



Infrared Microspectroscopy (IRM) Beamline

Overview and recent highlights on beamline capabilities

Jitraporn (Pimm) Vongsvivut

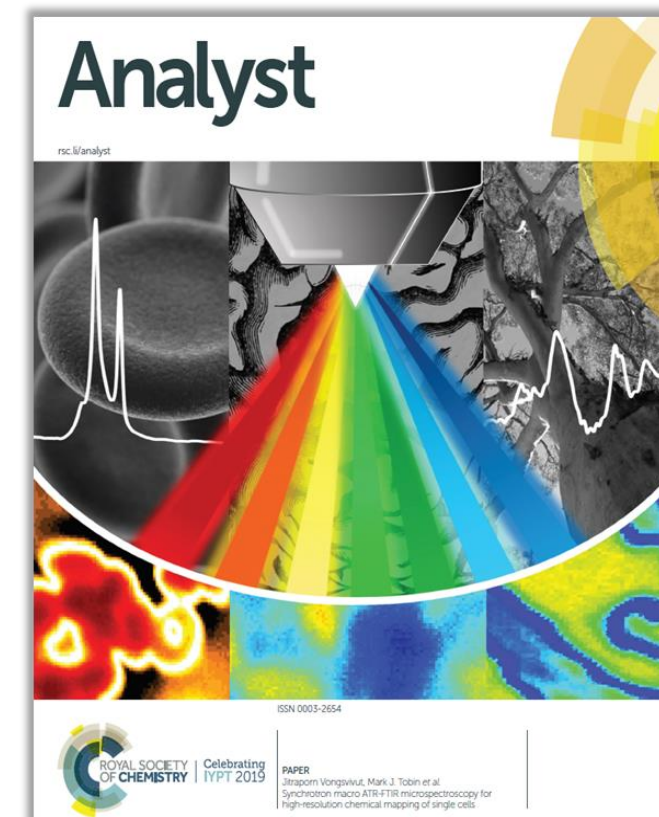
Senior Scientist – IRM Beamline
ANSTO – Australian Synchrotron

jitrapov@ansto.gov.au

Science. Ingenuity. Sustainability.

OVERVIEW

- **Traditional Sampling Methods**
 - *Transmission* with 4-angle polarisation analysis
 - *Reflectance* for *in-situ* monitoring of chemical and catalysis reactions
- **Macro-ATR Technique and Recent Applications***
 - Novel *Spirulina* bioactive wound healing coating
 - New β -carotene microcapsules using plant protein complexes
- **Progress on New Piezo-Controlled ATR Technique****
 - *In-situ* monitoring of electrochemical reaction in batteries

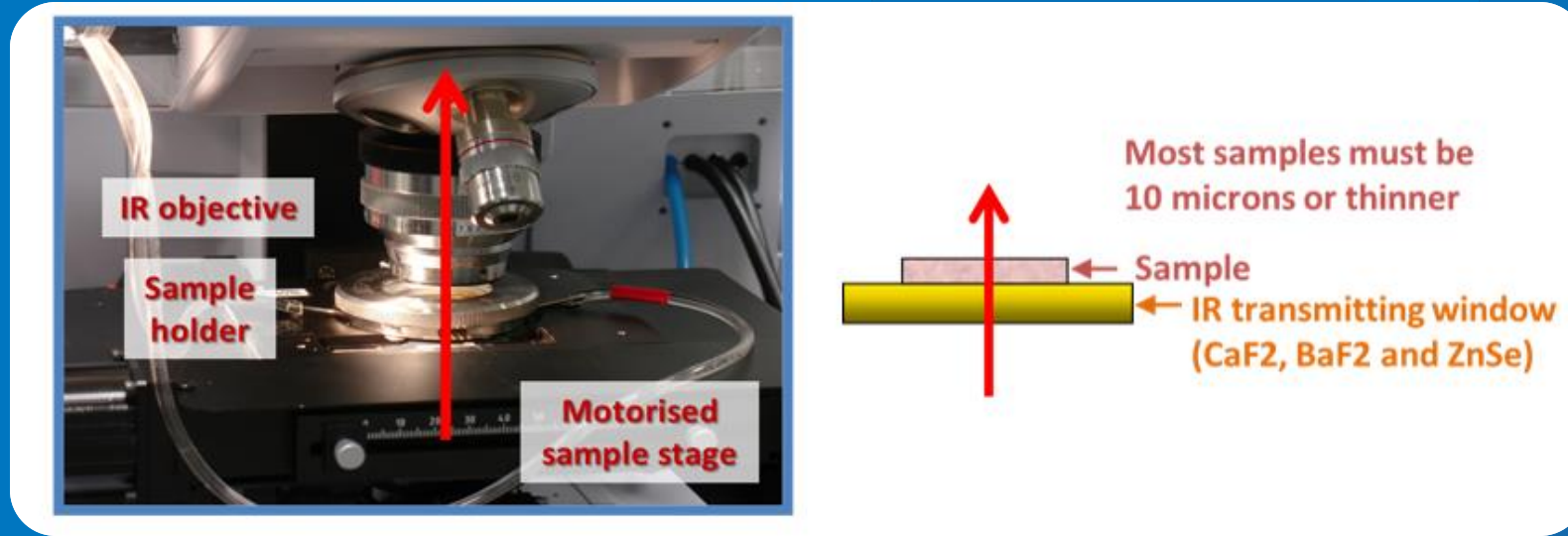


*Ref: J. Vongvivut, D. Perez-Guaita, B.R. Wood, P. Heraud, K. Khambatta, D. Hartnell, M. Hackett, M.J. Tobin, "Synchrotron macro ATR-FTIR microspectroscopy for high-resolution chemical mapping of single cells," *Analyst* (2019) **144**, 3226-3238.

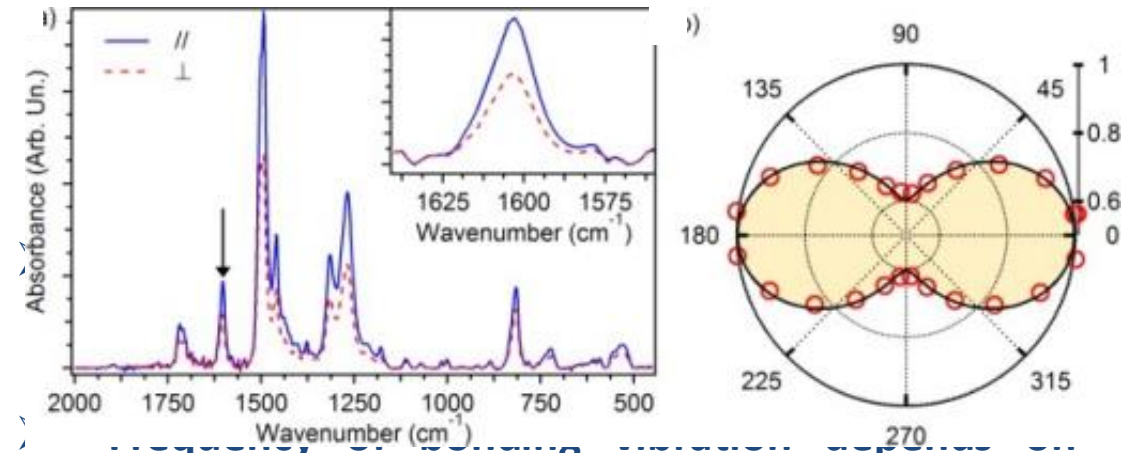
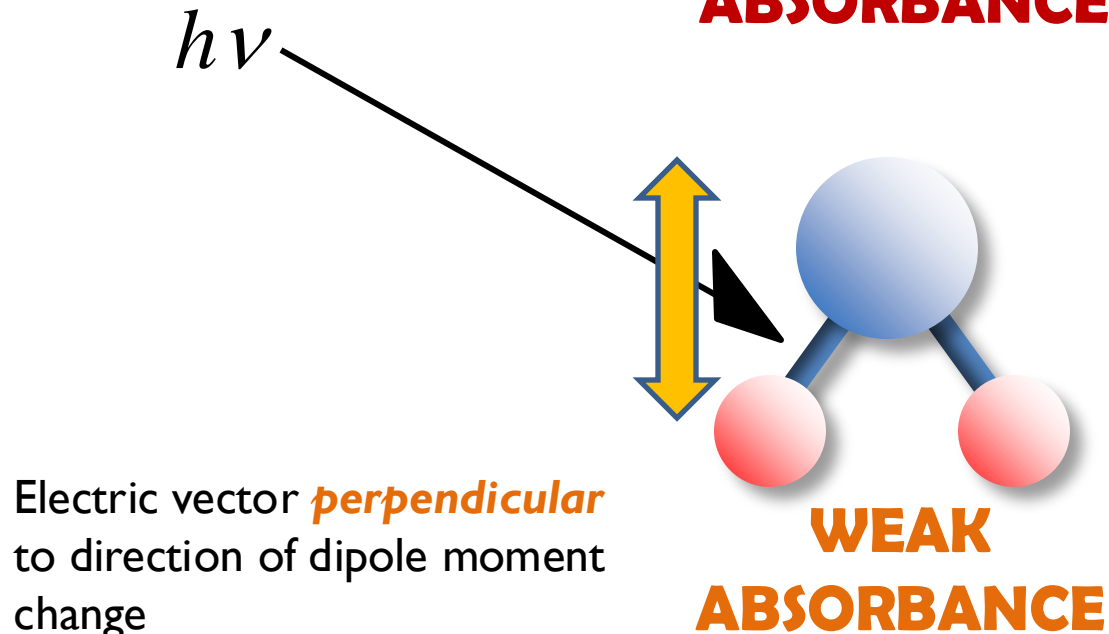
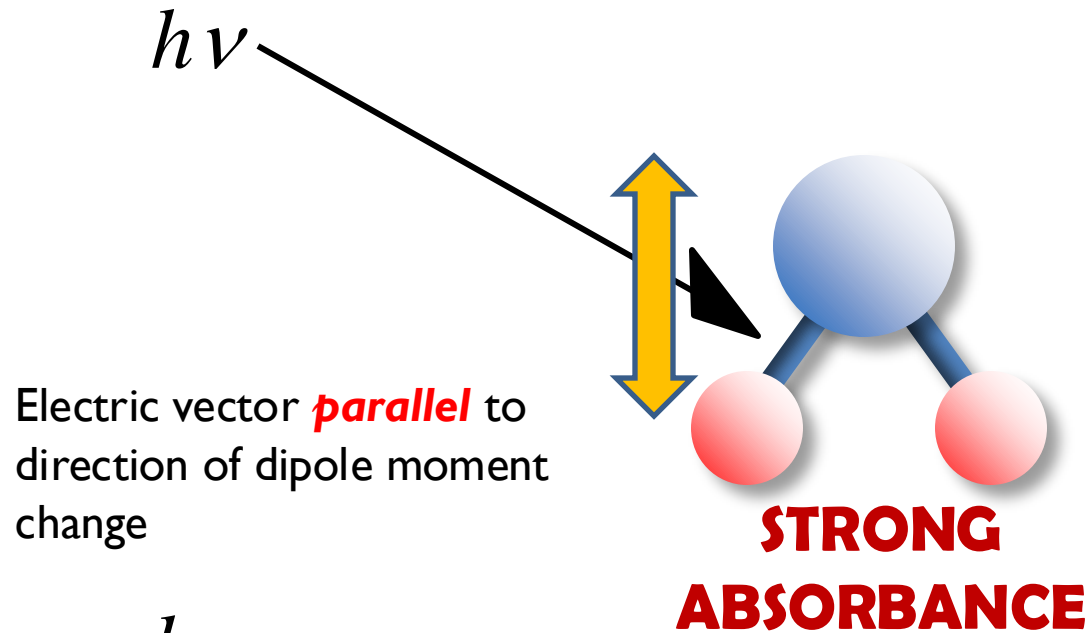
Ref: S. Liu, J. Vongvivut, Y. Wang, R. Zhang, F. Yang, S. Zhang, K. Davey, J. Mao, and Z. Guo, "Monolithic Phosphate Interphase for Highly Reversible and Stable Zn Metal Anode," *Angew. Chem. Int. Ed.* (2023), **62, 4, e202215600.

TRADITIONAL SAMPLING METHODS

– *Transmission* with 4-Angle Polarisation Analysis –



POLARISED-IR SPECTROSCOPY



mass of atoms and strength of bond

Reference: V. Fasano, A. Polini, G. Morello, M. Moffa, A. Camposeo, D. Pisignano, *Macromolecules* (2013), **46** (15), 5935–5942.

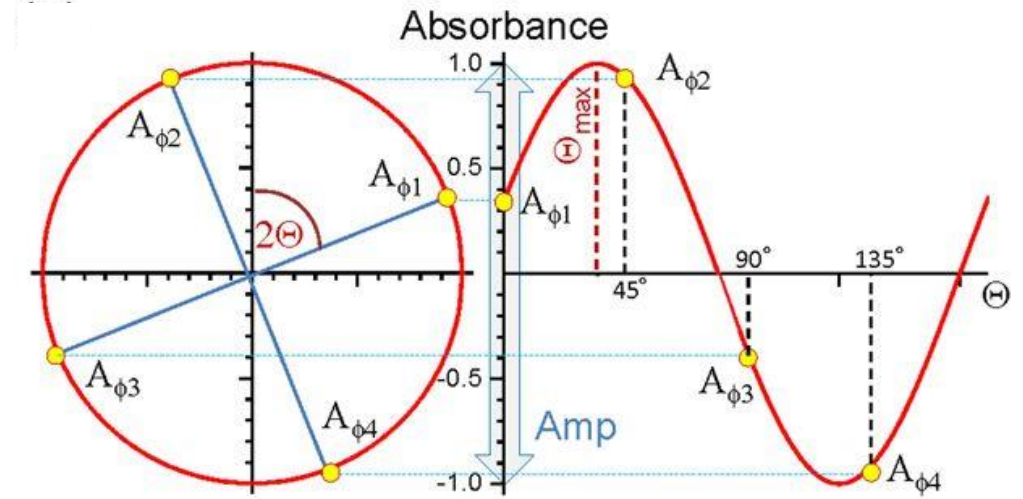
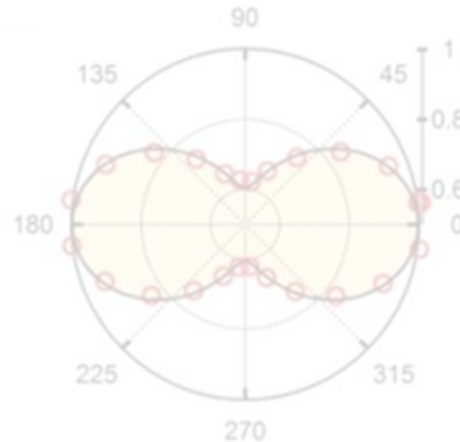
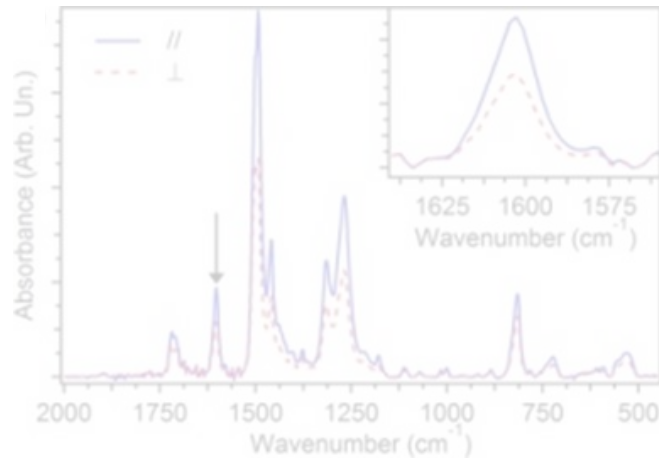
➤ Frequency is influenced by surrounding bonds and atoms.

Absorbance of oriented electrospun polymer fibres

➤ For IR absorption to occur, vibration must result in a net change in a dipole moment
Ring stretching mode of the fluorene unit, associated with vibrations prevalently directed along the molecular chain axis

✓ **Polarised-IR spectroscopy can therefore be used to probe the orientation of molecular bonds and functional groups ☺**

FOUR-ANGLE POLARISATION IR MICROSCOPY*



$$f_{\psi} = \frac{D-1}{D+2} \cdot \frac{2}{3 \cos^2 \alpha - 1}$$

This is the “orientation function”
a measure of how strongly oriented
the dipole is

Where: $D = \frac{\gamma - \sqrt{a^2 + b^2}}{\gamma + \sqrt{a^2 + b^2}}$ $a = A_0 - A_{90}$ $b = A_{45} - A_{-45}$

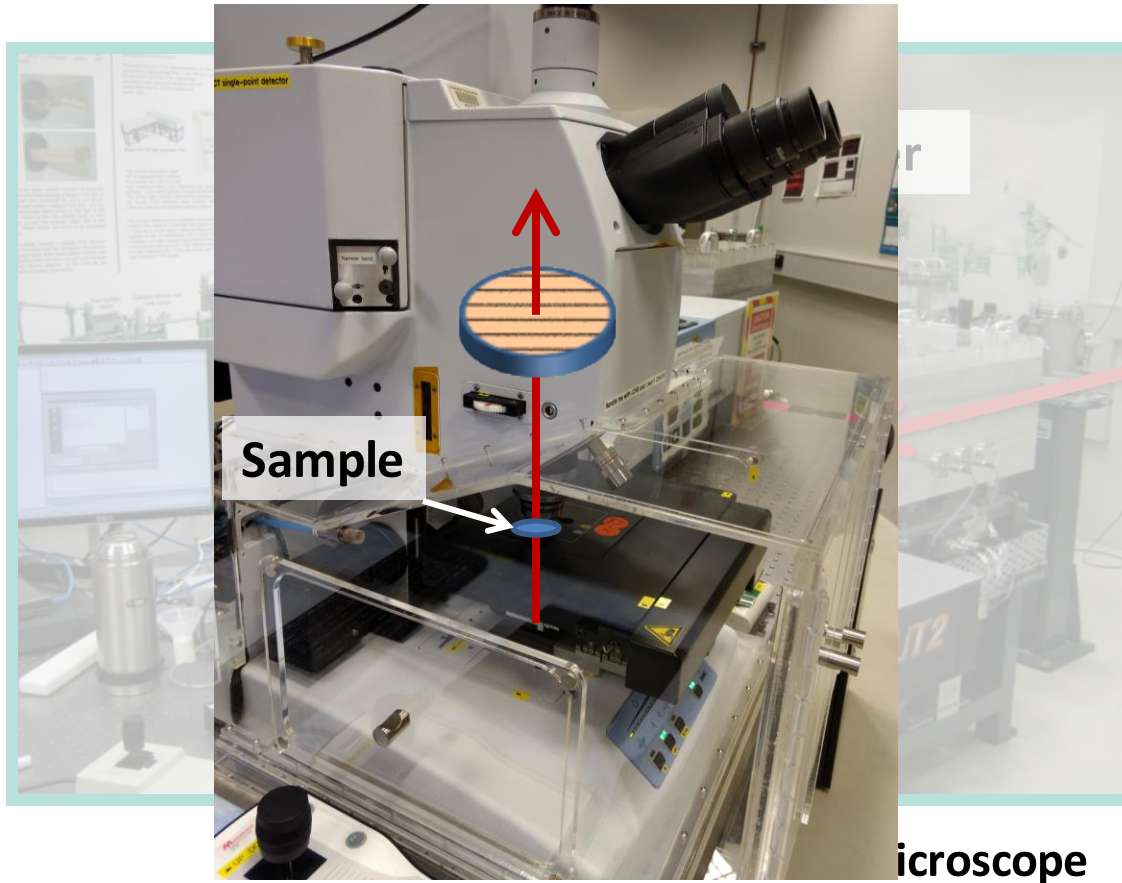
$$Amp = \sqrt{(A_{\phi_4} - A_{\phi_2})^2 + (A_{\phi_3} - A_{\phi_1})^2},$$

$$\theta = \frac{1}{2} \tan^{-1} \left(\frac{A_{\phi_3} - A_{\phi_1}}{A_{\phi_4} - A_{\phi_2}} \right),$$

This is the angle of the vibrating dipole

FOUR-ANGLE POLARISATION IR MICROSCOPY

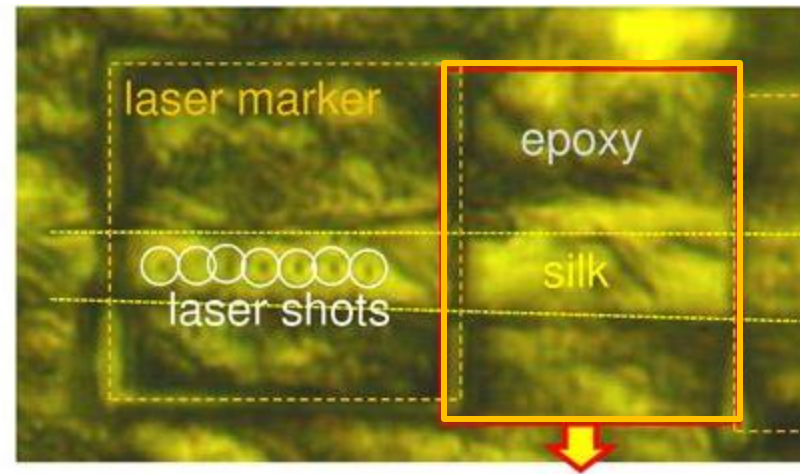
By coupling an FTIR spectrometer to an IR microscope, high quality (signal-to-noise) spectral data can be collected from microscopic samples.



Synchrotron Beam

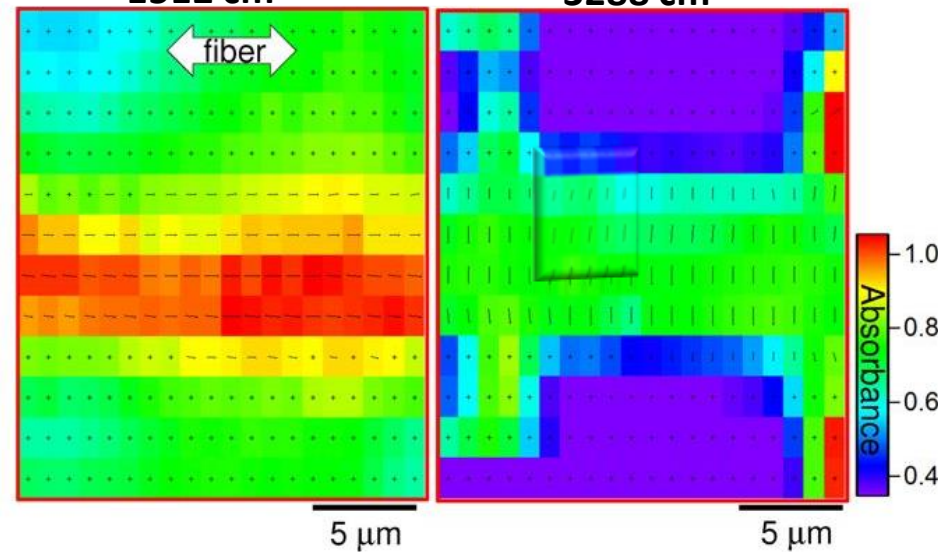
- ❖ Synchrotron-IR source and single-point MCT & FPA imaging detectors
- ❖ High spatial resolution down to 6-8 μm for transmission and reflectance
- ❖ Mid-IR range with MCT (3850-1000 cm^{-1})
- ❖ Mid-/Far-IR range with Si:B photodetector (6000-380 cm^{-1})

Laser modification of silk protein for tissue scaffold printing: orientational hyper-spectral imaging of silk



Amide II (C–N)
1512 cm⁻¹

Amide A (N–H)
3288 cm⁻¹

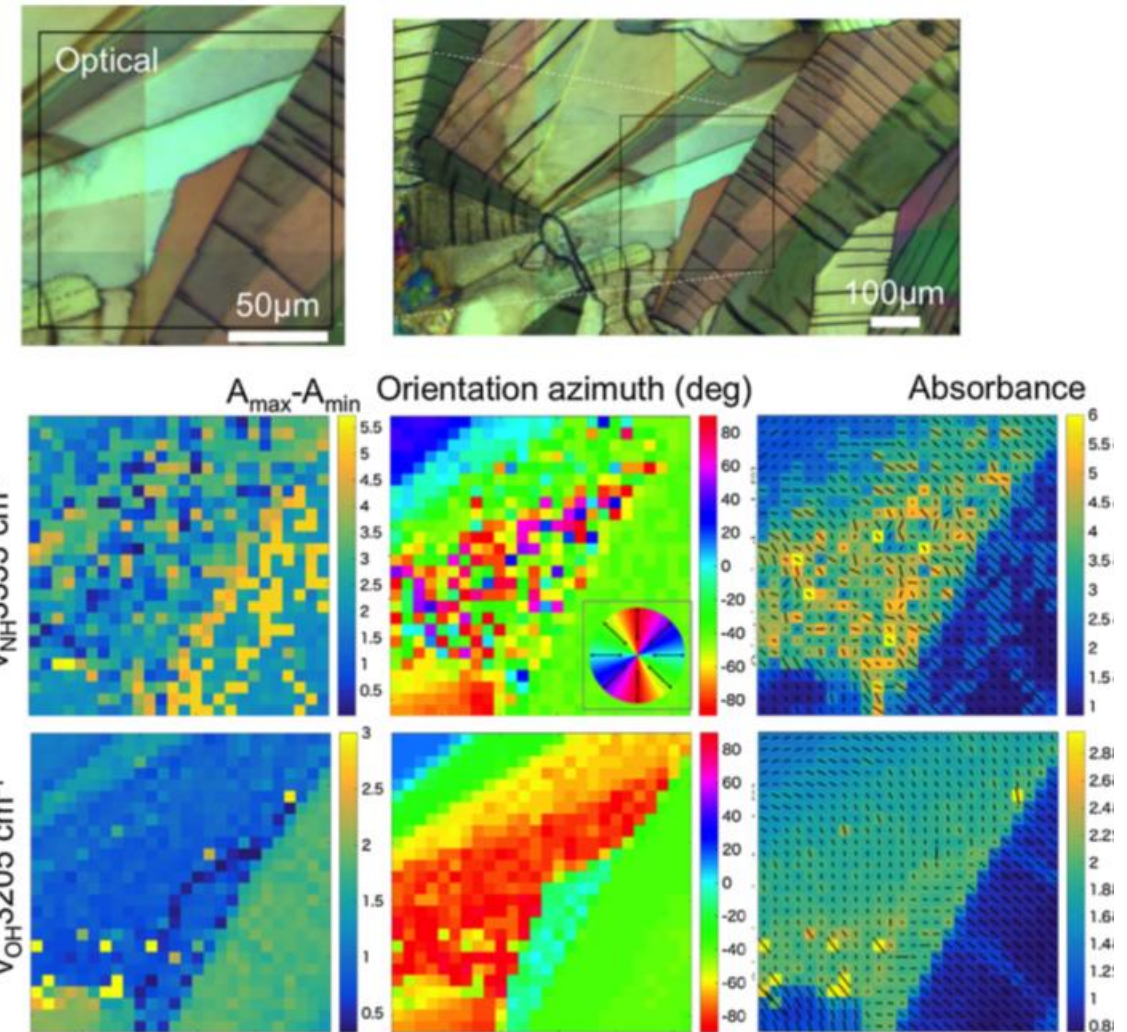
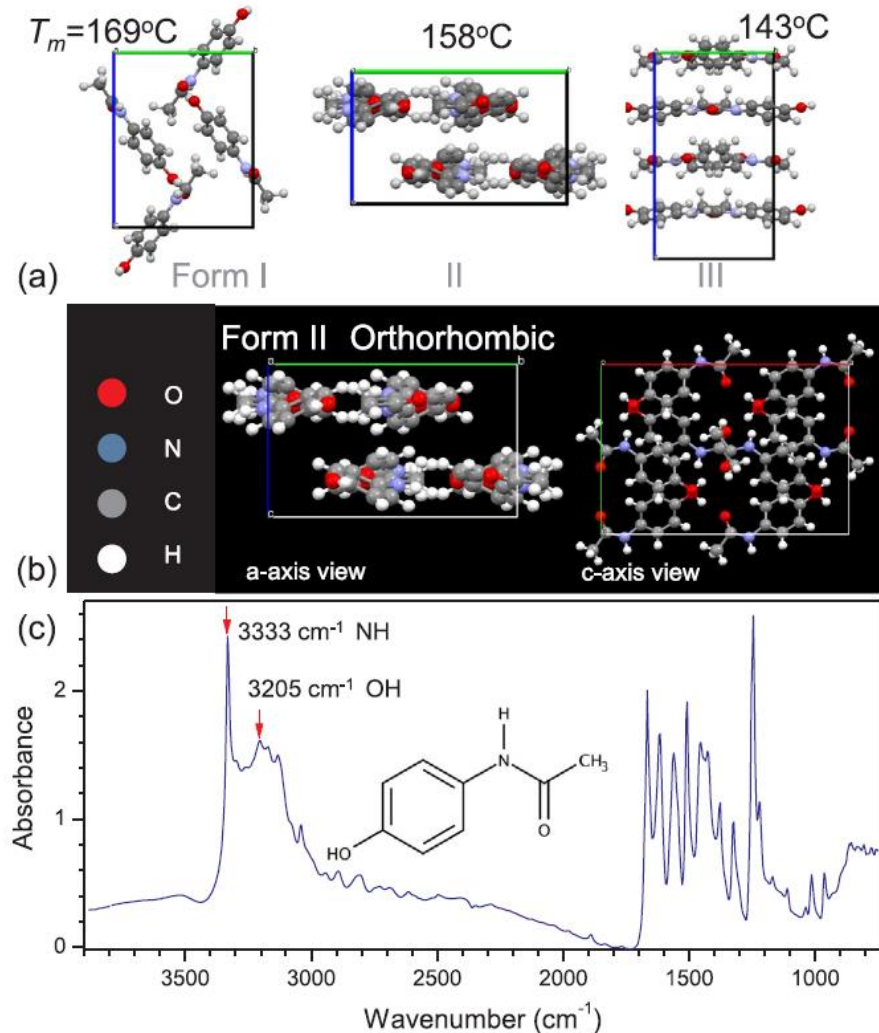


Bar direction = θ
dipole azimuth angle

Bar length = f_{ψ}
Orientation Function

TRANSMISSION 2

Gain a better understanding the enhanced solubility of paracetamol *form II* through their orientation using polarised IR mapping analysis



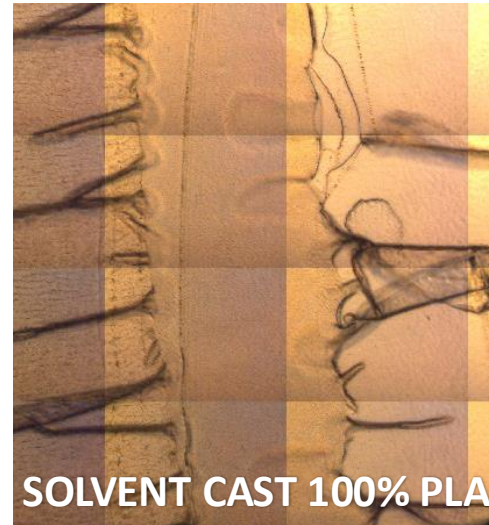
TRANSMISSION 3

Improving the mechanical performance of PLA by using nano-crystalline cellulose as fillers to produce durable biodegradable composite material

Use of additives such as nanocrystalline starch and cellulose has shown *improved mechanical properties of the PLA*.

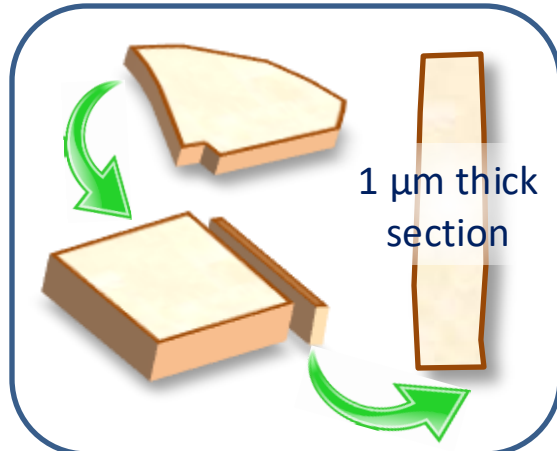
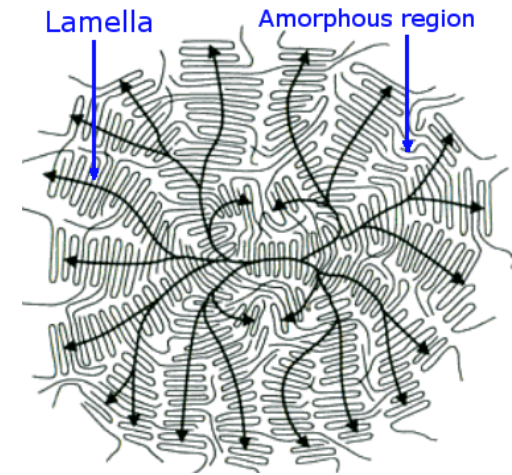
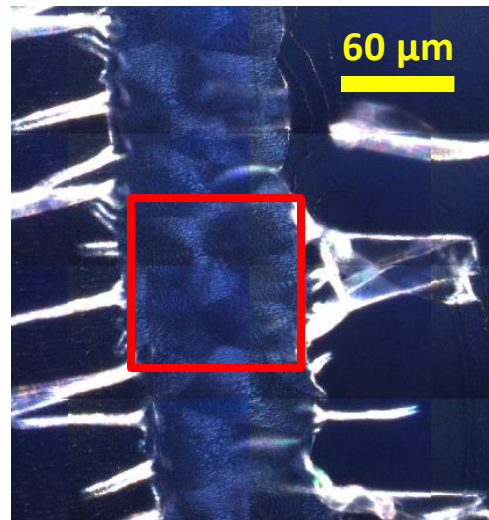


Transmitted visible light



SOLVENT CAST 100% PLA

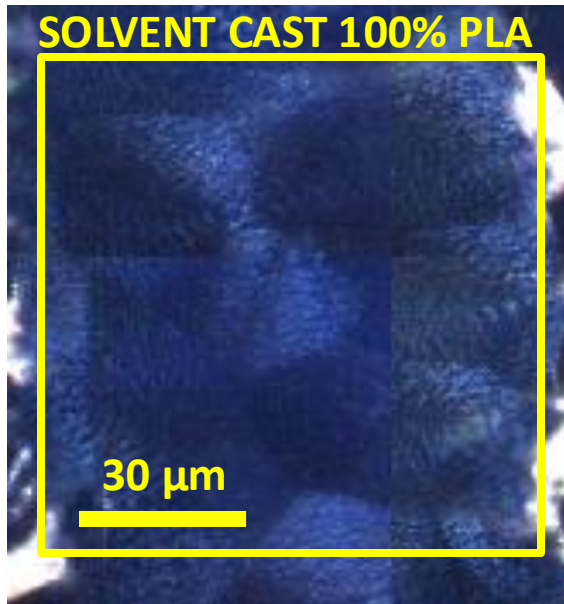
Polarised visible light



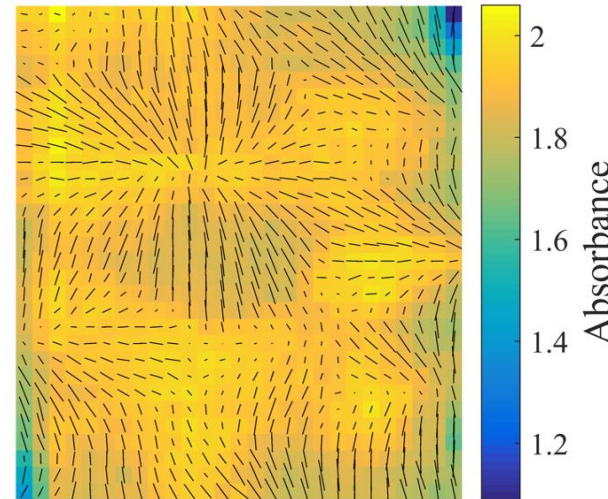
Sample preparation: thin microtomed sections

TRANSMISSION 3

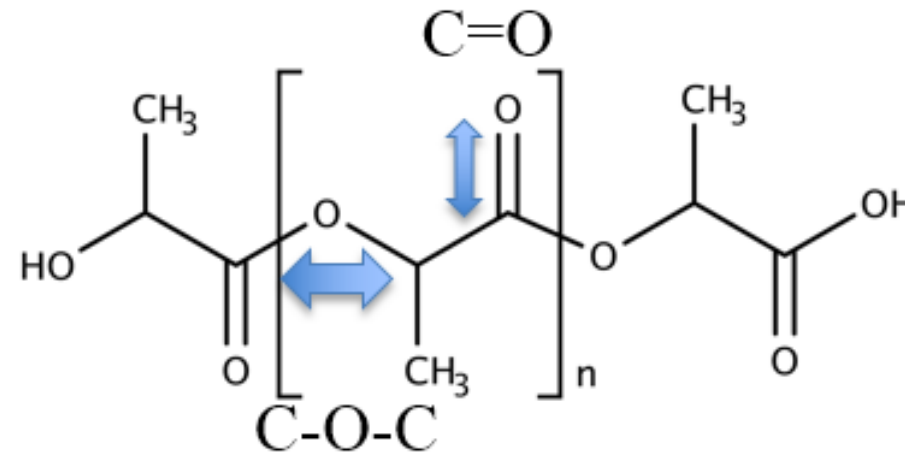
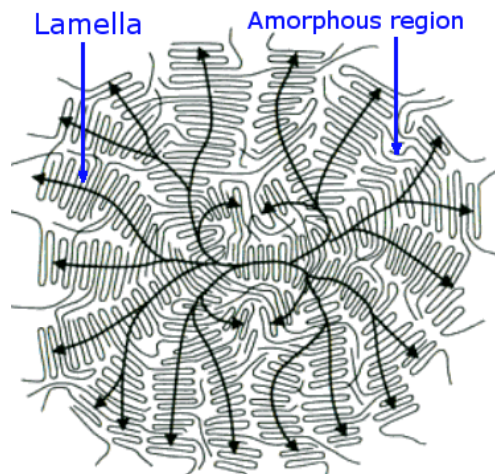
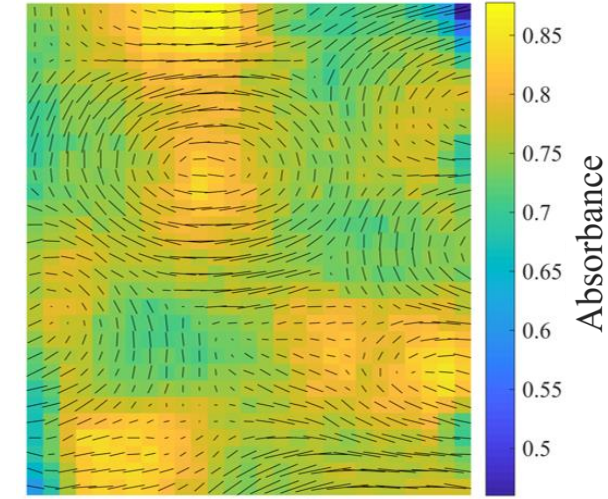
Improving the mechanical performance of PLA by using nano-crystalline cellulose as fillers to produce durable biodegradable composite material



$\nu(\text{C}=\text{O})$ sidechain



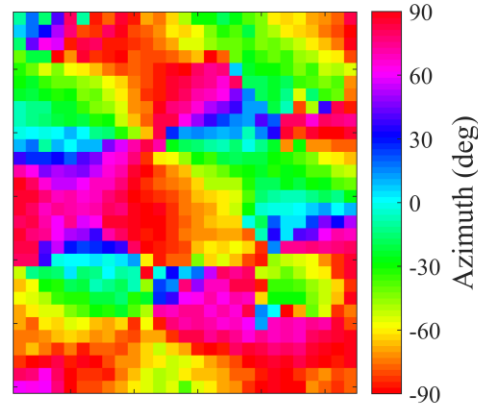
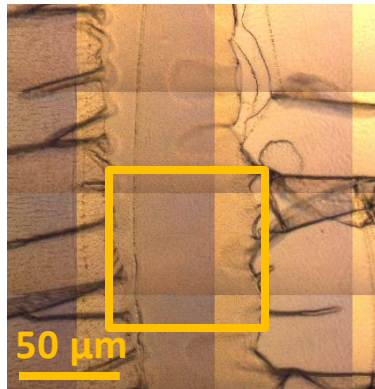
$\nu(\text{C}-\text{O}-\text{C})$ backbone



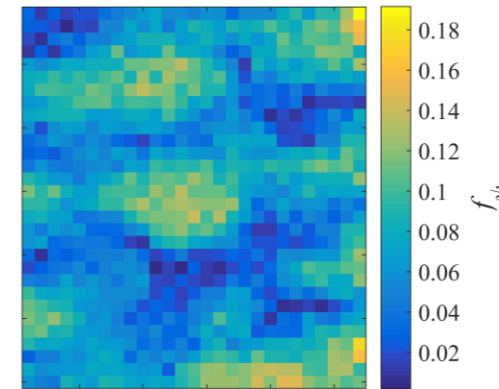
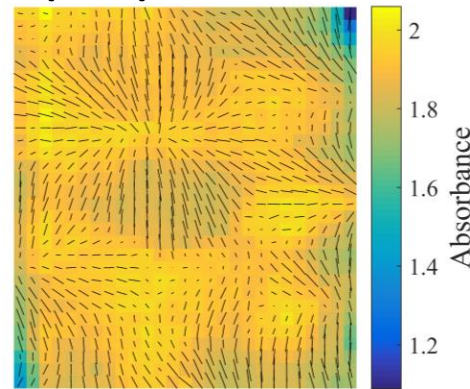
TRANSMISSION 3

Improving the mechanical performance of PLA by using nano-crystalline cellulose as fillers to produce durable biodegradable composite material

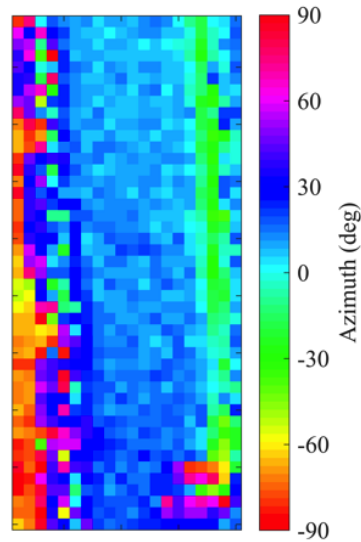
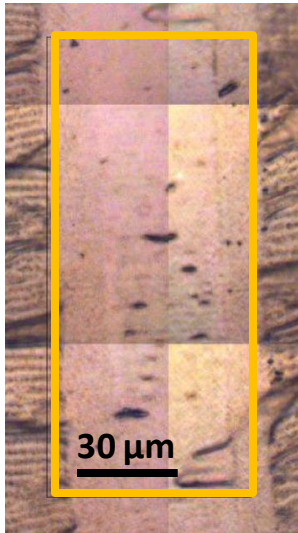
SOLVENT CAST 100% PLA



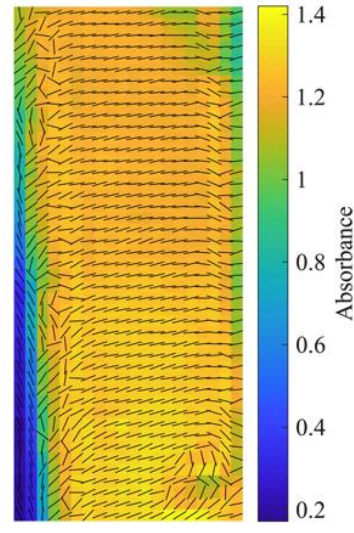
$\nu(\text{C=O})$ sidechain



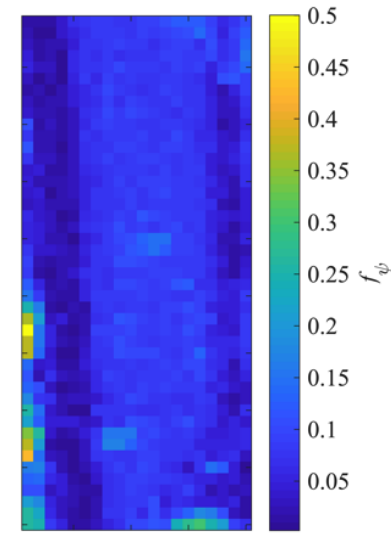
MELT PROCESSED* PLA 5% NANOCRYSTALLINE STARCH



Dipole angle



Dipole angle
Orientation Function
Absorbance



Orientation Function

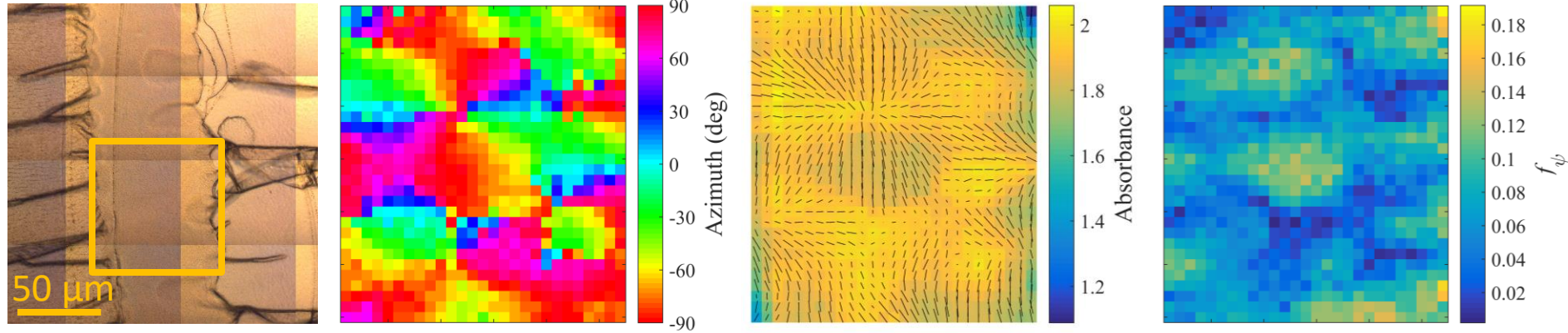
*MELT PROCESS:

another way of casting out solvent from polymer.

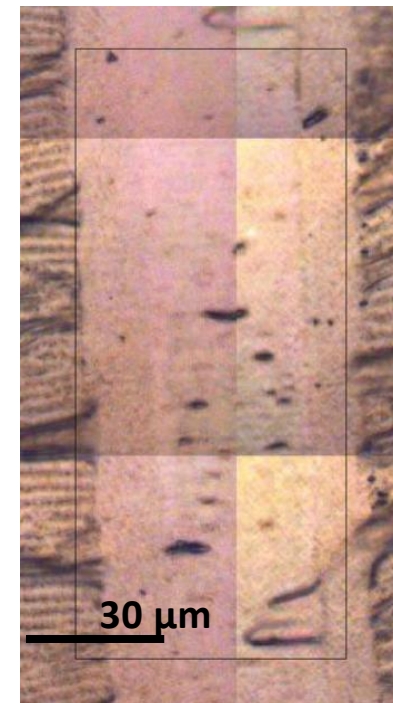
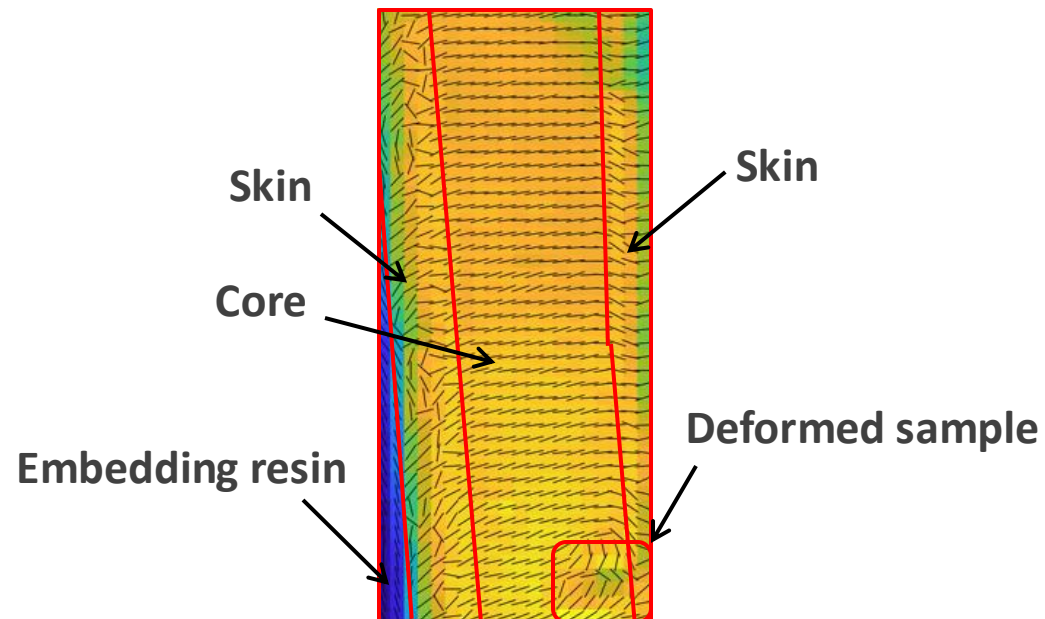
In this process, the pellet was first heated up, pressed into a dye press and then allowed to cool.

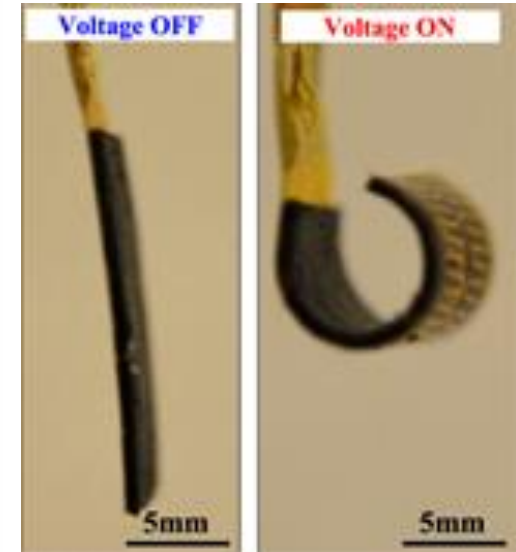
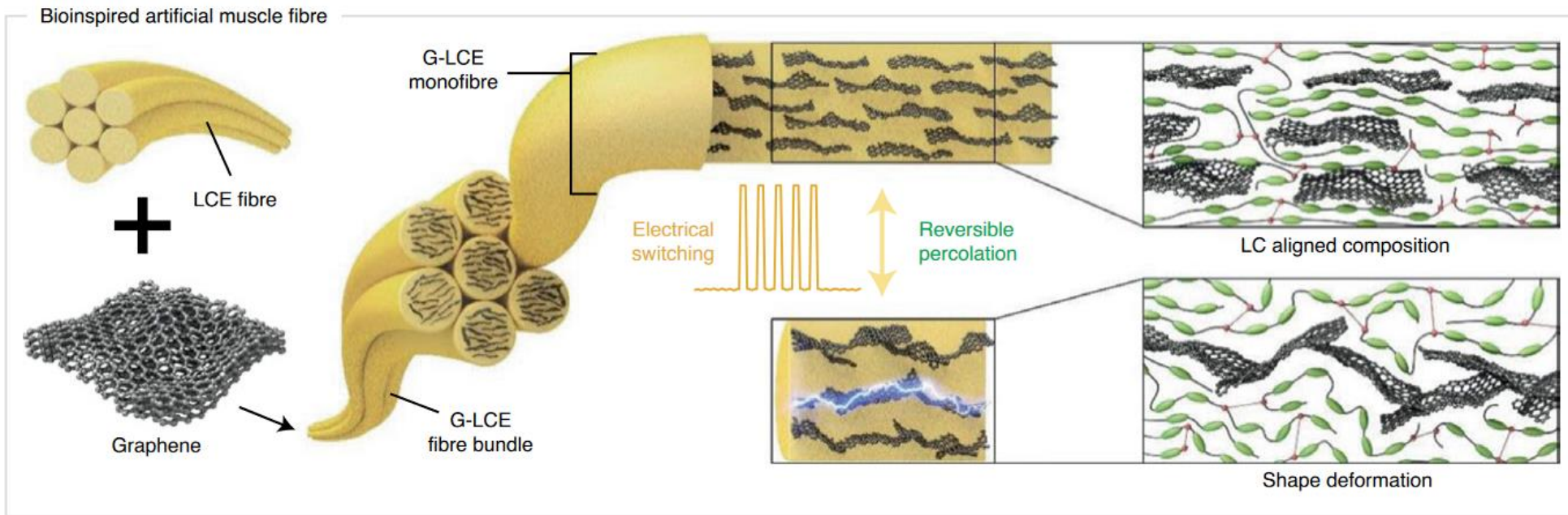
Improving the mechanical performance of PLA by using nano-crystalline cellulose as fillers to produce durable biodegradable composite material

SOLVENT CAST 100% PLA



MELT PROCESSED PLA 5% NANOCRYSTALLINE STARCH

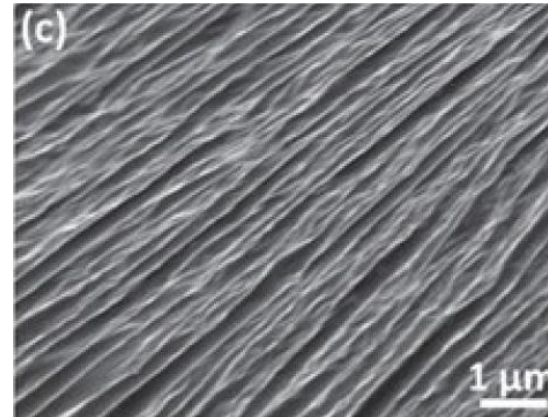




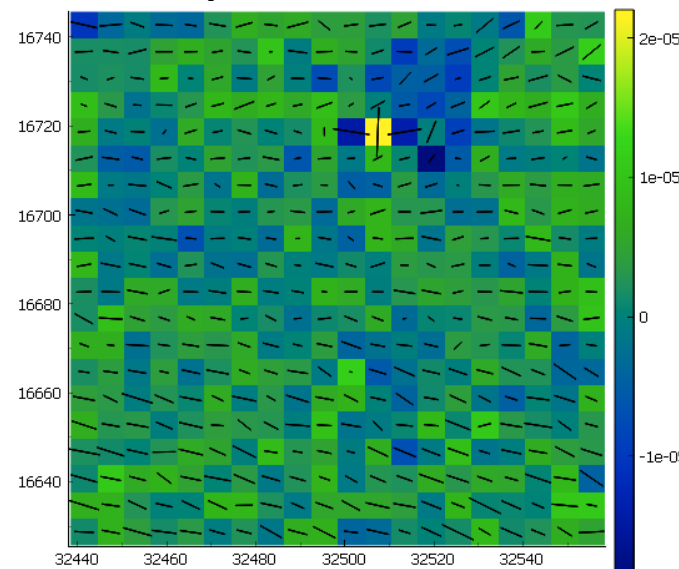
- Using **reduced graphene oxide (rGO)** to enhance the conductivity of thermally responsive LCEs, that have been used as artificial muscles and soft actuators for robotic and sensor applications.
- This project aims at investigating the effect of applied electrical fields on the alignment of rGO embedded within the matrix of LCE, to gain insights into its structure-property relationship critical for underpinning the performance enhancement of these artificial muscles.**

Characterization of electrically aligned reduced graphene oxide (rGO) sheets in liquid crystalline elastomer (LCE) used as artificial muscles and soft actuators

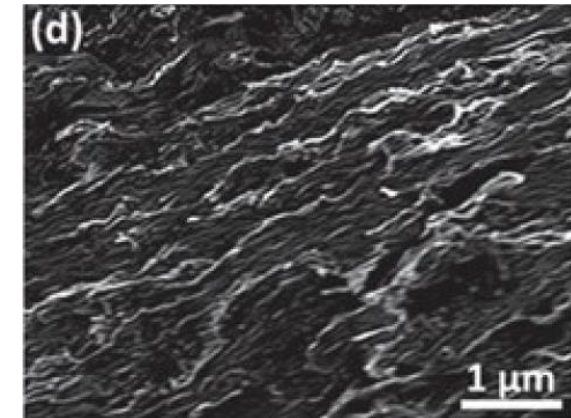
Aligned rGO sheets in LCE matrix



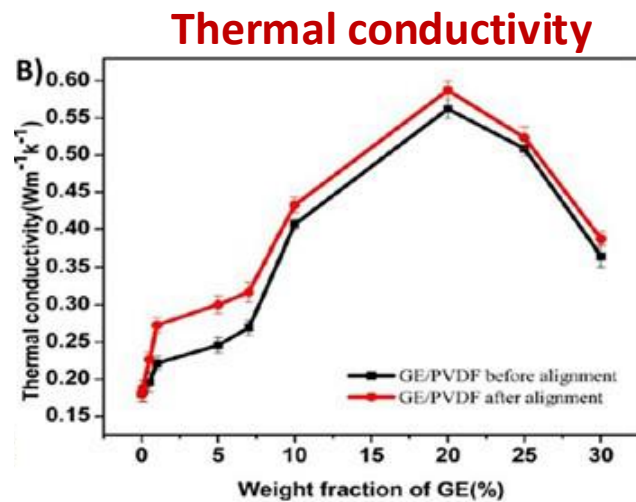
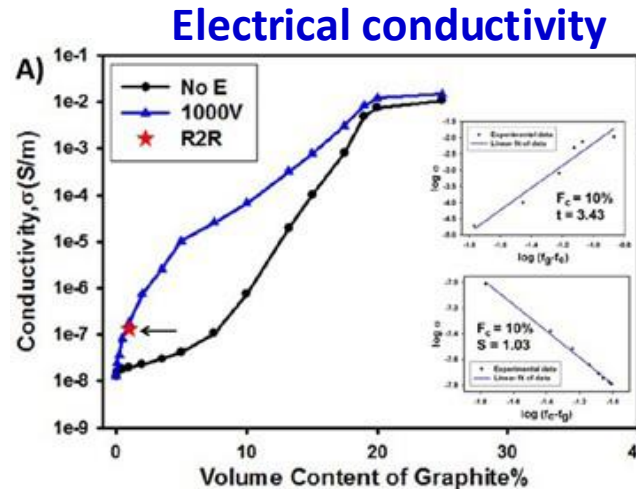
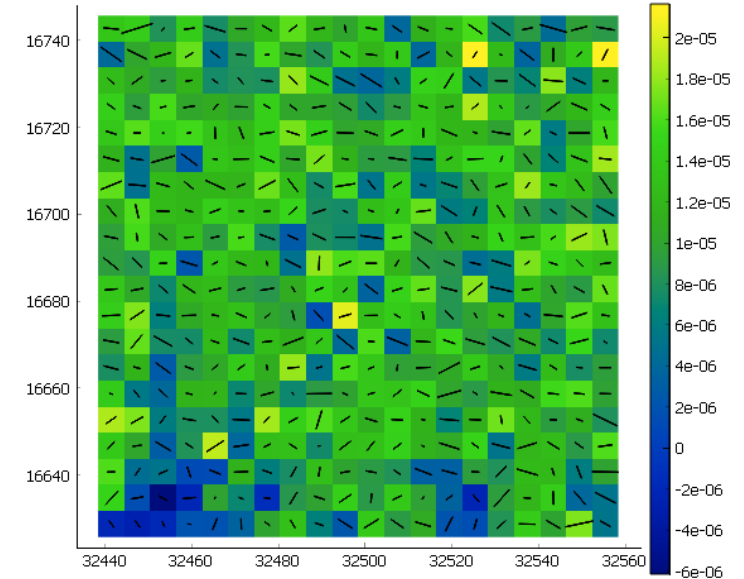
rGO peak at 3443 cm^{-1}



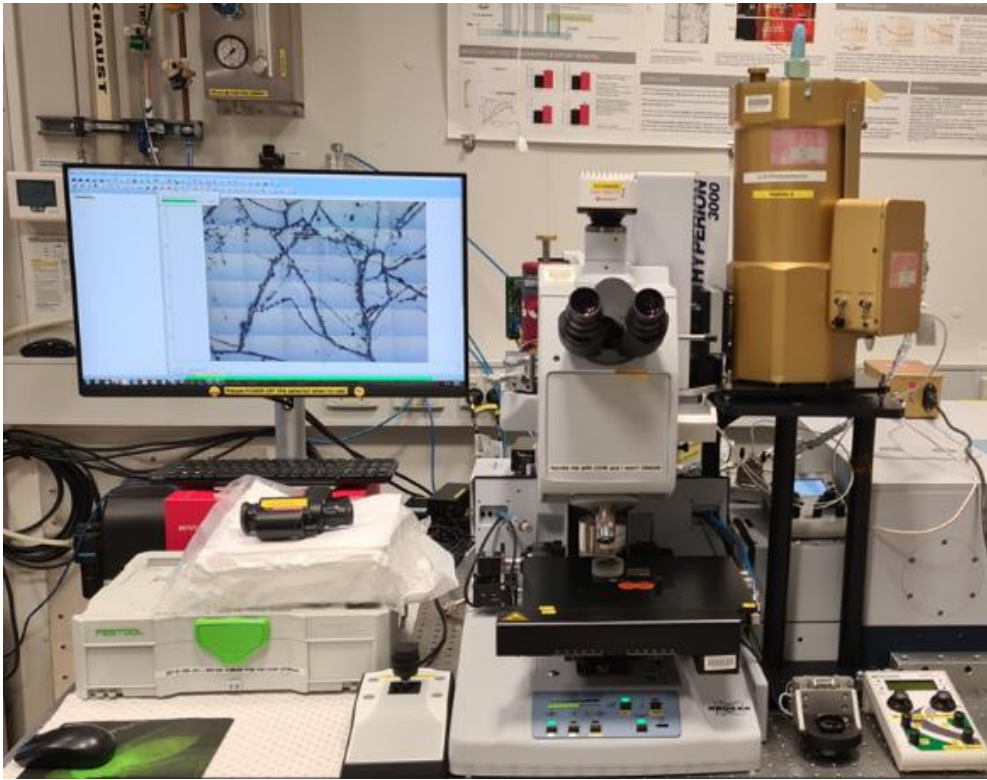
Randomly oriented rGO sheets in LCE matrix



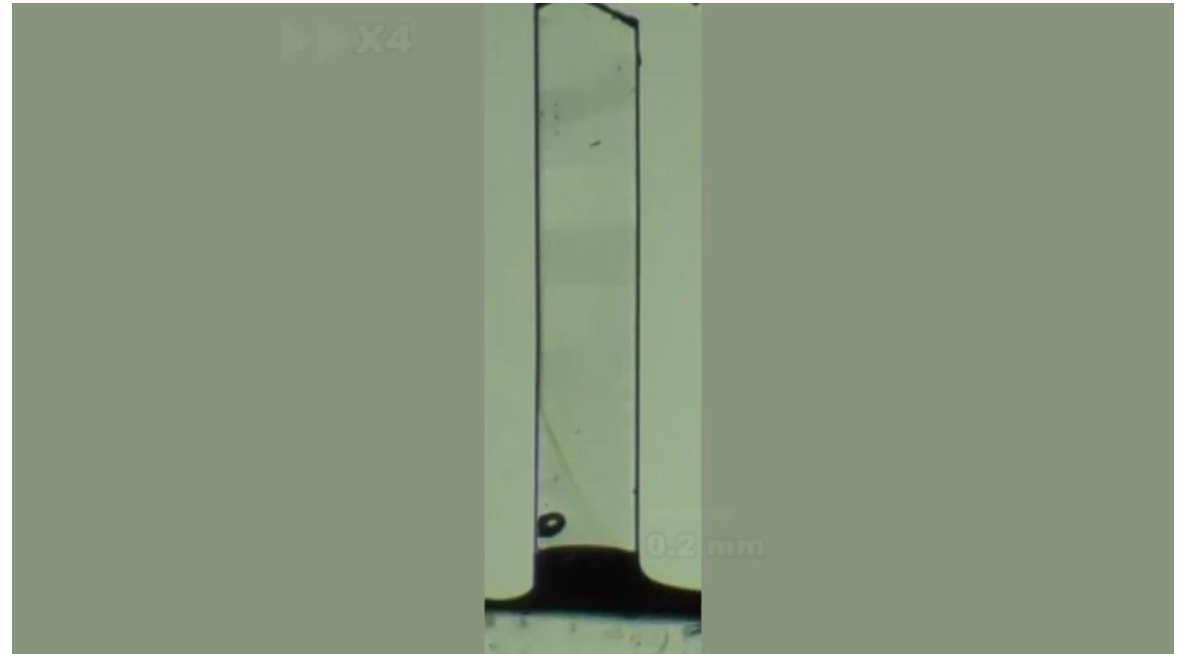
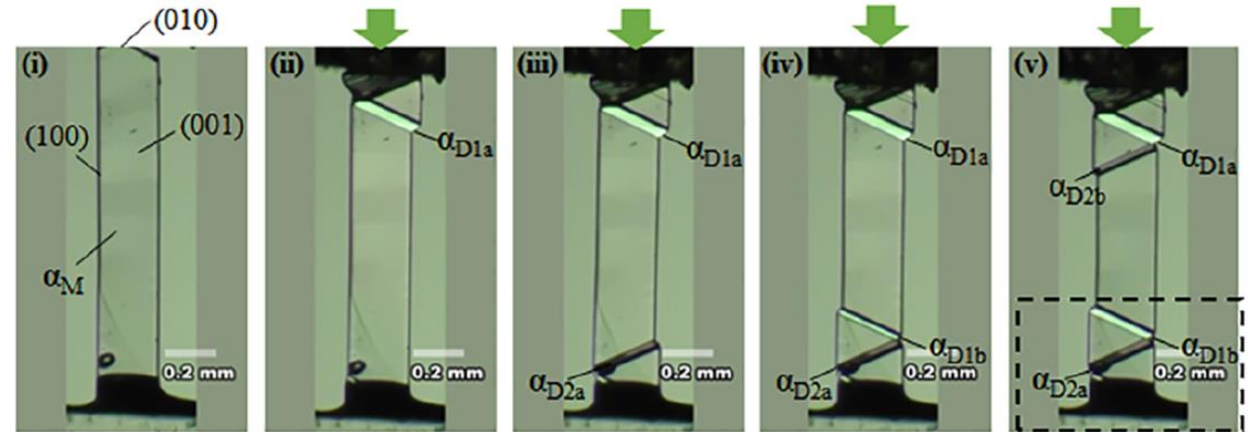
rGO peak at 3443 cm^{-1}



Insights into changes of molecular orientation in scissor-like two-directional deformation of *Ferroelastic Organic Crystals* (FEOCs) during compression

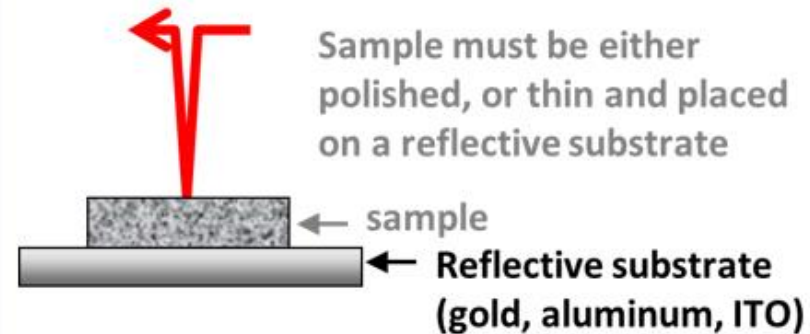
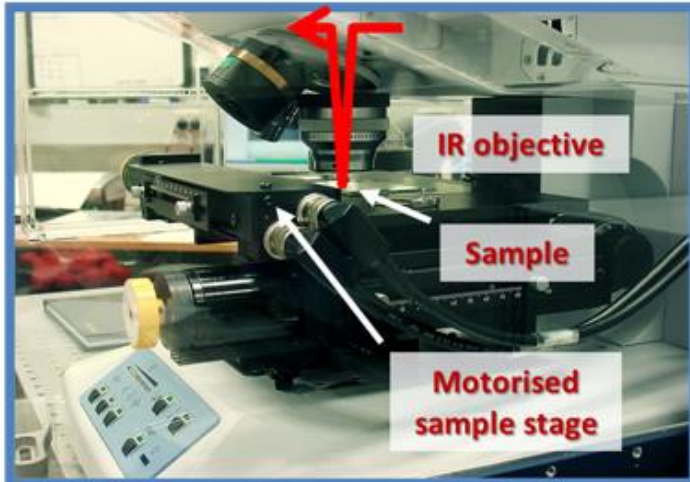


Coupling Si:B photodetector on IRM's FTIR microscope

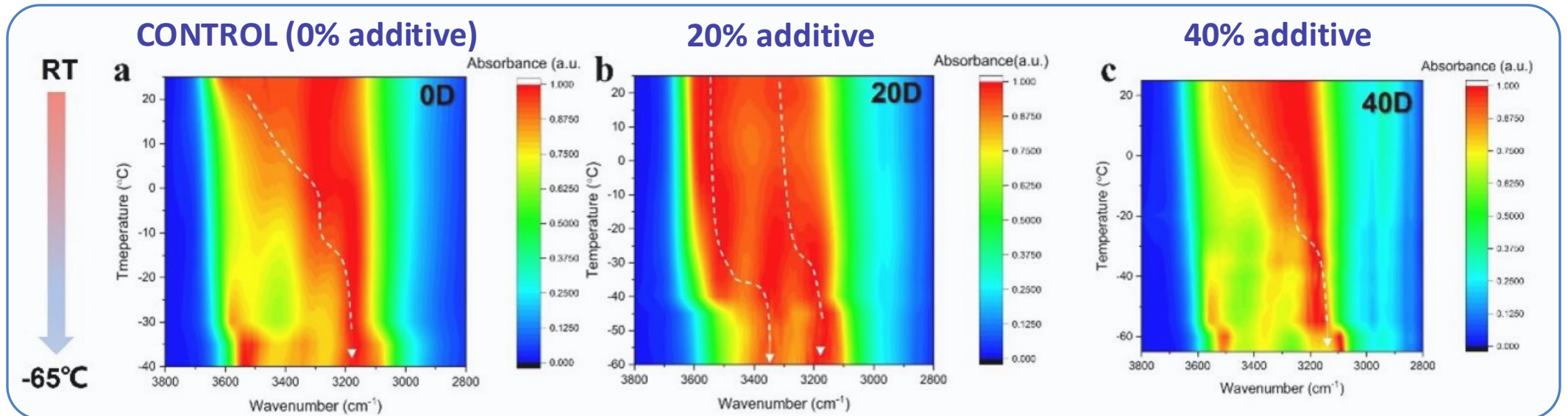
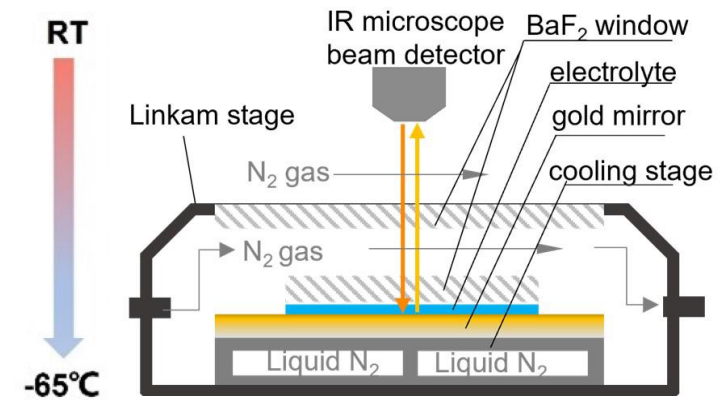
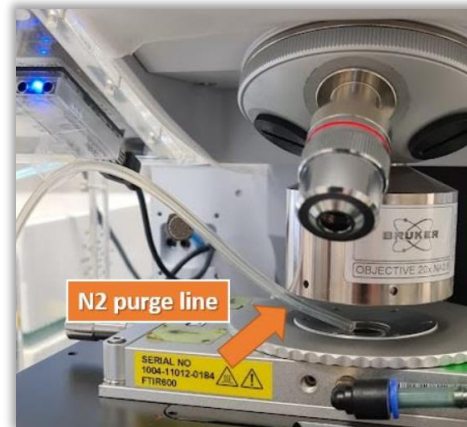


TRADITIONAL SAMPLING METHODS

– *Reflectance* for In-Situ Catalysis Reactions –



REFLECTANCE 1 In-situ monitoring of anti-freezing electrolytes for aqueous Zn battery



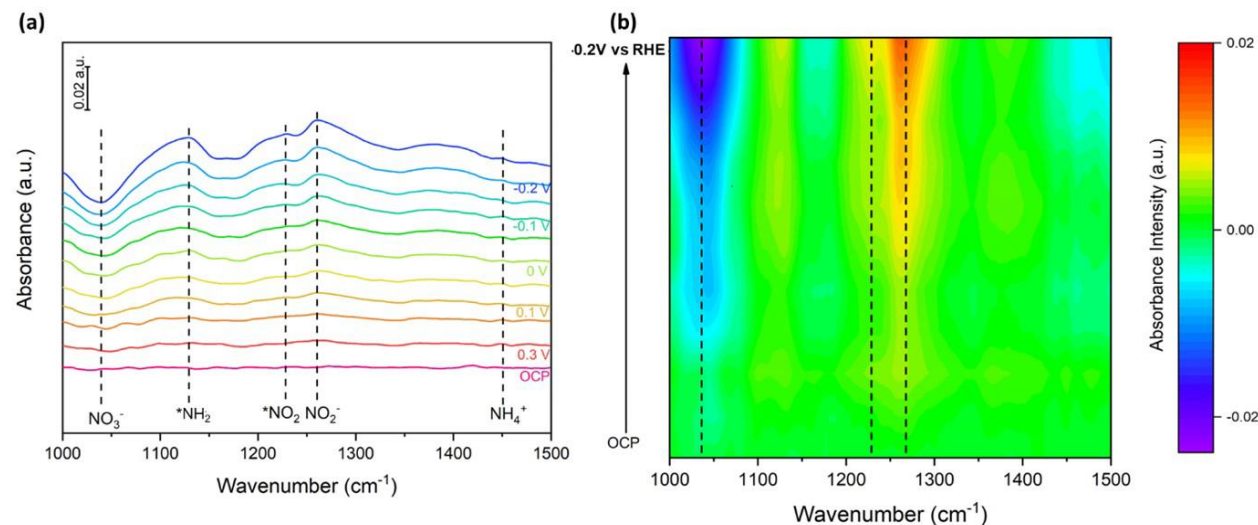
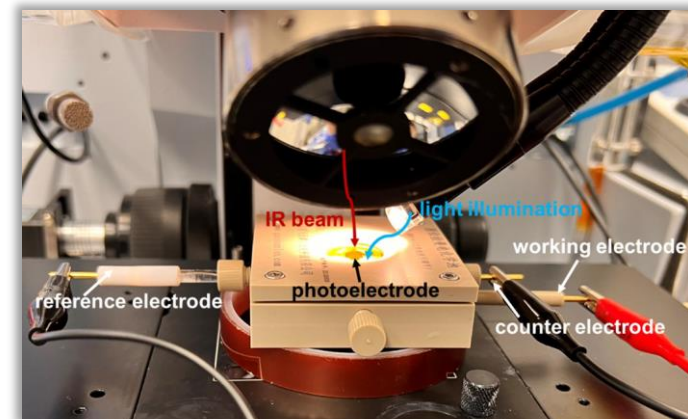
- Changes of intensity at different wavenumbers across the temperature range suggest altered interactions between the additives and co-solvents at the sub-zero conditions, leading to a new understanding of their anti-freezing mechanism(s).

REFLECTANCE 2

Gaining insights into reaction mechanism of photoelectrochemical urea synthesis using *in-situ* synchrotron-FTIR technique



UNSW
SYDNEY



➤ Spectral series collected over a range of applied voltage revealed the production of nitrogen intermediates over the course of the reaction that led to insights into the mechanism, important for optimizing the production and yields.

Ref [1]: C. Han *et al.*, "Nanostructured Hybrid Catalysts Empower the Artificial Leaf for Solar-Driven Ammonia Synthesis" *Energy Environ. Sci.* (2024), **17**, 5653-5665.

Ref [2]: S. Zhou *et al.*, "Solar driven Ammonia Synthesis with Co-TiO_x and Ag Nanowires Enhanced Cu₂ZnSnS₄ Photocathodes" *Appl. Catal. B.* (2024), **348**, 123836.

IN-HOUSE DEVELOPED HYBRID MACRO ATR-FTIR TECHNIQUE

– Recent Highlighted Applications –

OVERVIEW

Background
“Macro-ATR”



Macro-ATR
Devices



Applications

(A) Hybrid macro ATR-FTIR



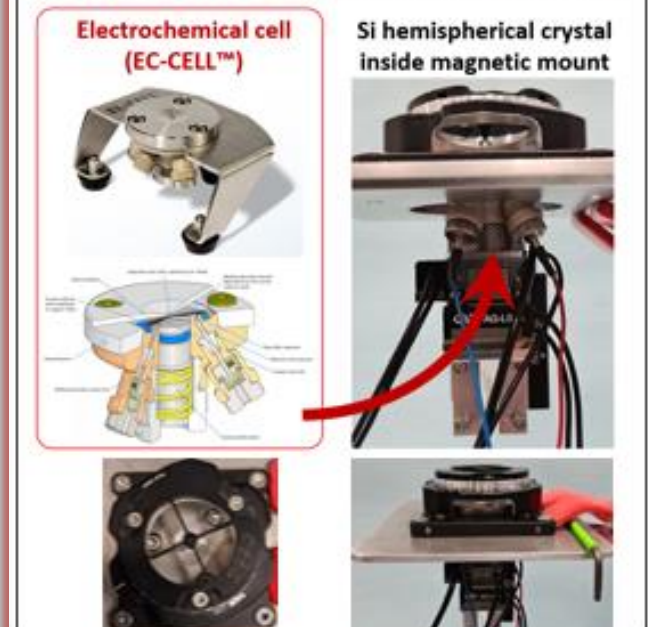
(B) Temperature-controlled
hybrid macro ATR-FTIR



(C) Soft-contact piezo-controlled
macro ATR-FTIR (chemisorption)

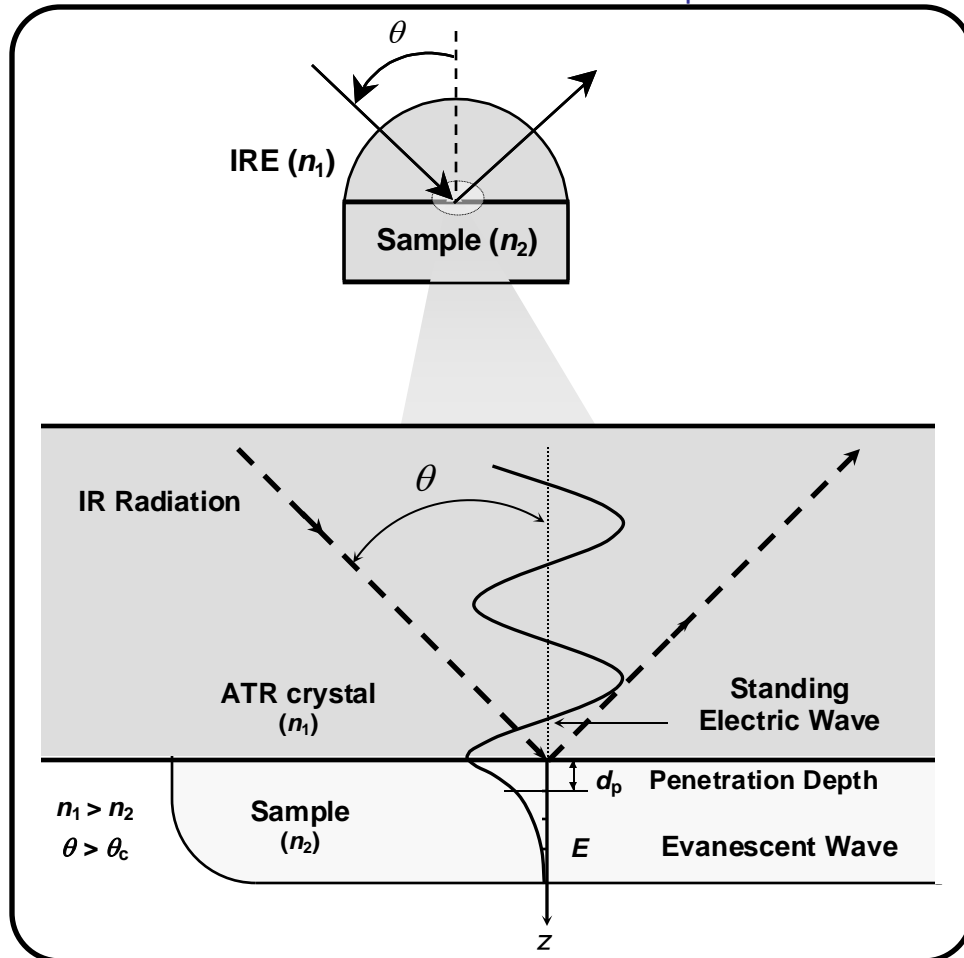


(D) Soft-contact piezo-controlled
macro ATR-FTIR (electrochemical cell)

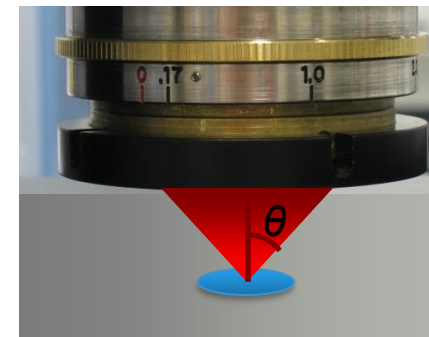
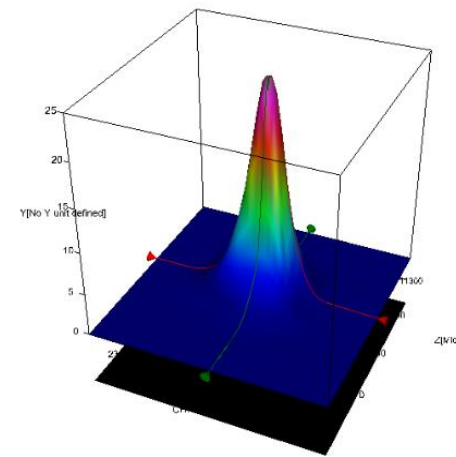


PRINCIPLE OF (MACRO) ATR-FTIR SPECTROSCOPY

ATR-FTIR utilizes **TOTAL INTERNAL REFLECTION** phenomenon when IR radiation travels through high index ATR crystal and impinges on low-index sample surface at $\theta_{\text{incident}} > \theta_c$ resulting in evanescent wave, which decays exponentially into sample surface (d_p).



spatial resolution with total internal reflection



Rayleigh Equation:

$$r = 1.22 \lambda / 2 \times \boxed{NA}$$



Numerical aperture
NA = $n(\sin\theta)$

At $\lambda = 6 \mu\text{m}$

For **NA (air) = 0.65**

$$r = 5.6 \mu\text{m} \text{ (TRANS \& REFL)}$$

At $\lambda = 6 \mu\text{m}$

For **NA (ZnSe) = 1.56**

$$r = 2.3 \mu\text{m}$$

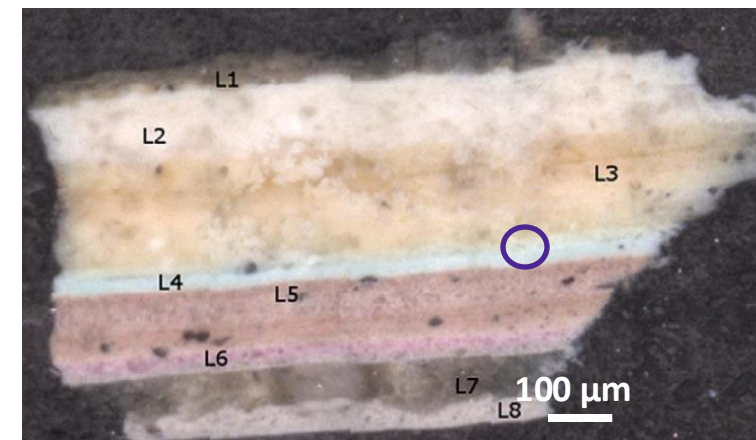
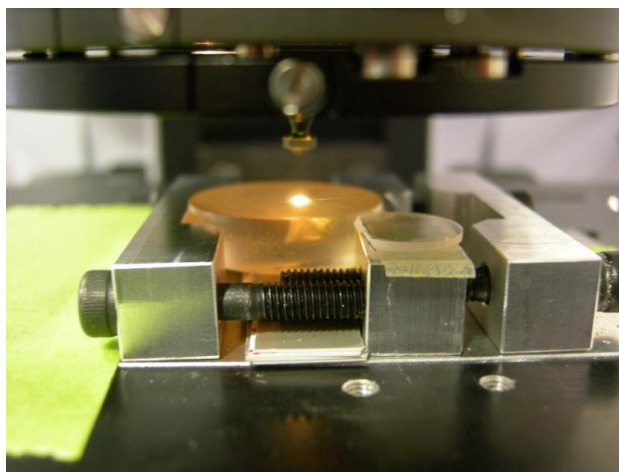
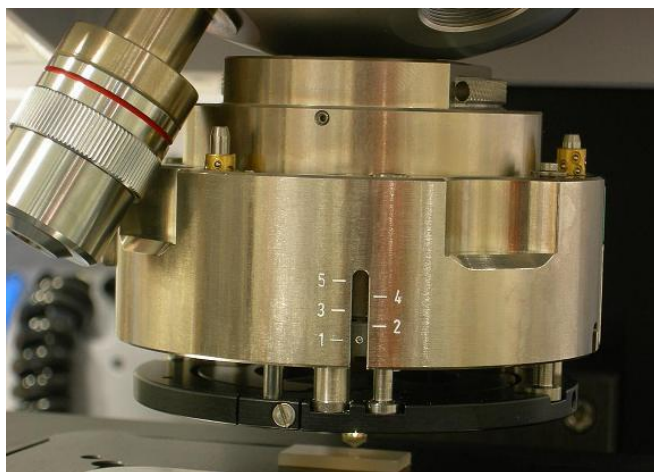
At $\lambda = 6 \mu\text{m}$

For **NA (Ge) = 2.6**

$$r = 1.4 \mu\text{m} \text{ (Ge ATR)}$$

TRADITIONAL MICRO-ATR TECHNIQUE

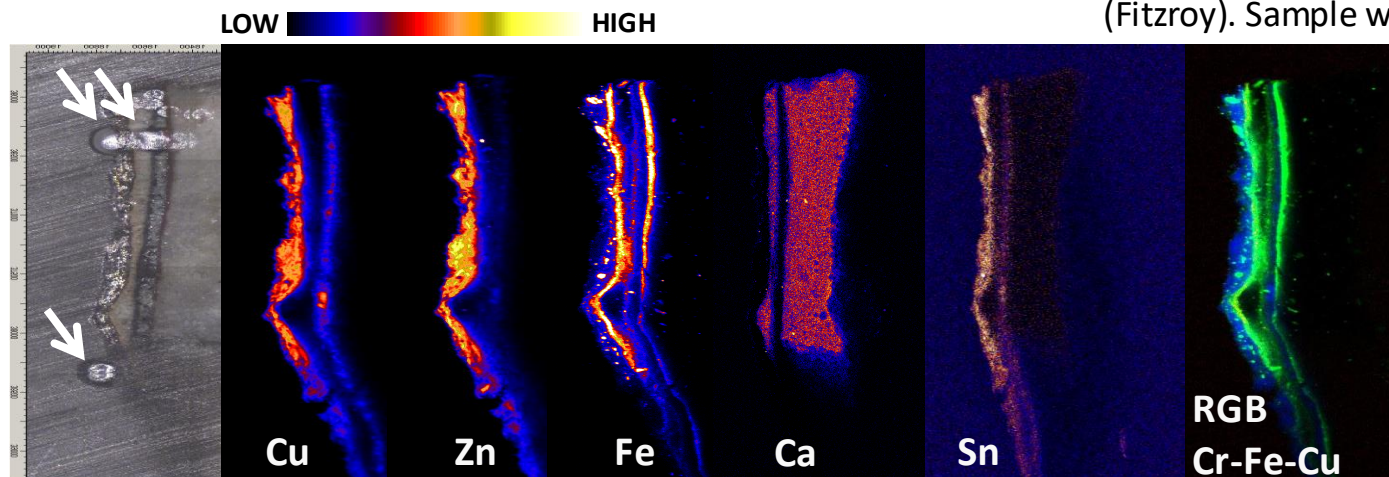
Commercial Bruker ATR 20× objective equipped with Ge-ATR crystal



Multilayer paint fragment from exterior of Provincial Hotel (Fitzroy). Sample was not suitable for thin sectioning.



- × Sample damage
- × Contamination
- × Slow scan



Visible image of a paint cross section recorded after standard micro-ATR “mapping” measurements (*left*), showing indentation marks damaged by the high pressure from the ATR crystal (*arrowed*)

Ref: R. Sloggett *et al.* Microanalysis of artworks: IR microspectroscopy of paint cross-sections, *Vib. Spectrosc.* (2010) **53**, 77-82.

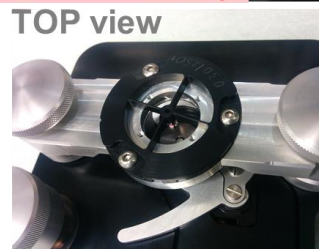
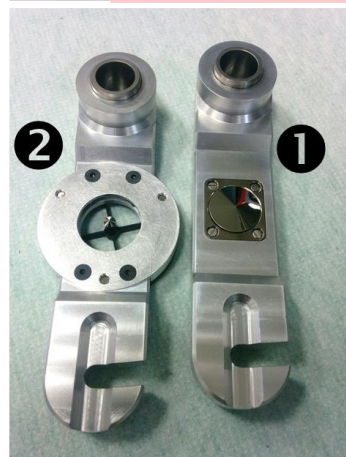
MODEL 1: “HYBRID” MACRO-ATR WITH 20× OBJECTIVE



Bruker Macro-ATR unit and setup



TOP view



BOTTOM view

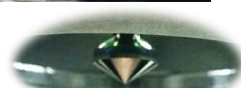


Sample

MACRO-ATR cantilever arm:

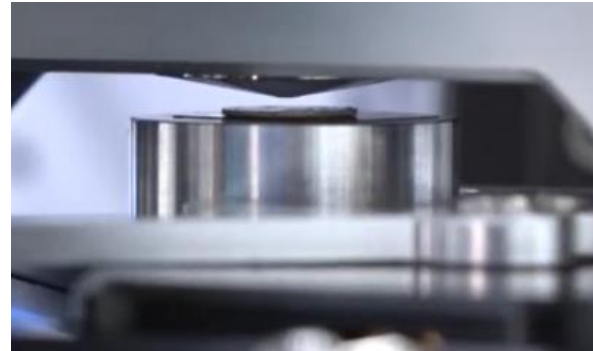
① ORIGINAL model supplied with 1-mm-dia facet Ge crystal.

② HYBRID version: in-house modification to accept 250- μ m-dia and 100- μ m-dia facet Ge crystals from commercial micro-ATR objectives.

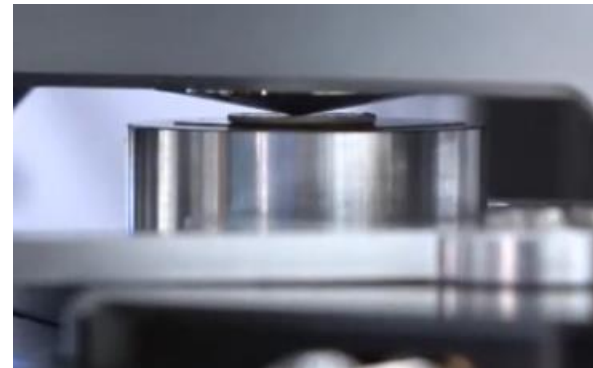


250- μ m-dia tip

Non-contact position for background measurement



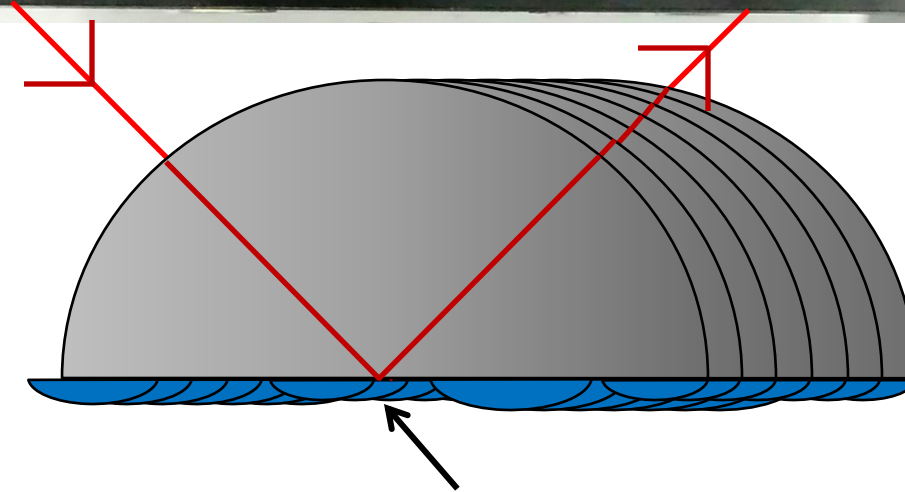
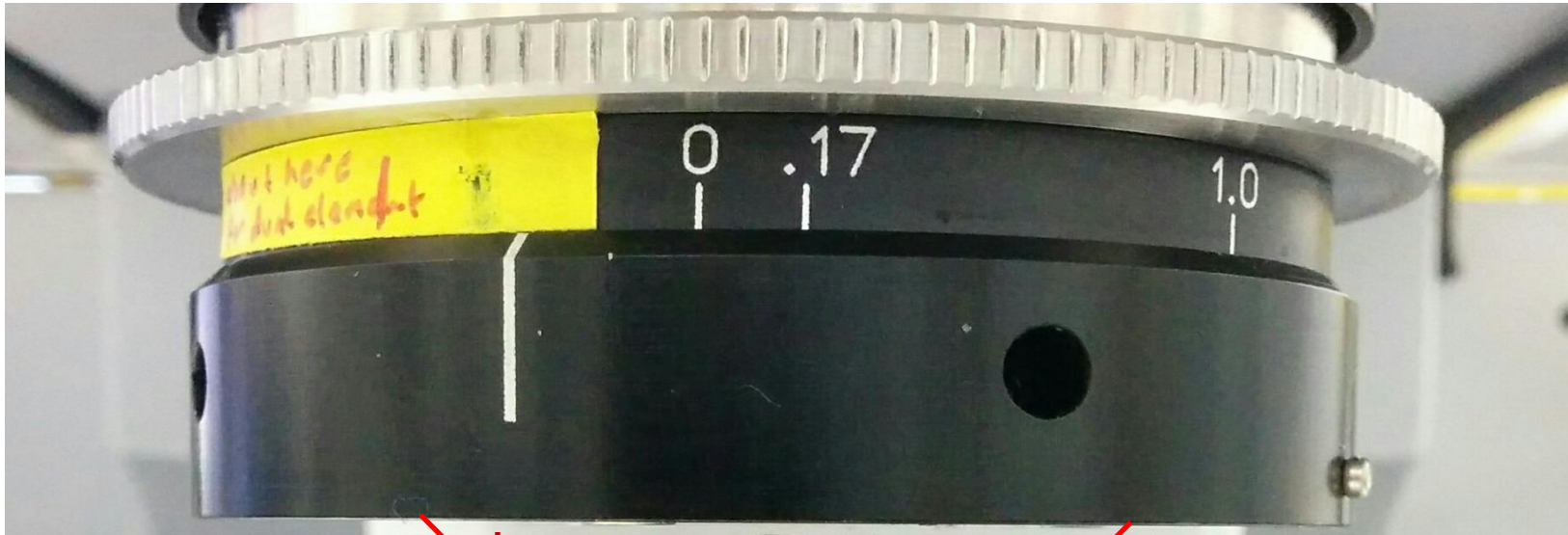
Contact position for mapping measurement



- ✓ No cross contamination
- ✓ Faster scan
- ✓ Minimal sample damage

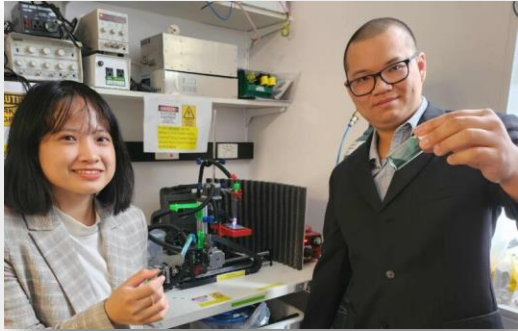
Available sizes of Ge facet tip: 1 mm, 250 μ m and 100 μ m offering a good range of contact pressure on samples.

MODEL 1: "HYBRID" MACRO-ATR WITH 20× OBJECTIVE

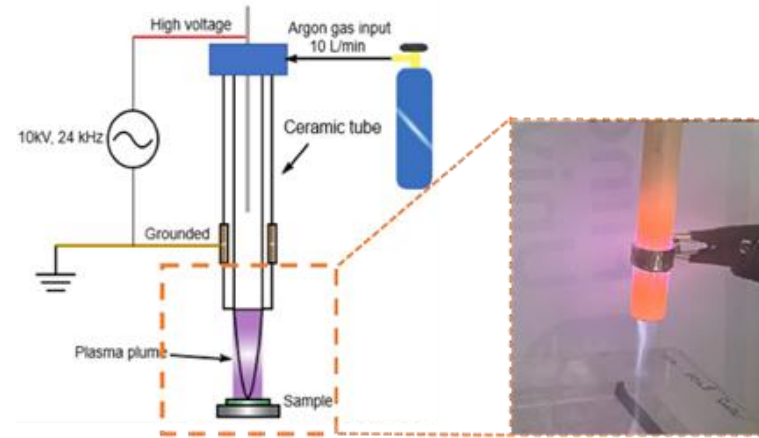


Step interval of the beam between measurement points is also reduced by a factor of 4 for Ge crystal ($n_{\text{Ge}} = 4$)

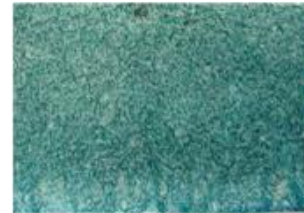
smallest projected aperture available $\sim 1 \mu\text{m}$ | smallest step (lateral) resolution = 250 nm



Plasma jet transforms blue-green *Spirulina* microalgae into ultrathin bioactive coatings for anti-bacterial wound healing applications (Patent No. AU2023902971)



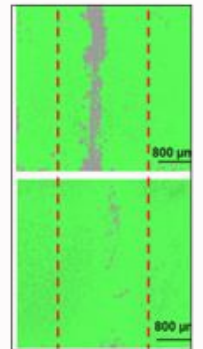
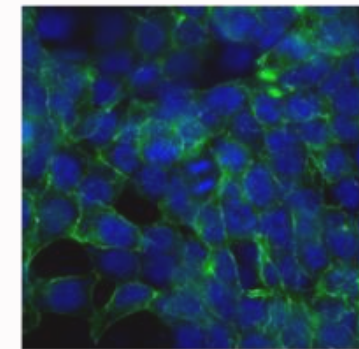
Blue-green *Spirulina* microalgae



Synchrotron Macro-ATR analysis



Antibacterial and antibiofilm



Wound healing

➤ **Argon plasma jet technique:** an innovative sustainable approach to harness antibacterial compound “phycocyanin” by breaking down *Spirulina* cell wall creating uniform bioactive coating on the surface of the substrate in just one single step.

Ref: T. T. Nguyen, N. H. Nguyen, A. Hayles, W. Li, D. Q. Pham, C. K. Nguyen, T. Nguyen, **J. Vongsivut**, N. Ninan, Y. Sabri, W. Zhang, K. Vasilev, V. K. Truong, “Transforming *Spirulina maxima* Biomass into Ultrathin Bioactive Coatings Using an Atmospheric Plasma Jet – A New Approach to Healing of Infected Wounds,” *Small* (2023) **2305469**.

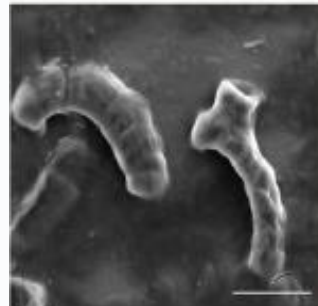
Plasma jet transforms blue-green *Spirulina* microalgae into ultrathin bioactive coatings for anti-bacterial wound healing applications (Patent No. AU2023902971)

Scanning Electron Microscope

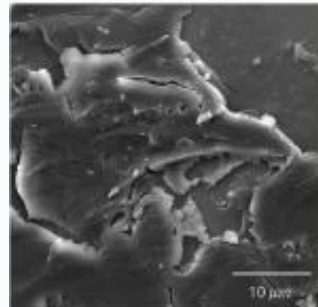
**Control
(untreated)**



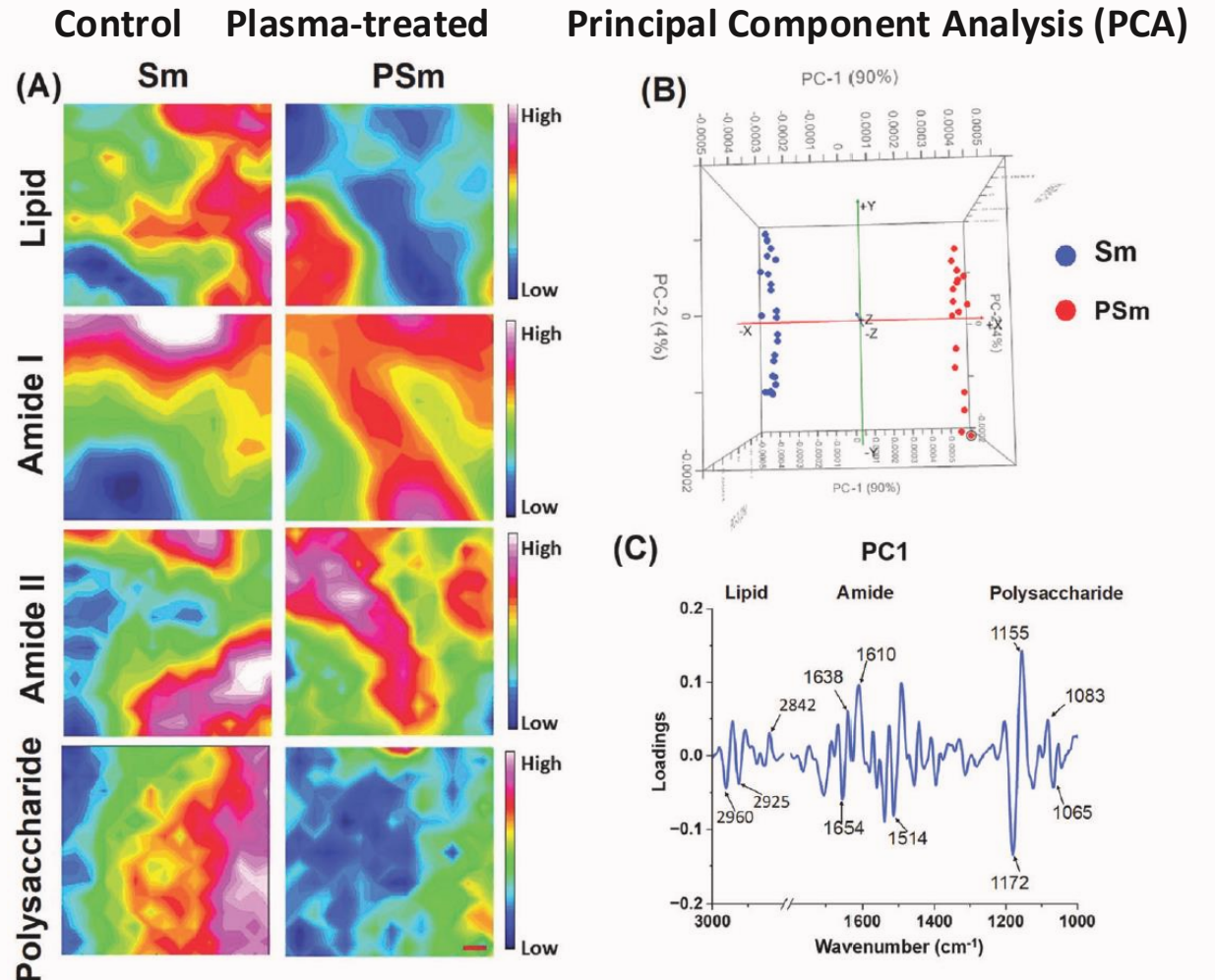
**Plasma treated
(100 s/cm²)**



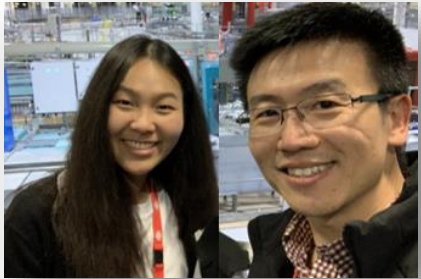
**Plasma treated
(200 s/cm²)**



Synchrotron Macro ATR-FTIR technique

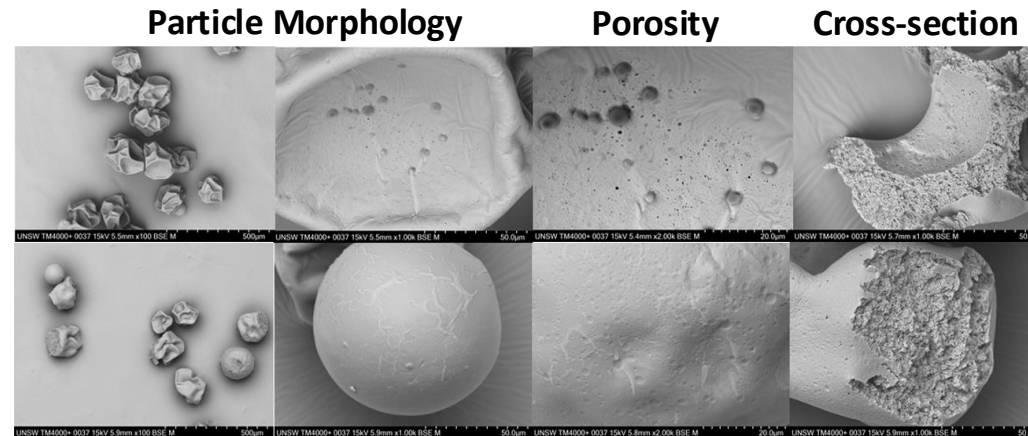


Investigating surface composition and encapsulation stability of novel β -carotene microcapsules produced using pea/whey protein complexes

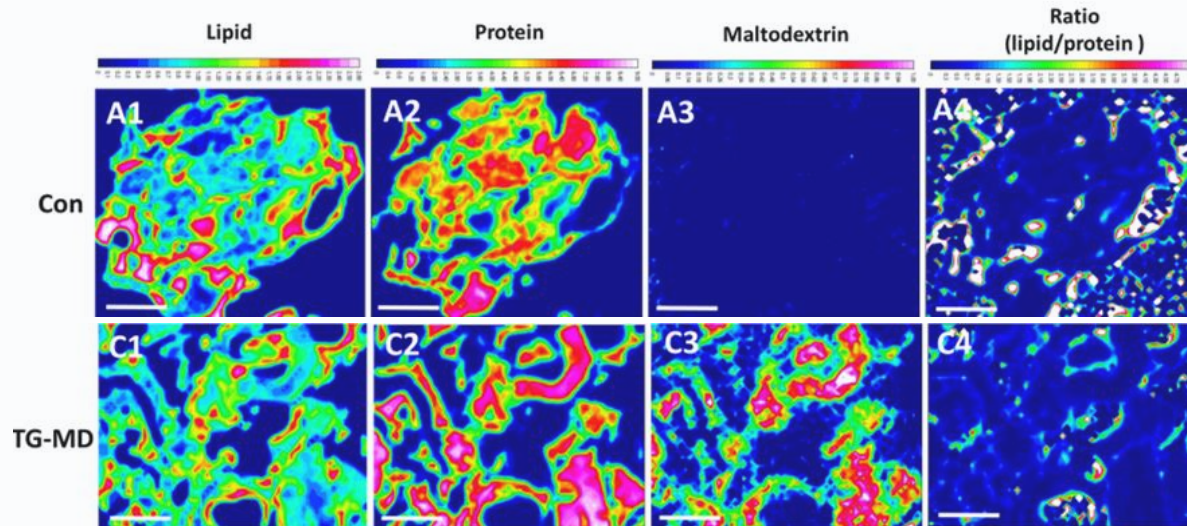
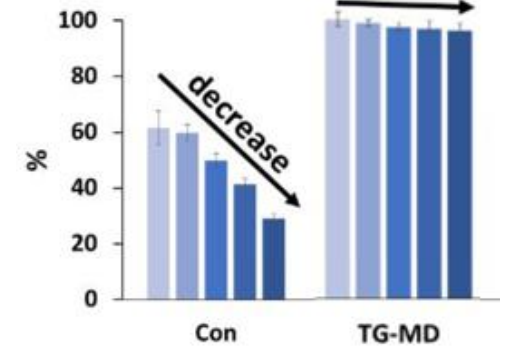


Control
(pea/whey protein
blends)

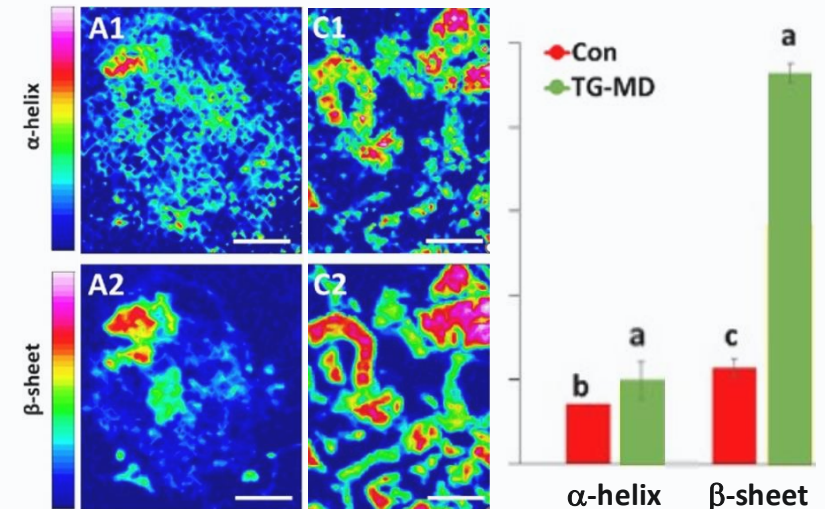
TG-MD
(cross-linked
pea/whey protein
blends + maltodextrin)



Encapsulation efficiency
over 8 weeks



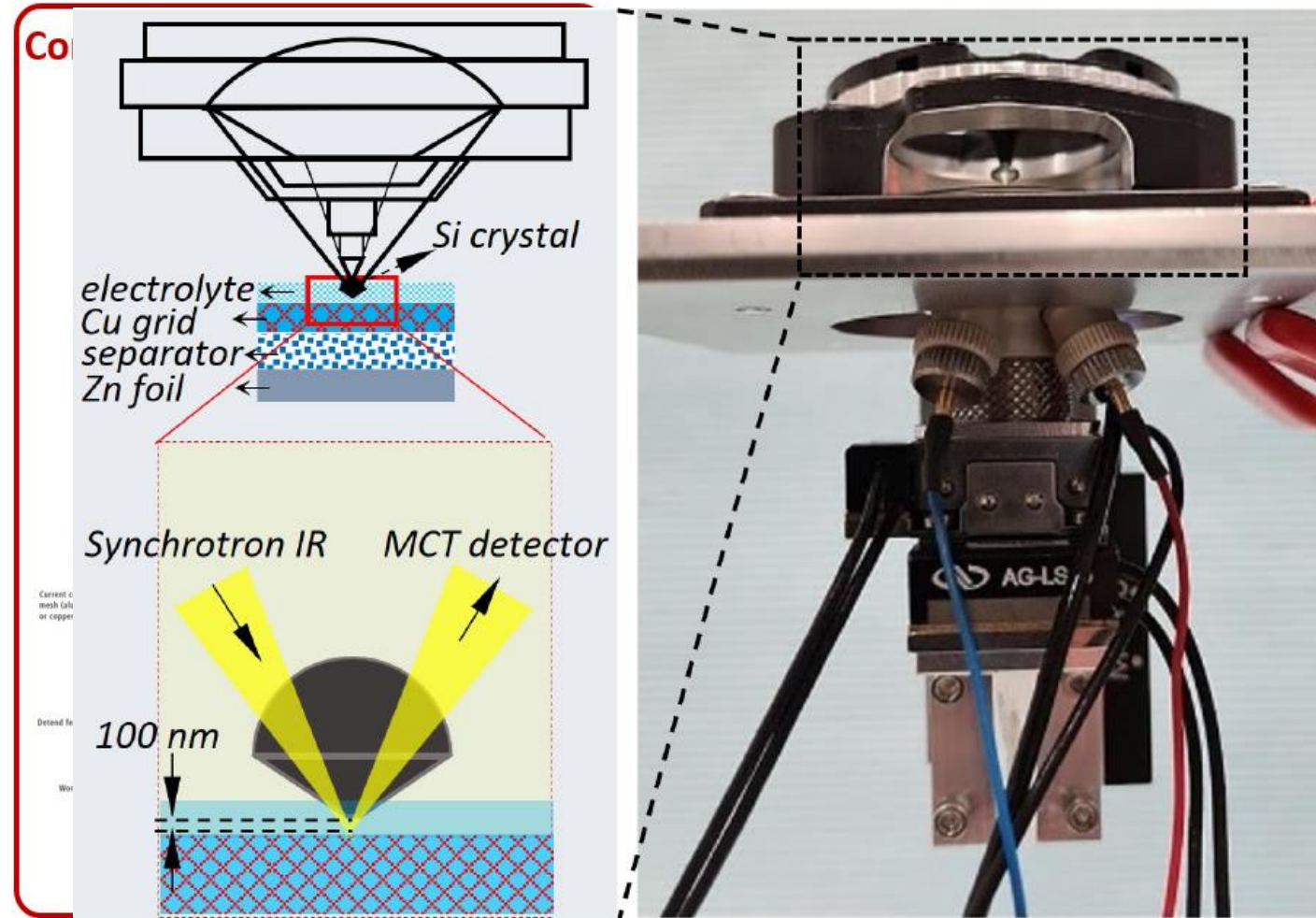
Surface composition (lipid:protein ratio)



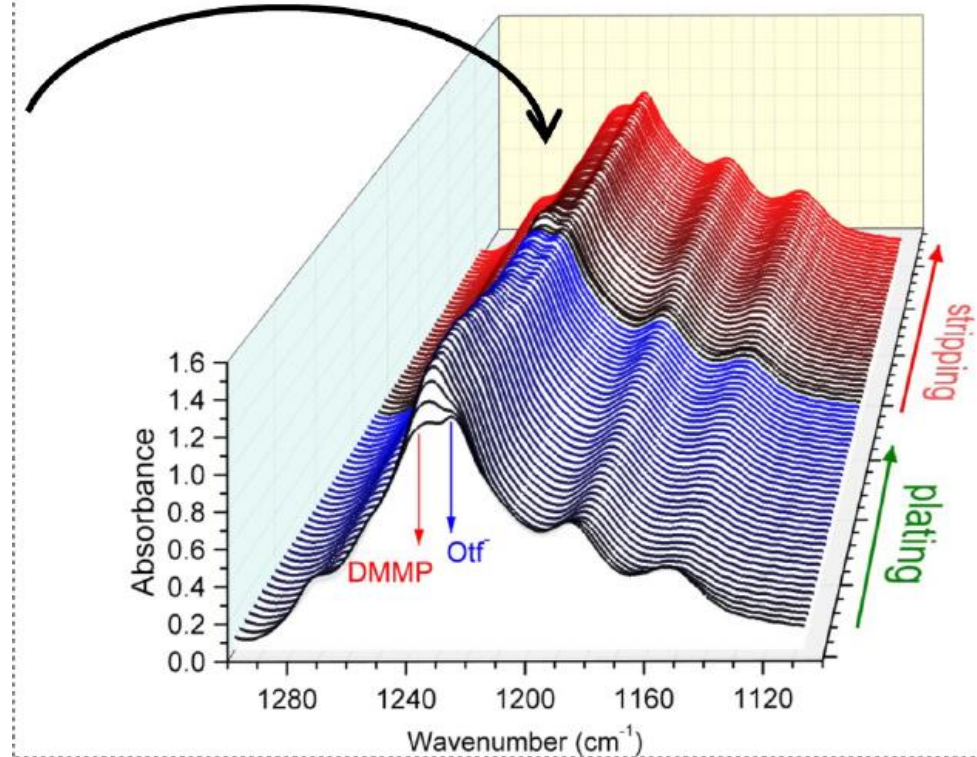
Protein secondary structure

IN-HOUSE DEVELOPED PIEZO-CONTROLLED MACRO ATR-FTIR TECHNIQUE

– Current Progress in Battery Research –



The success on observing the intensity changes of solvent (DMMP) and anion (Otf⁻) during electrochemical reactions

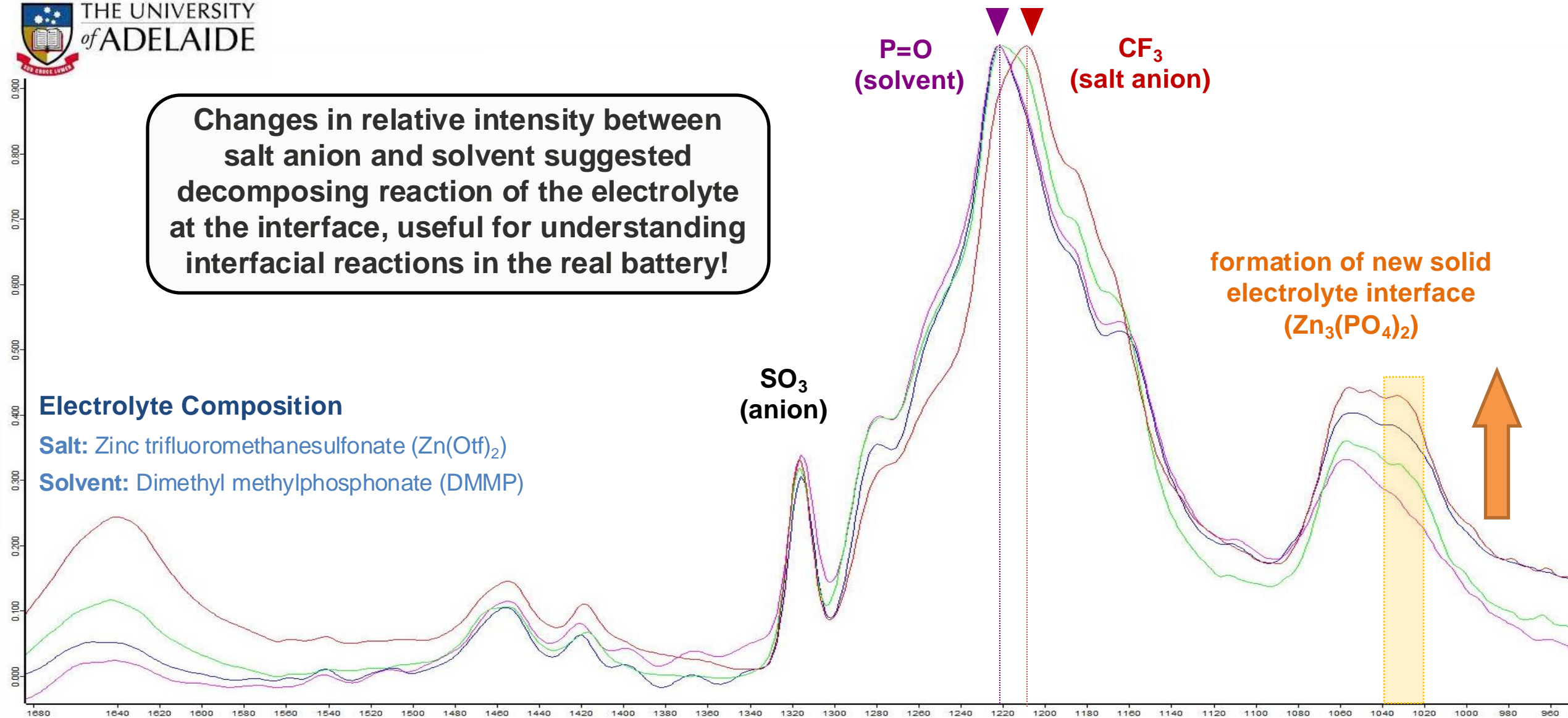


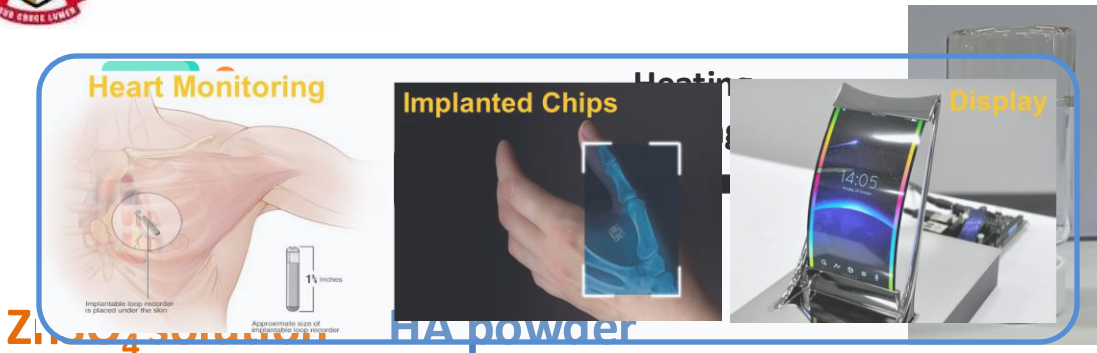
Changes in relative intensity between salt anion and solvent suggested decomposing reaction of the electrolyte at the interface, useful for understanding interfacial reactions in the real battery!

Electrolyte Composition

Salt: Zinc trifluoromethanesulfonate ($\text{Zn}(\text{Otf})_2$)

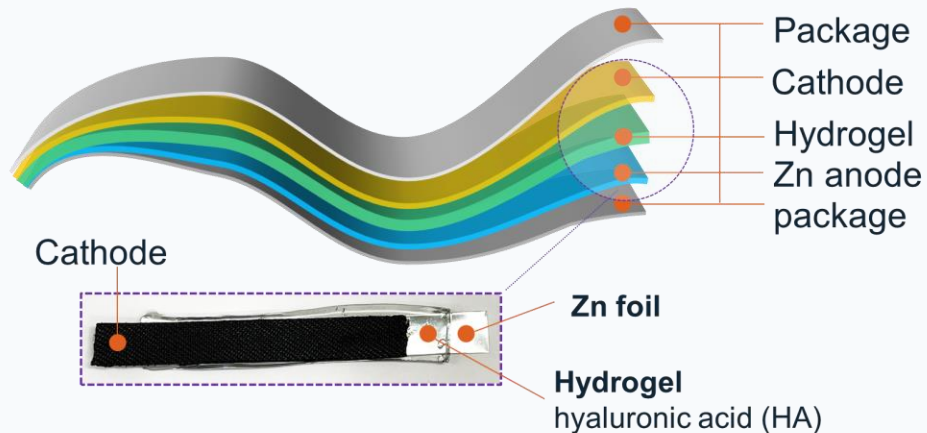
Solvent: Dimethyl methylphosphonate (DMMP)





Zn₄ anode HA powder

Flexible zinc metal batteries

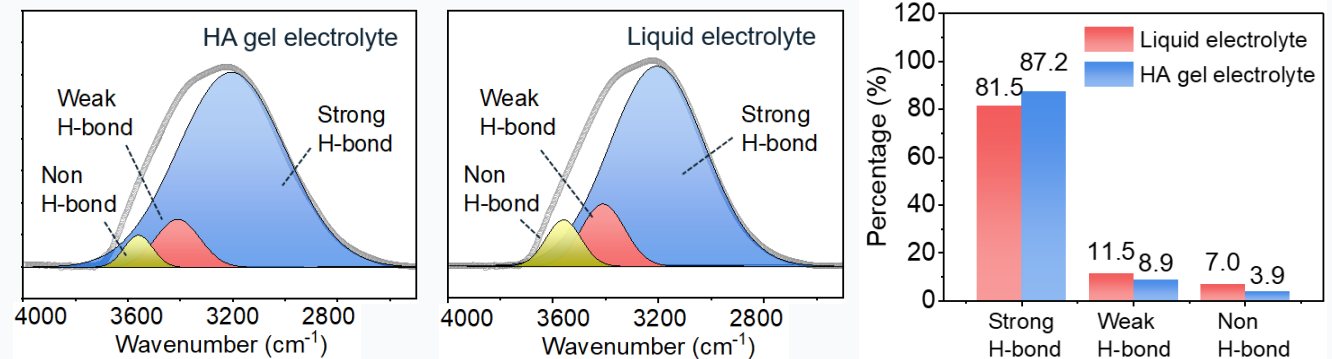


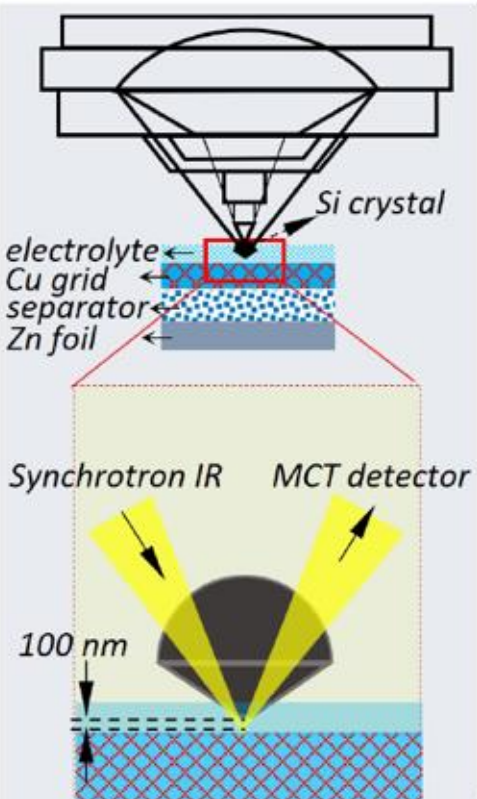
Good flexibility, non-flammable, low cost

Superior performance of HA electrolyte (over liquid electrolyte):

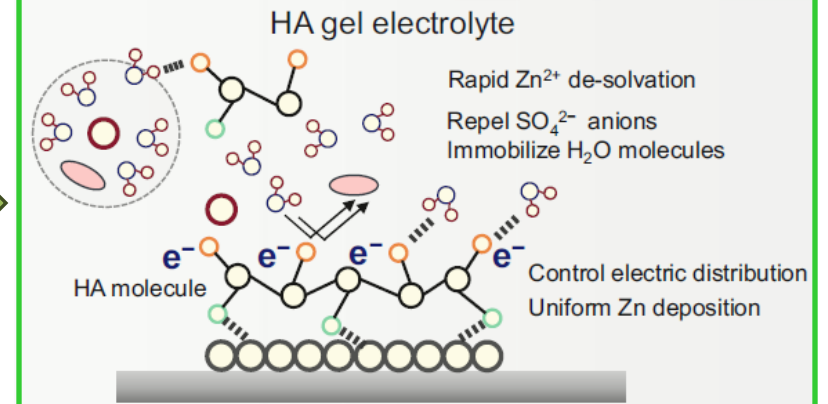
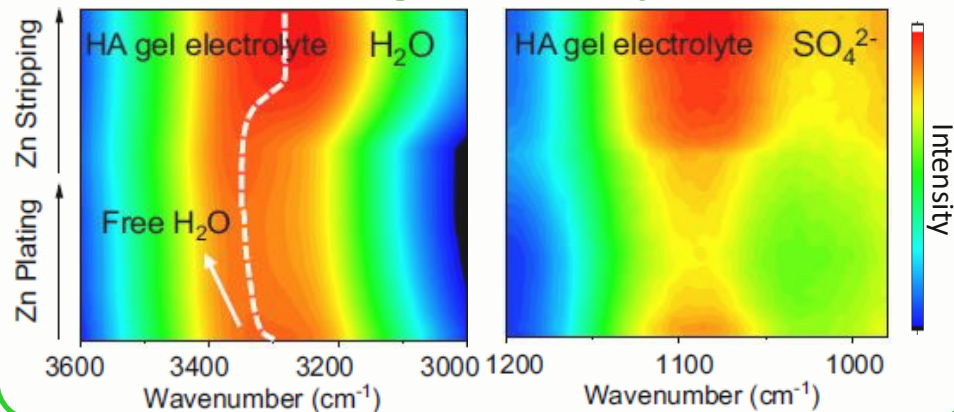
- ✓ Long life span (~5,500 hours = 230 days)
- ✓ High Coulombic efficiency (99.71% high reversible)
- ✓ Wider electrochemical stable window (ESW)
- ✓ Good anti-corrosion property (i.e. negligible by-products generated)
- ✓ More uniform growth of Zn deposition
- ✓ Excellent flexibility to be made for flexible battery applications

Benchtop-FTIR: gaining insights into the electrochemical mechanism

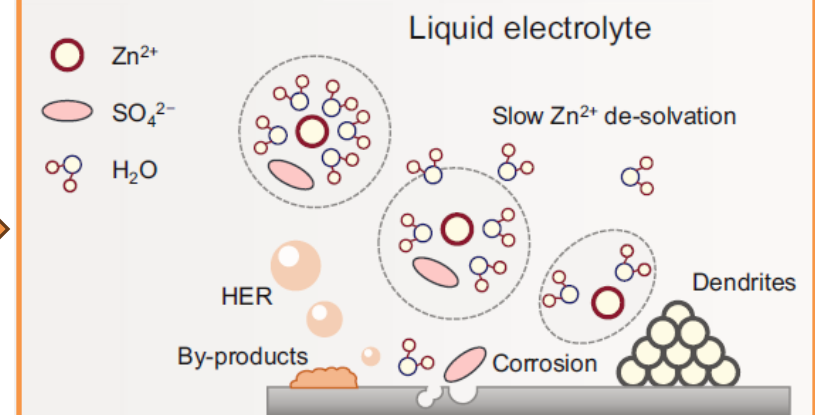
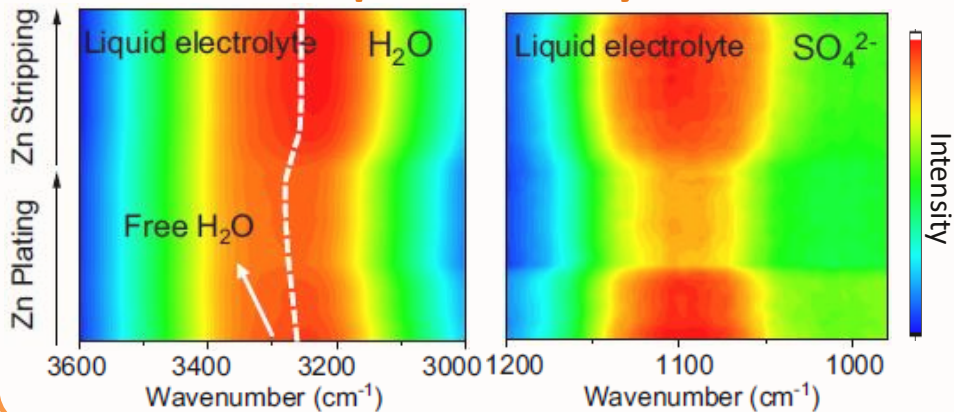




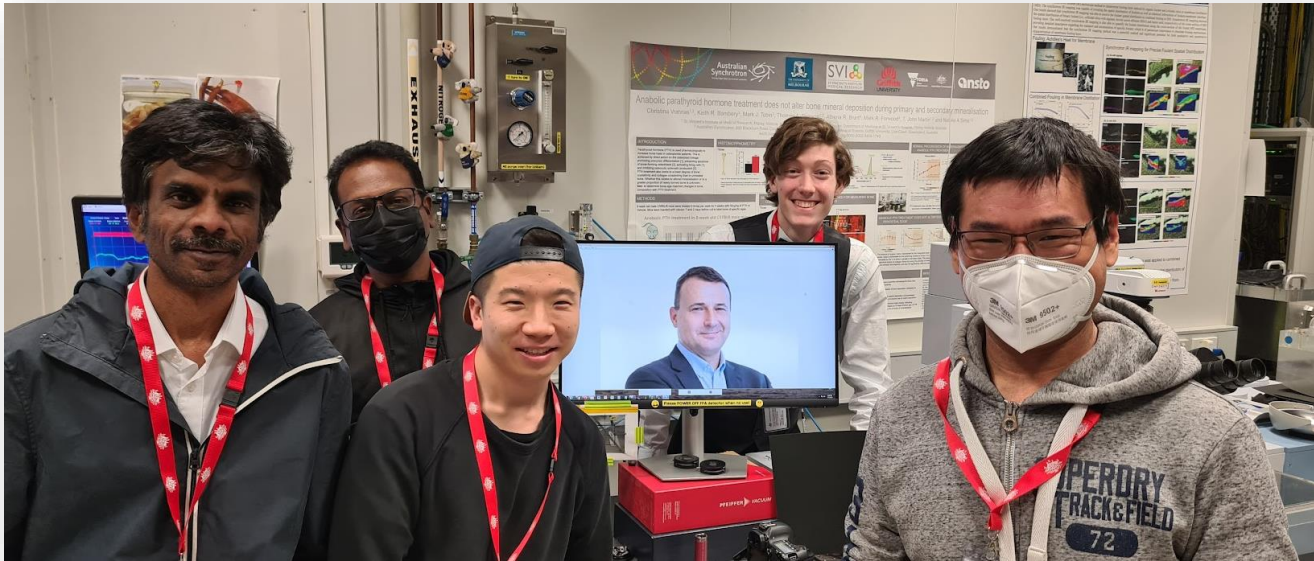
HA gel electrolyte



Liquid electrolyte



ACKNOWLEDGEMENTS



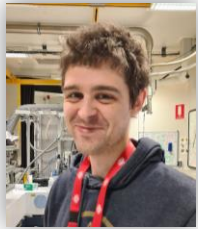
Saulius Juodkazis
Soon Hock Ng
Vijayakumar Anand
Molong Han
Daniel Smith
Armandas Balčytis



Junko Morikawa
Meguya Ryu
Reo Honda



Callum Gassner
Bayden R. Wood



Pooja Takkalkar
Nhol Kao
Gregory Griffin
Tapasi Mukherjee



Nishar Hameed
Nisa V. Salim
Ahmed Al-Qatatsheh
Jaworski C. Capricho
Premika Govindaraj

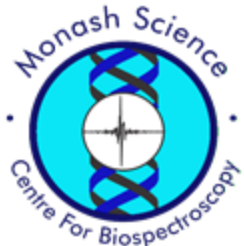


Natalie A. Sims
Martha A. Blank
Christina Vrahnas
Ingrid Poulton
Blessing Crimeen-Irwin




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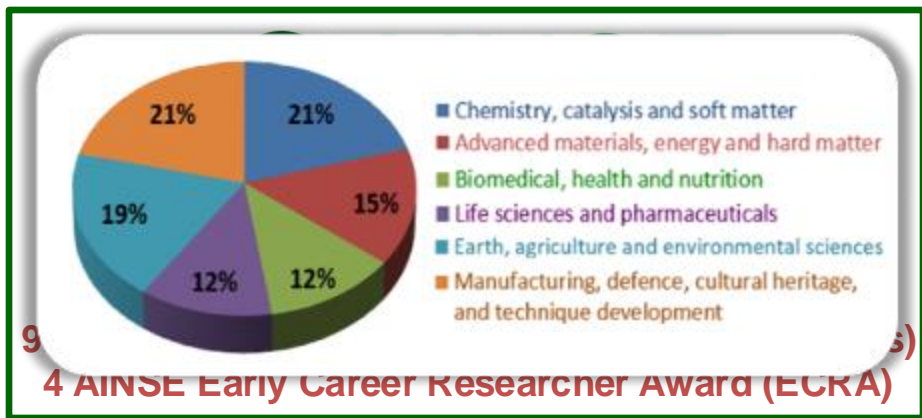
Junko Morikawa
Meguya Ryu
Reo Honda




Simon Lewis
Wilhelm van Bronswijk
Mark J. Hackett
Georgiana Sauzier (AINSE-ECRA)
Elena Dallerba (AINSE-ECRA)
Ashley Hollings (AINSE-PGRA)
Rhiannon E. Boseley (AINSE-PGRA)
Karina Khambatta (AINSE-PGRA)
Kea Inder-Smith (AINSE-PGRA)
Meg Willans (AINSE-Honours)




Sally Gras
Lydia Ong
Anita Pax







Cordelia Selomulya
Yong Wang
Woojeong Kim




Ingrid Ward
Kane Ditchfield
Nikola Ristovski (AINSE-Honours)




Thomas Scheibel
Christian Haynl
Vanessa J. Neubauer
Kai R. H. Mayer




Elena P. Ivanova
James Chapman
Vi Khanh Truong
Aaron Elbourne
Saffron Bryant
Zoe Shaw (AINSE-PGRA)
Louisa Huang (AINSE-PGRA)
Erim Kosyer (AINSE-Honours)
Soroosh Gharehgozlo (AINSE-Honours)
Nhol Kao
Gregory Griffin
Pooja Takkalkar
Benu Adhikari
Yakindra Timilsena





Saulius Juodkazis
Armandas Balčytis
Soon Hock Ng
Nishar Hameed
Premika Govindaraj (PGRA)
Lingxue Kong
Ludo Dumee
Jingshi Wang (AINSE-PGRA)
Srinivas Nunna



Zaiping Guo
Wei Kong Pang
Sailin Liu (AINSE-PGRA/ECRA)
Shilin Zhang
Ruizhi Zhang
Guanjie Li







IRM BeamTeam: past & current



Mark J. Tobin
Previous Principal Scientist
(IRM & THz)



Alan Easdon
Senior Mechanical
Technician



Pimm Vongsvivut
Senior Scientist – IRM



Keith Bambery
Senior Scientist – IRM



Annaleise Klein
Scientist – IRM

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THANK YOU 😊

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