetrical molecule

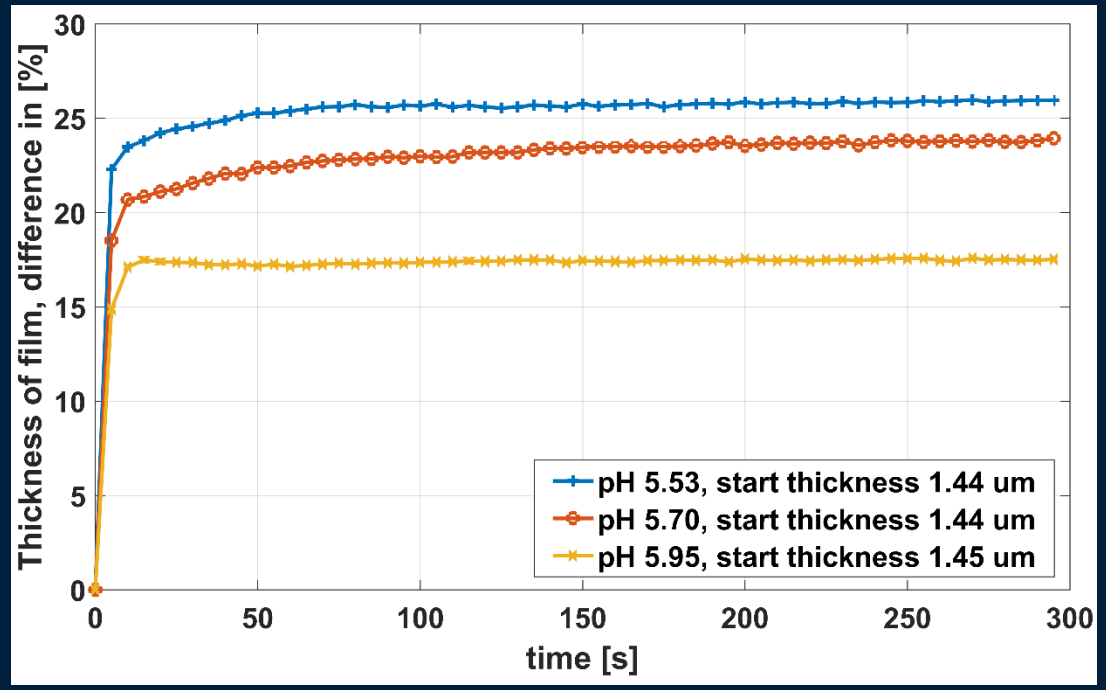
1,3-butanediol diacrylate



Piperazine



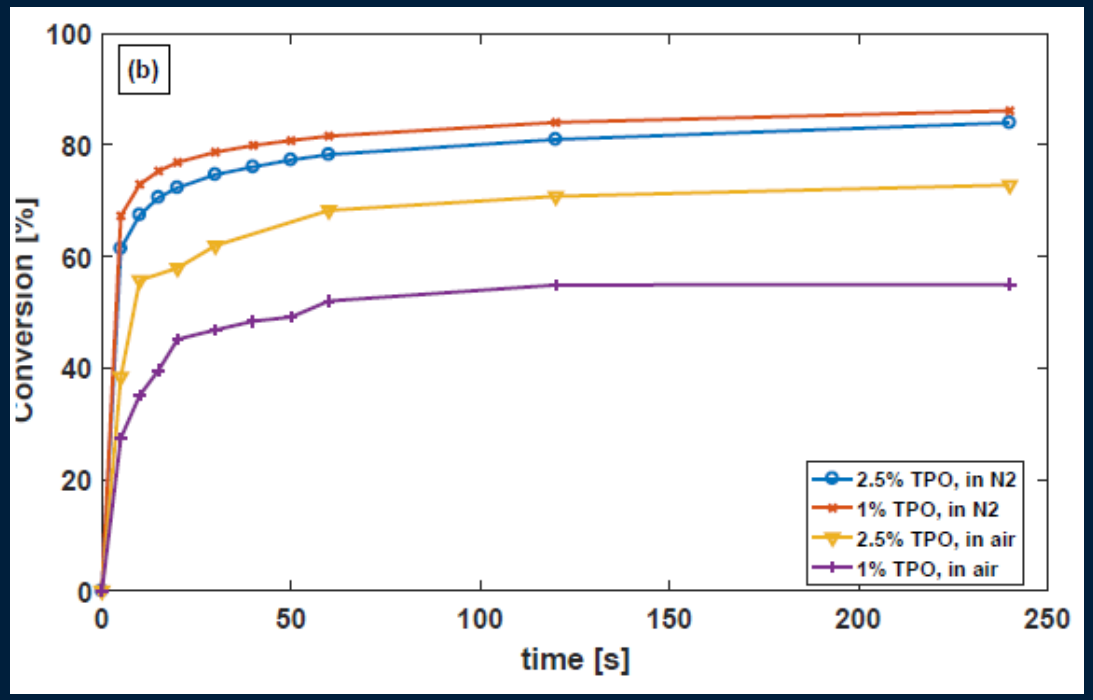
Experimental results



Main findings

- pH sensitive
- Does not crystallize
- Mol ratio 2:1
  - Large expansion degree
  - Challenging to make thin films

Experimental results

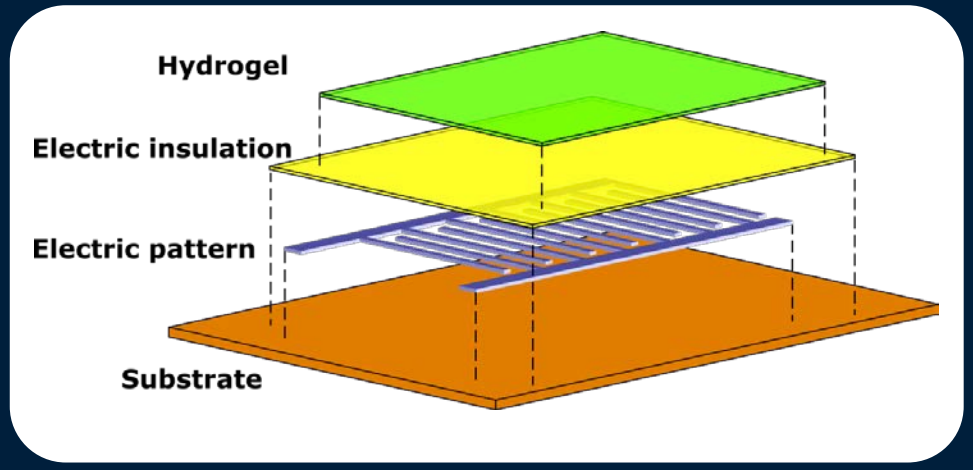


Main findings

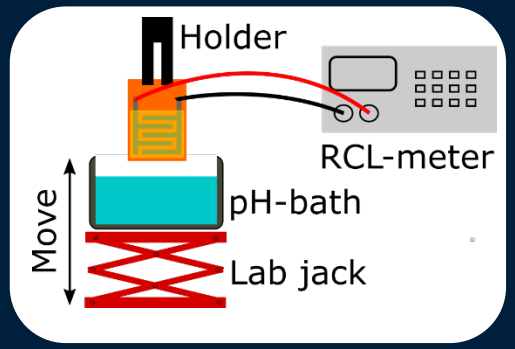
- Best to cure thin films in an inert atmosphere

Flexible capacitive pH-sensor

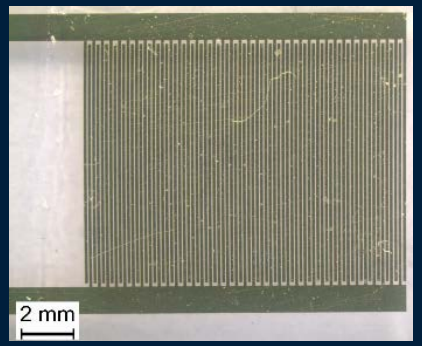
Sensor layout



- Print an electric pattern
- Electric insulation
- Sensing layer

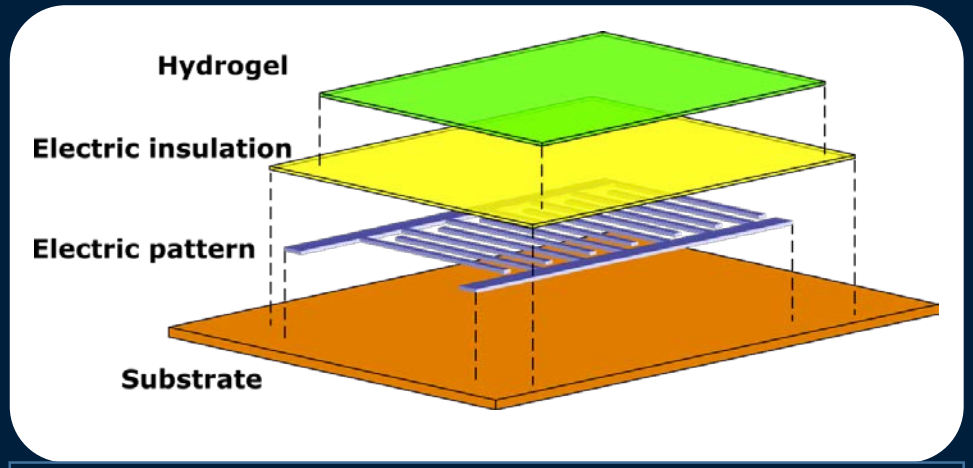


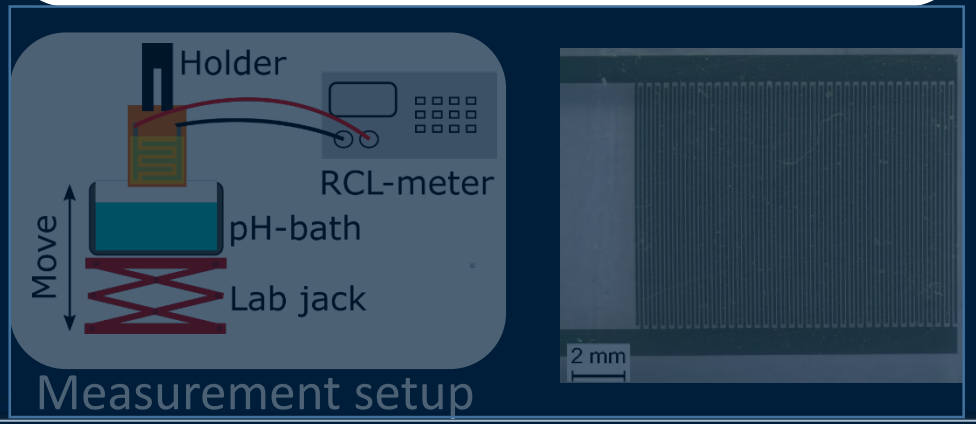
Measurement setup



Flexible capacitive pH-sensor

Sensor layout





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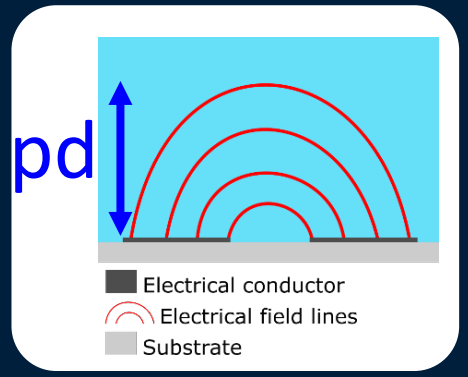
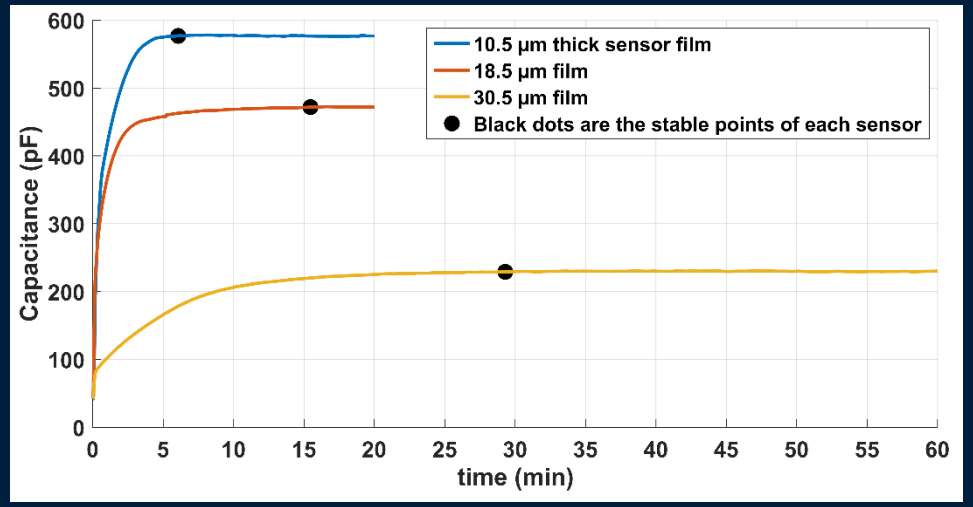


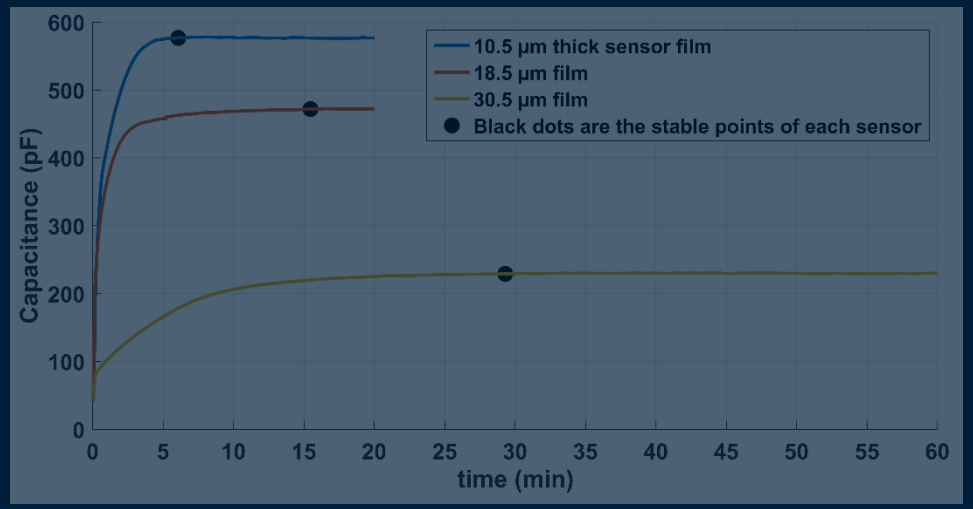
Penetration depth

Experimental measurements



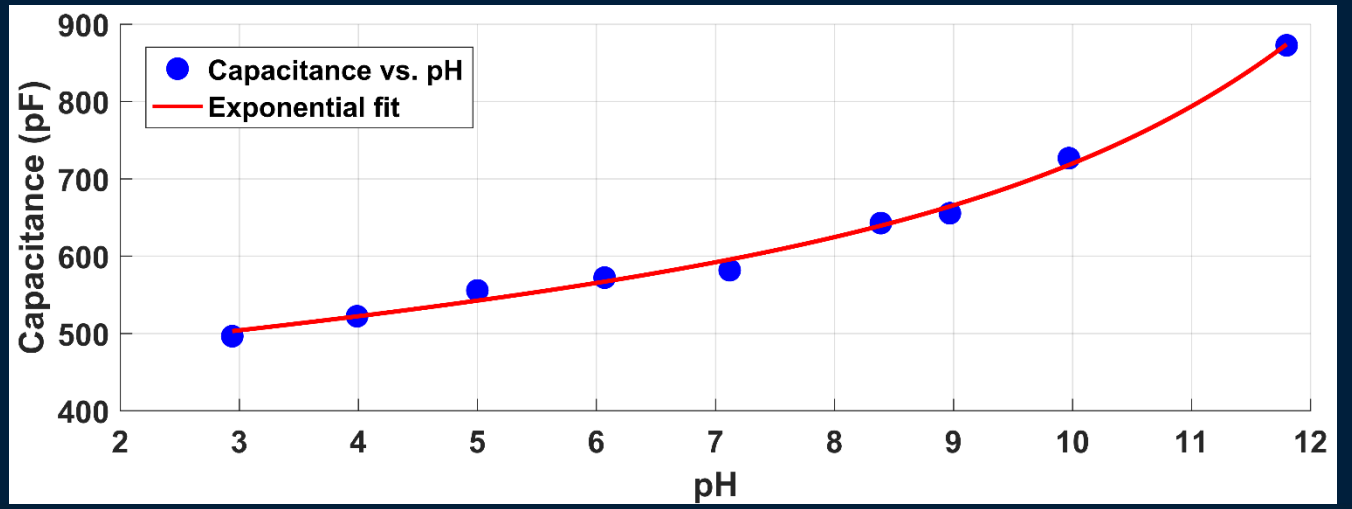
Time to stable sensor at pH 7 for different thicknesses

Experimental measurements

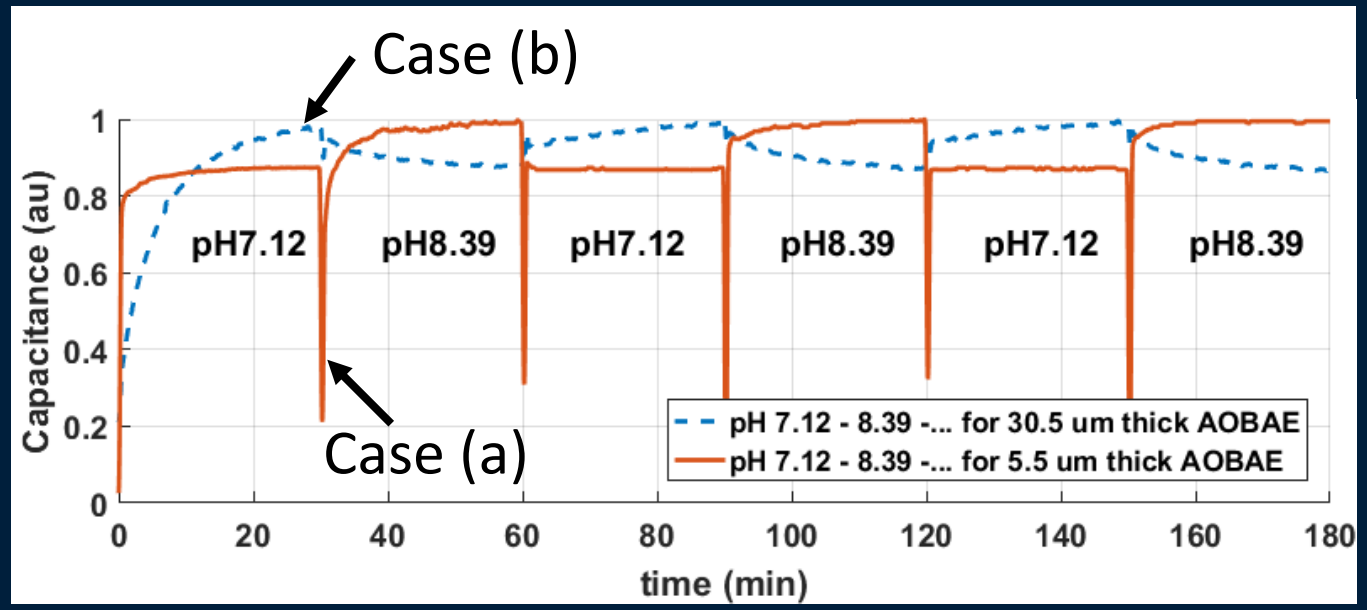


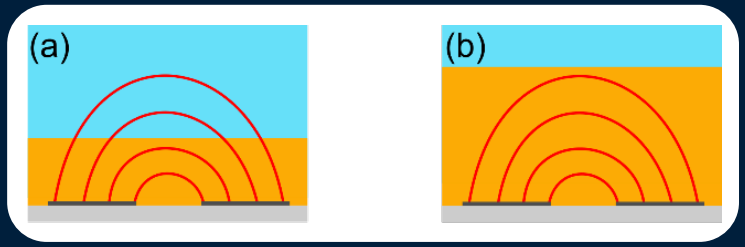
Time to stable sensor at pH 7 for different thicknesses

Capacitance response to pH

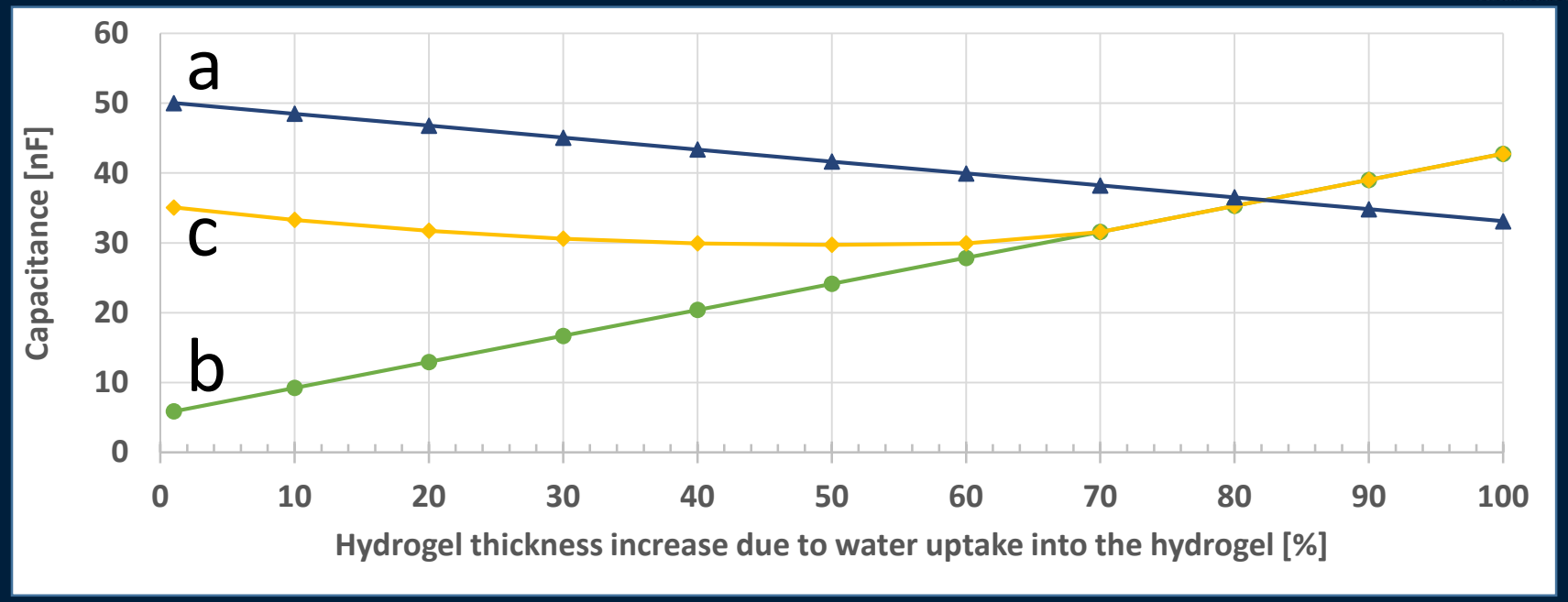


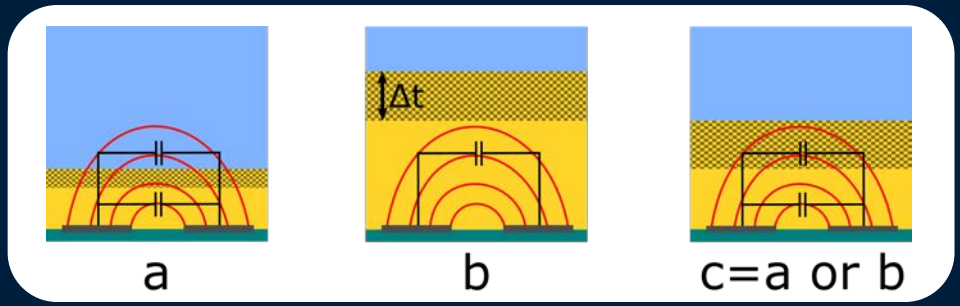
Experimental measurements





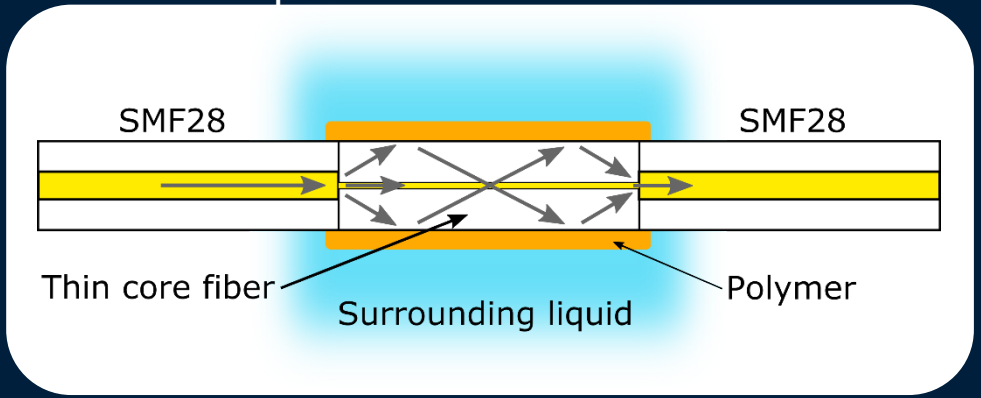
Experimental measurements



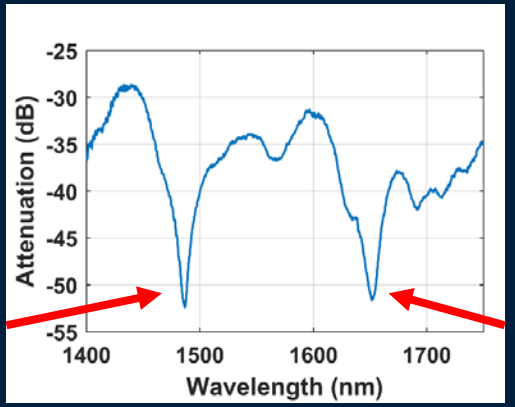


Fiber optic pH-sensor

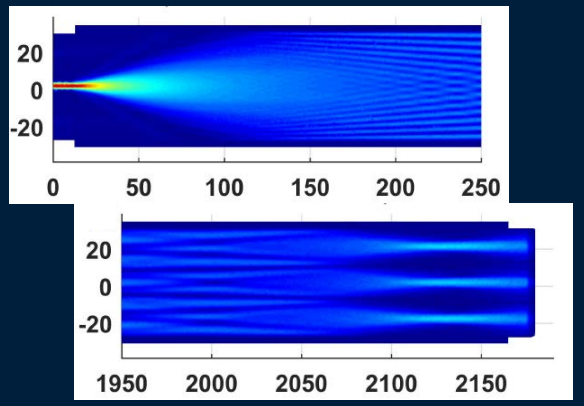
Inline fiber optic Mach-Zehnder interferometer



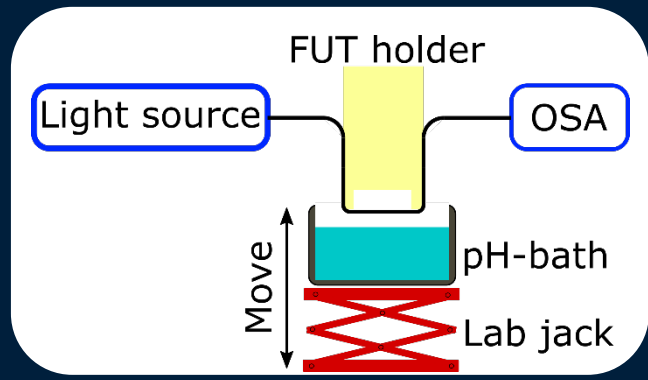
- Splice a thin core fiber between two single mode fibers
- Coat and cure the hydrogel layer



Typical output spectrum

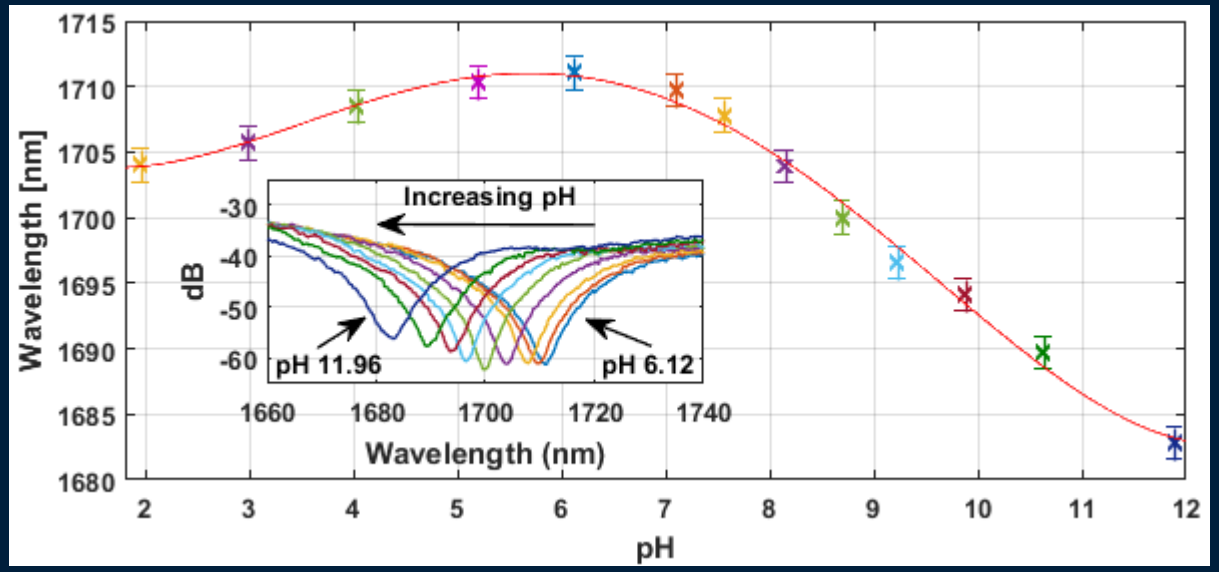


Simulation, in- and out-put spectrum

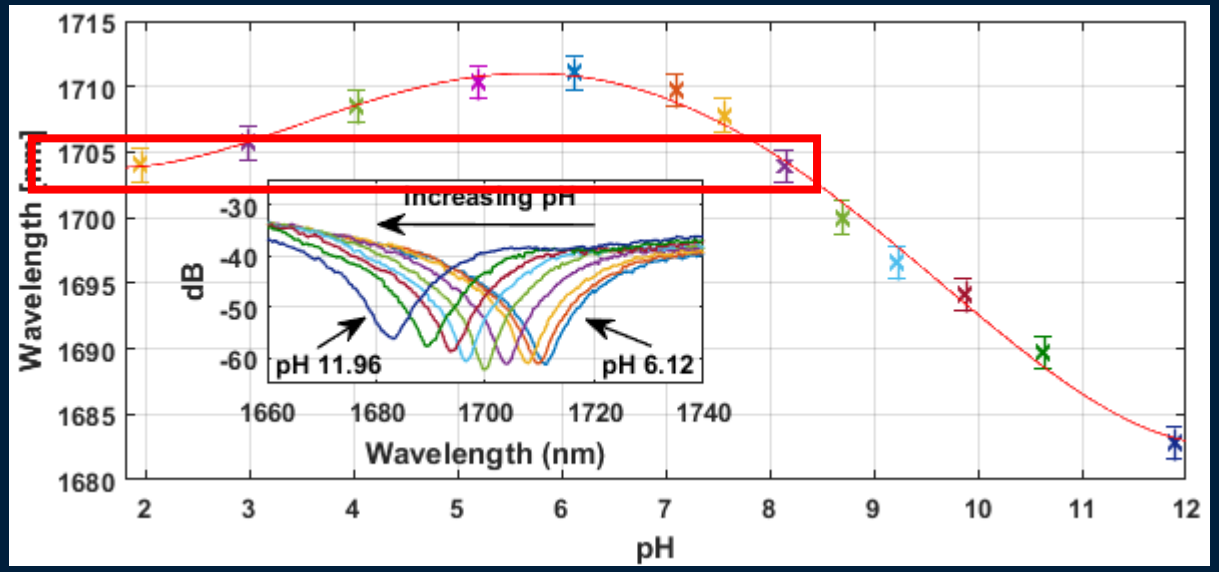


Measurement setup

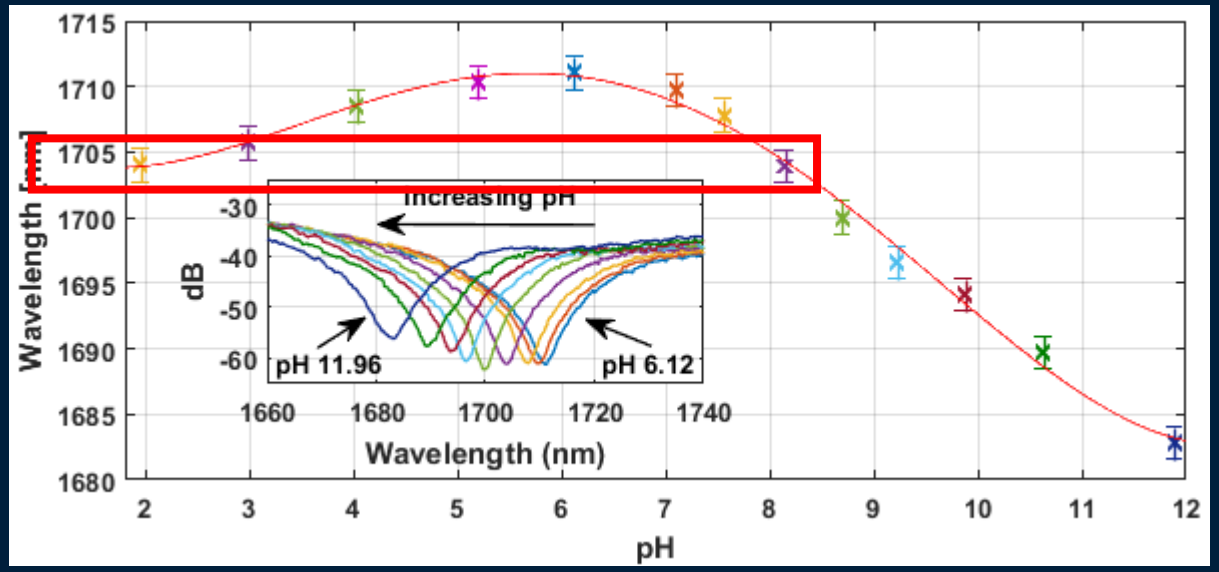
Fiber optic pH-sensor

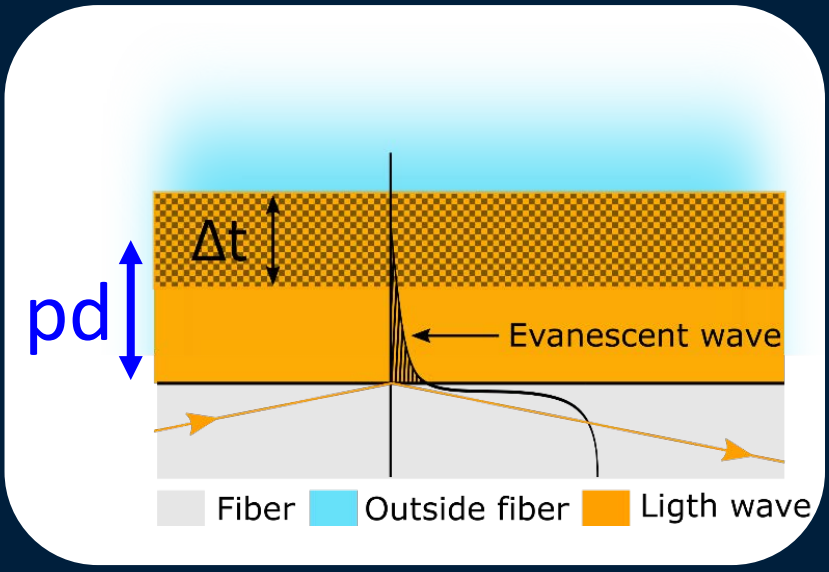


Fiber optic pH-sensor

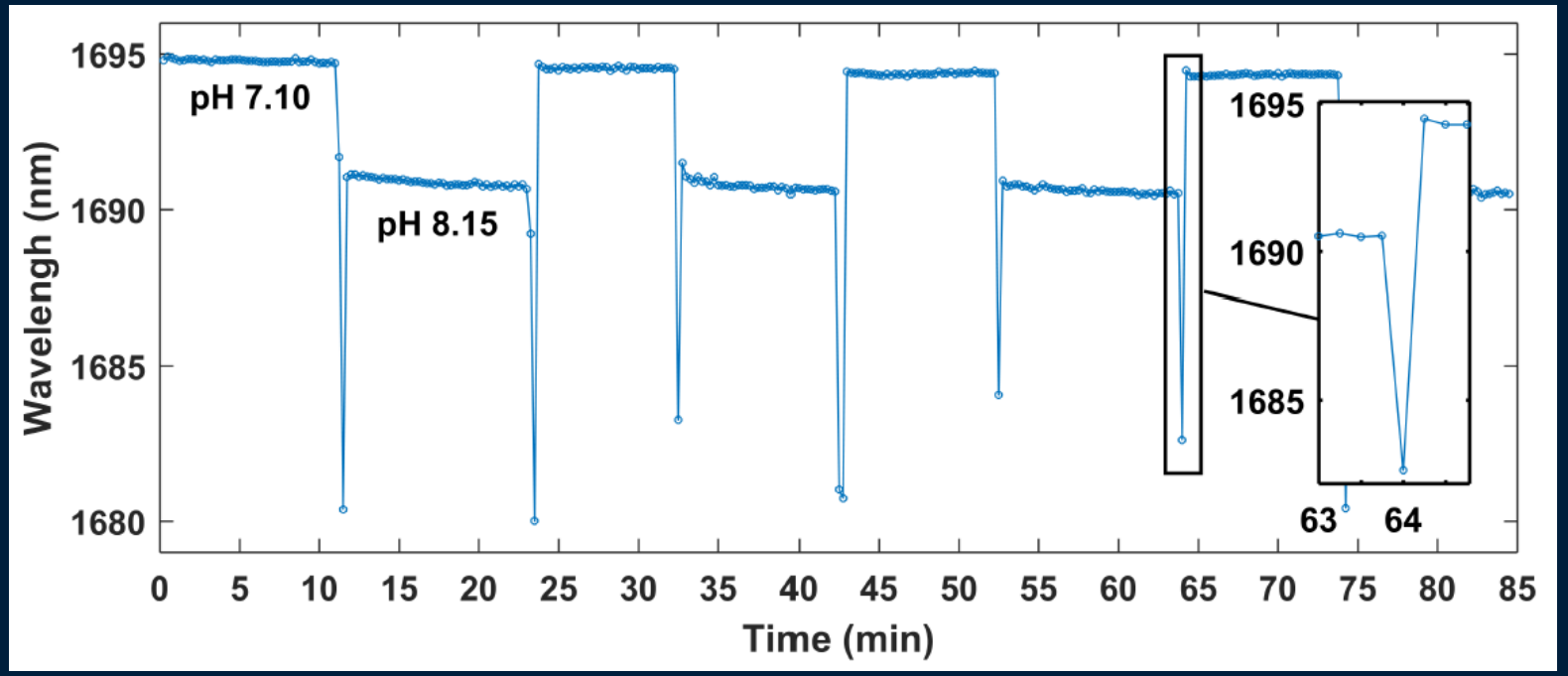


Fiber optic pH-sensor

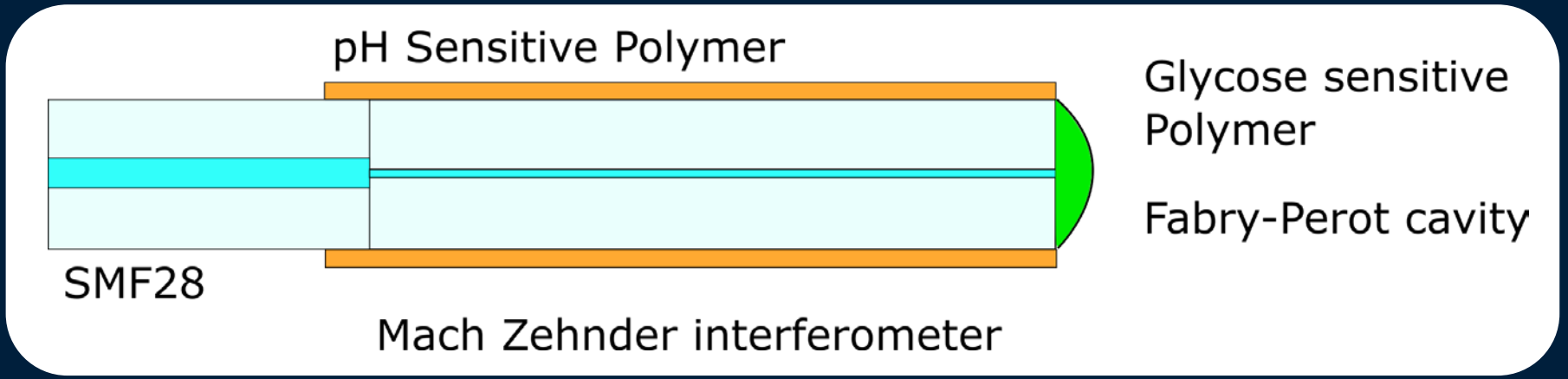




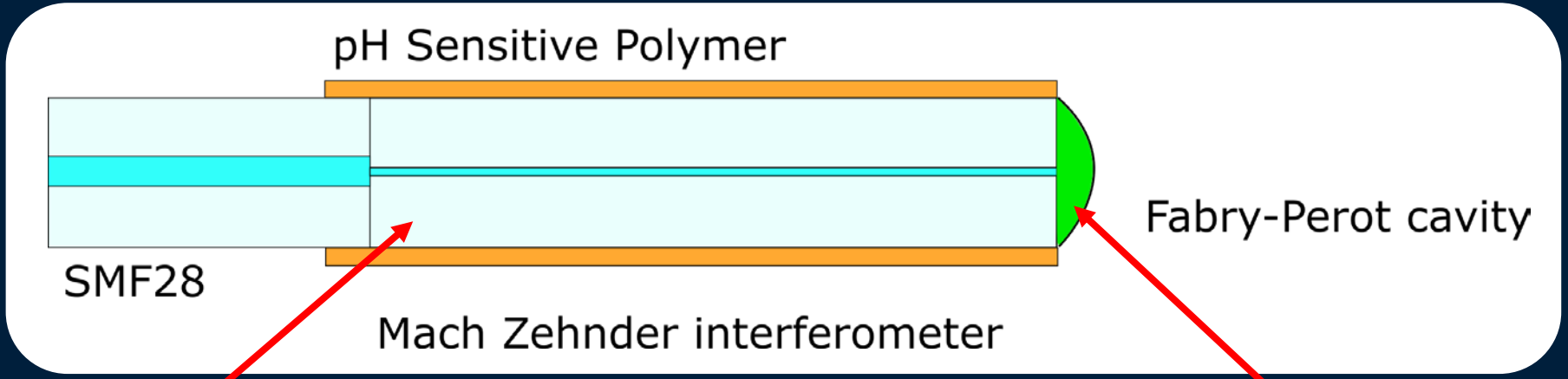
Fiber optic pH-sensor

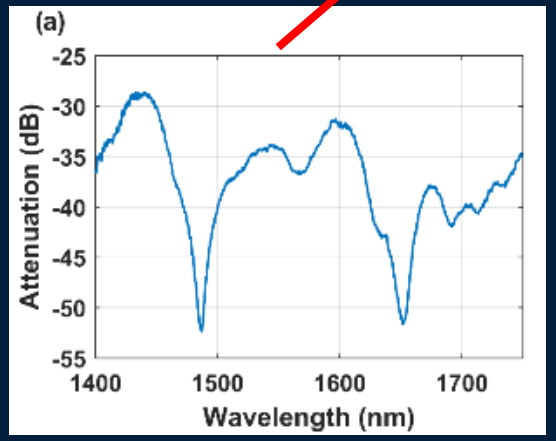


Dual parameter sensor

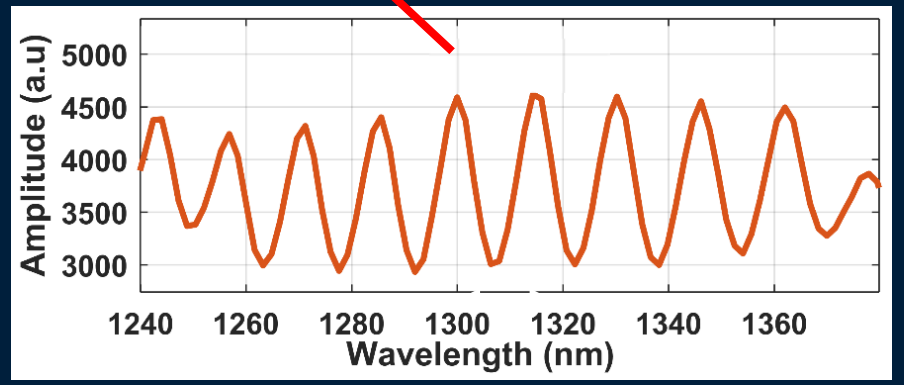


Dual parameter sensor



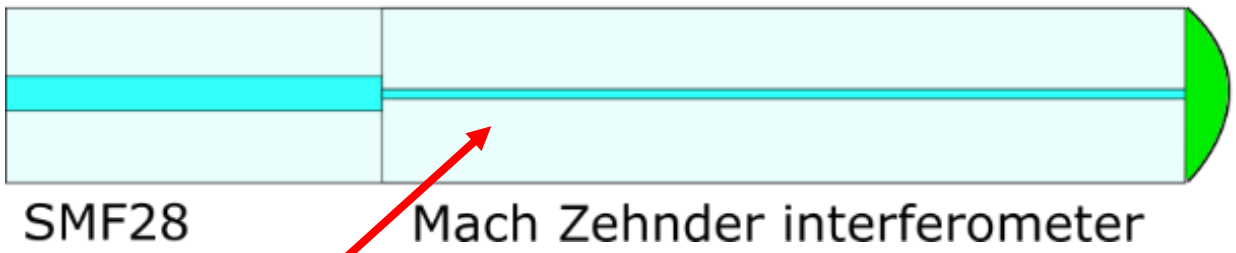


Low frequency interferometer
App. 150 nm between minimas

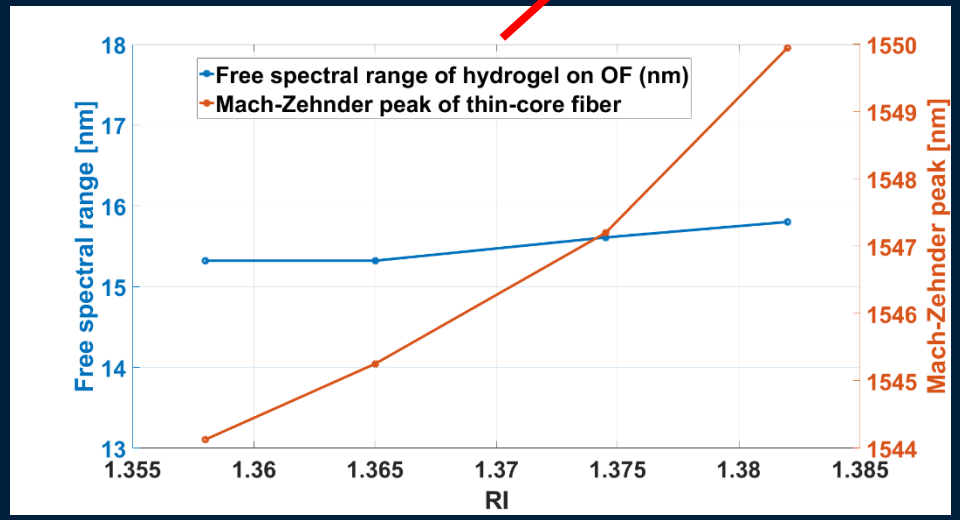


High frequency interferometer
App. 15 nm between minimas

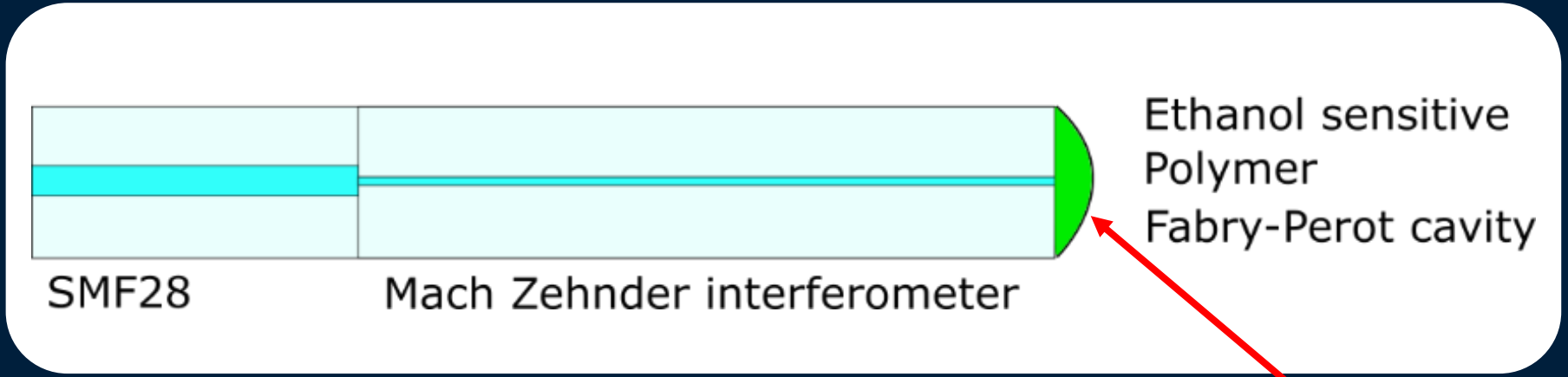
Dual parameter sensor

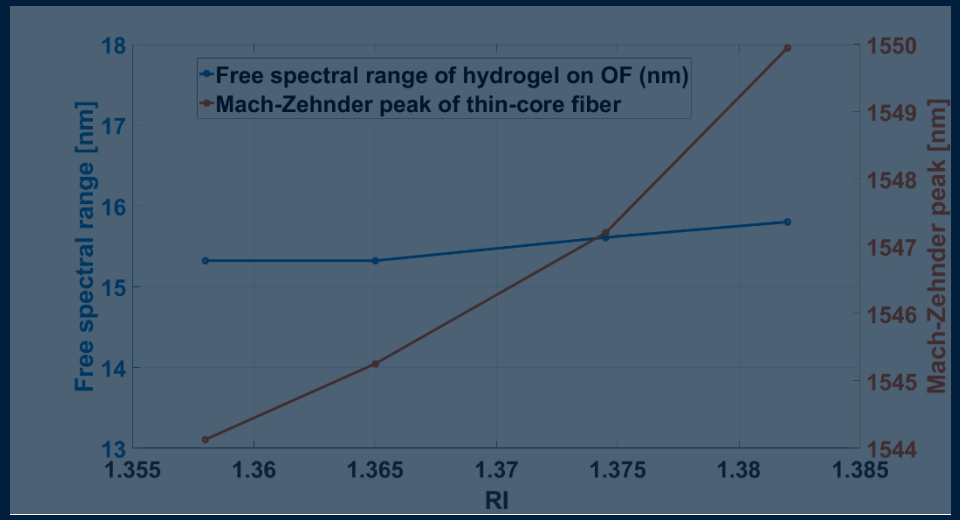


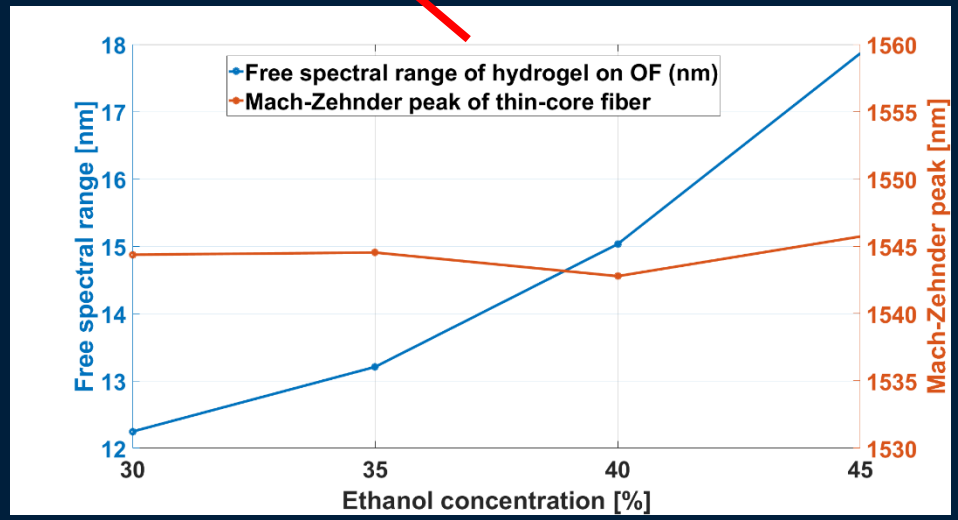
Ethanol sensitive Polymer
Fabry-Perot cavity



Dual parameter sensor







Conclusions

- The investigated hydrogels are very promising for pH-sensitive sensor applications
- The hydrogels are suitable to be used in both optical and electrical sensor configurations
  - Optical sensors showed response to pH between 2 and 12
  - Electrical sensors showed response to pH between 3 and 12
- The conceptual dual parameter sensor showed small crosstalk and is thus a promising technique

Future research

- Further characterisation of the hydrogel
- Redesign the Mach-Zehnder interferometer to work in telecom wavelength ranges
- Develop methods for better adhesion
- Further investigate the dual parameter sensor

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Thank you for your time