Nanocrystalline Cellulose Hydrogel Encapsulated Plasmonic Nanosensors for Detection of Reactive Oxygen Species (ROS): Towards a Sensing Bandage

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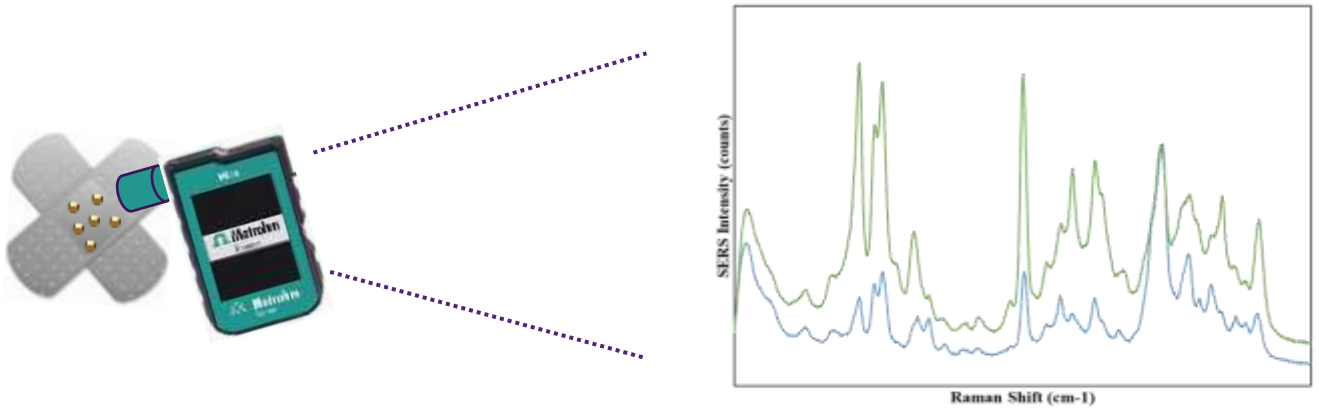
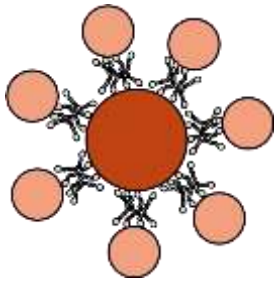
Overview

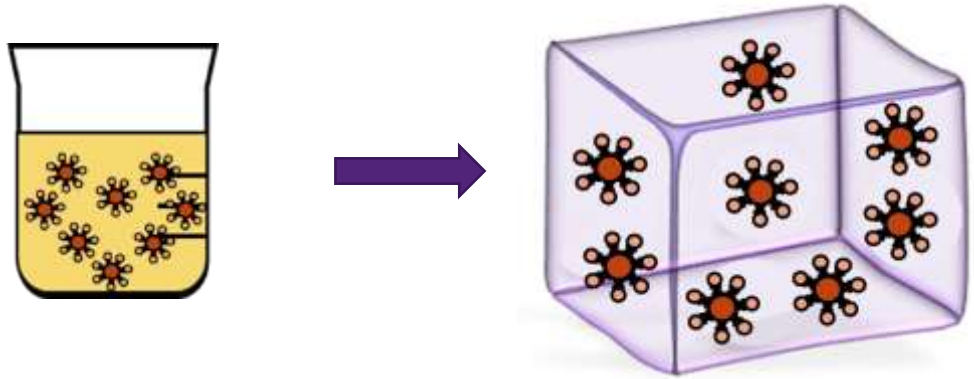
1. Introduction to Raman Spectroscopy



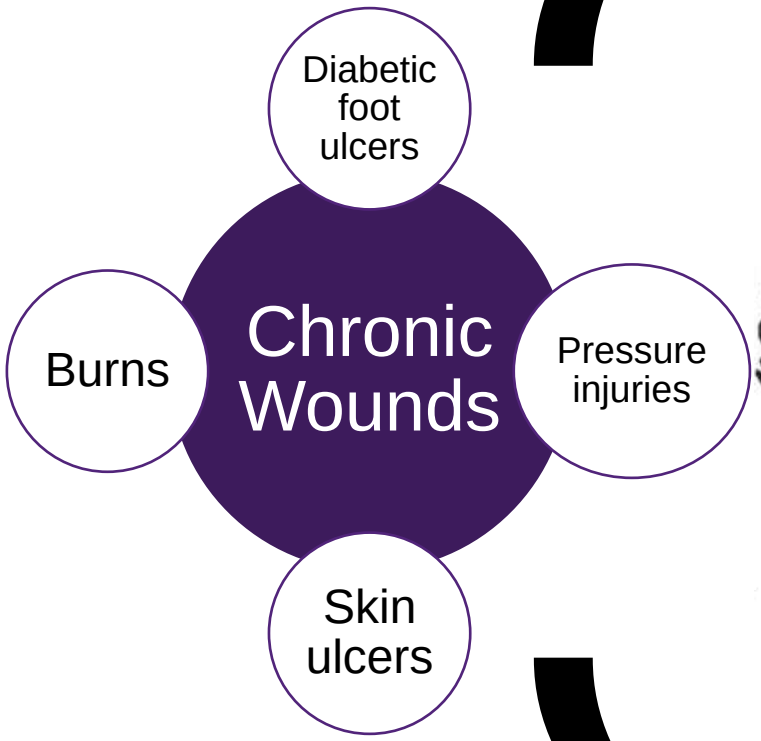
2. Au-nanoassemblies – Core-Satellite Nanoassemblies to provide high SERS enhancements

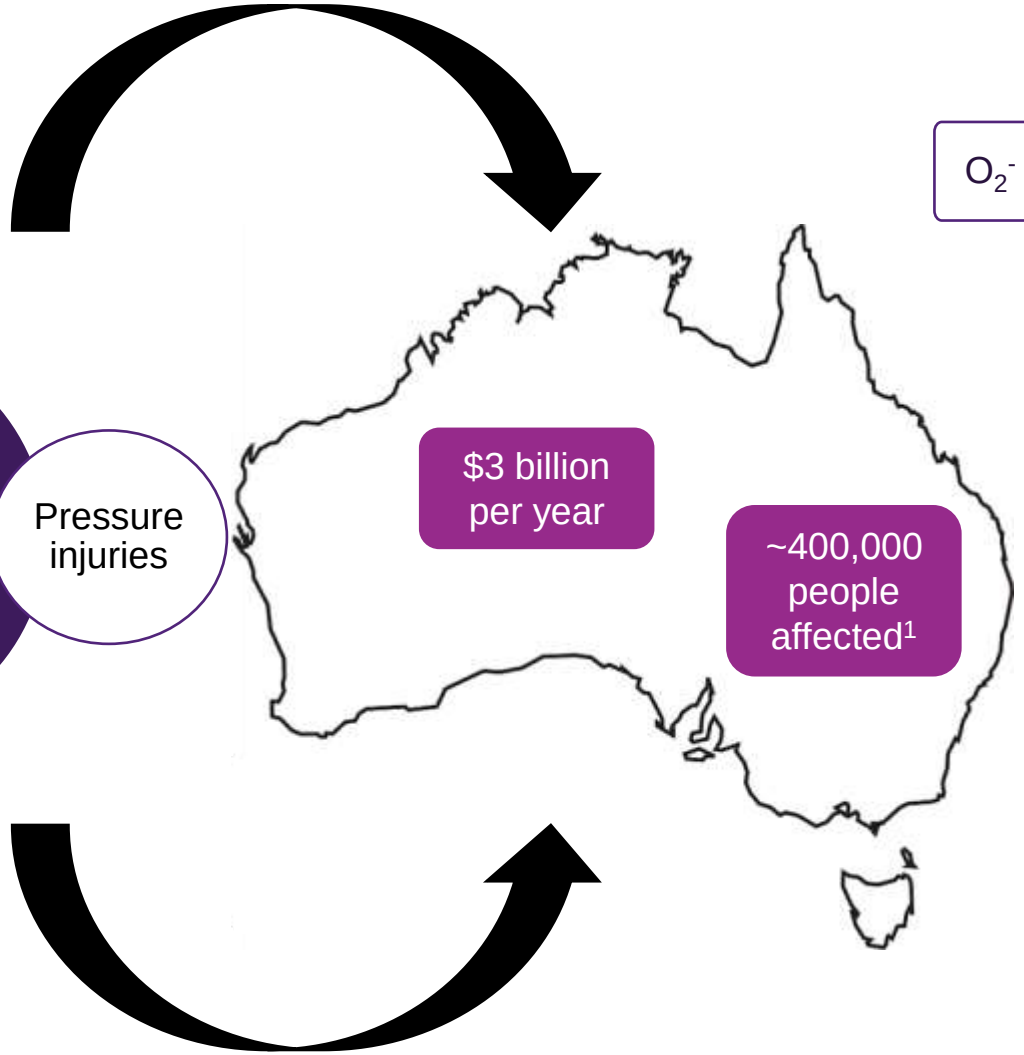


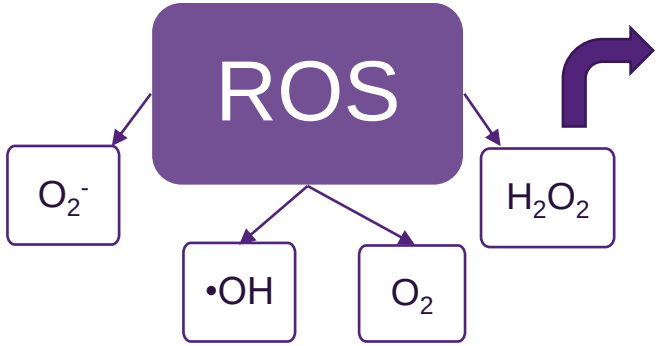
3. NCC Hydrogel SERS sensor – trapping NA in NCC hydrogel to maintain their high SERS enhancements and facilitate diffusion.



Chronic Wounds and Reactive Oxygen Species (ROS)







~1-5 µM normal plasma range

10 mM promoted wound healing

166 mM delayed wound healing[2]

Sensor

- Selective and sensitive
- Monitors in real-time non-invasively
- Incorporated into a bandage

Optimize healing conditions

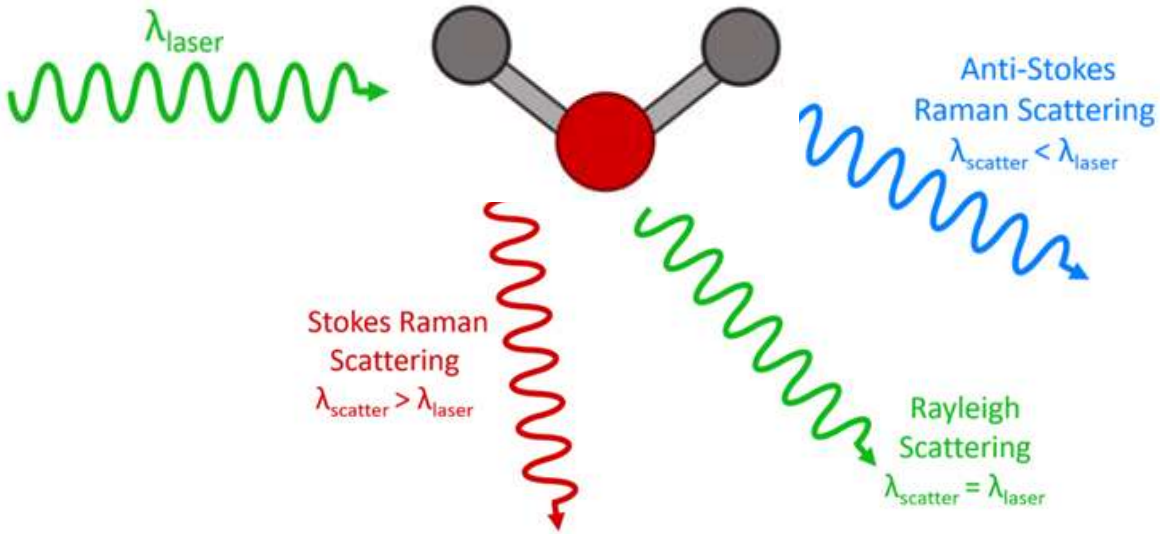
Minimize costs

[1]Dr Rosana Pacella, Issue Paper: "Chronic Wounds in Australia, July (2017)

[2]Loo, A. E., et al : Effects of hydrogen peroxide on wound healing in mice in relation to oxidative damage, 2012

Introduction to Raman Spectroscopy

Raman spectroscopy is a vibrational spectroscopy technique depending on the chemical structure.

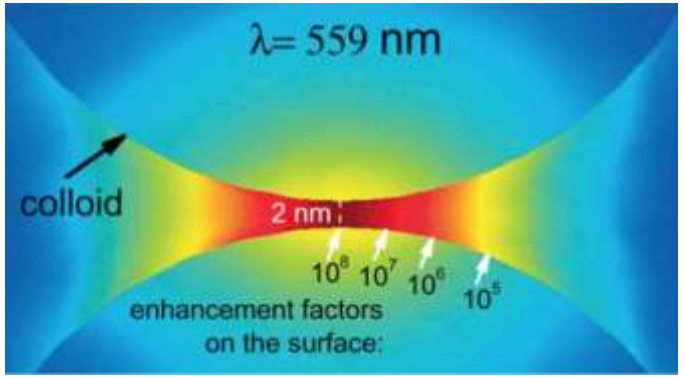


Raman Scattering

- Unique Raman 'fingerprint'
- Excellent for aqueous samples
- Weak Scattering (1 in 1,000,000)

Surface Enhanced Raman Spectroscopy (SERS)

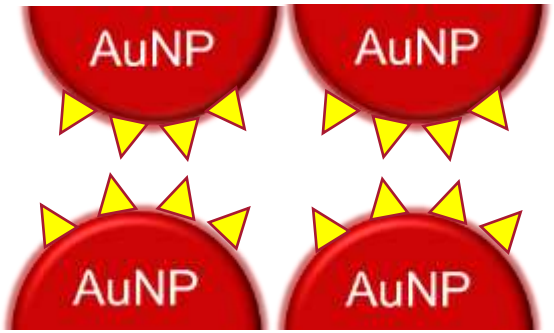
- Plasmonic Nanostructures
- Enhance Raman signals



Smith & G. Dent, Modern Raman Spectroscopy: A Practical Approach 1st ed. , Wiley (2005)

Reactive Probe Detection

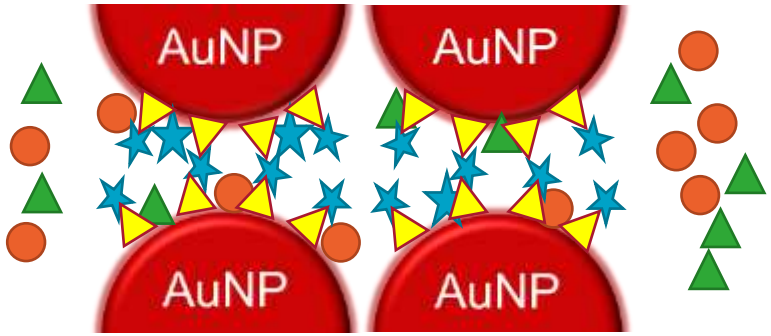
AuNP Substrate



Reactive Probe

Analyte solution

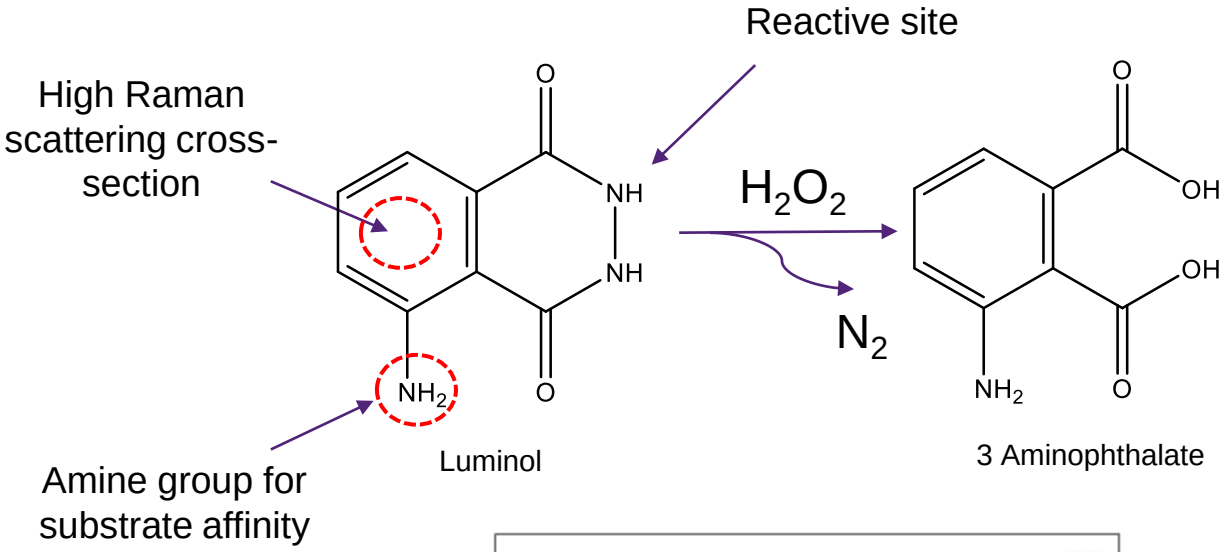
Detection

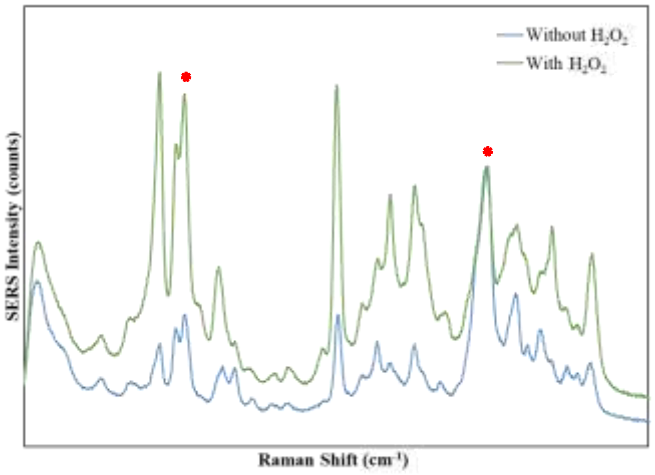


Specific detection of analyte

Potentially detect multiple signals
but interference of signal for complex systems

Reactive Probe

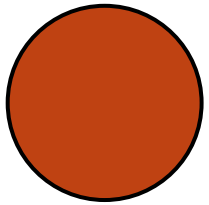




❖Ratiometric response

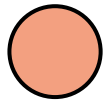
- Acts as an internal standard
- Signals become easy to quantify

Synthesis of Core-Satellite Nanoassemblies



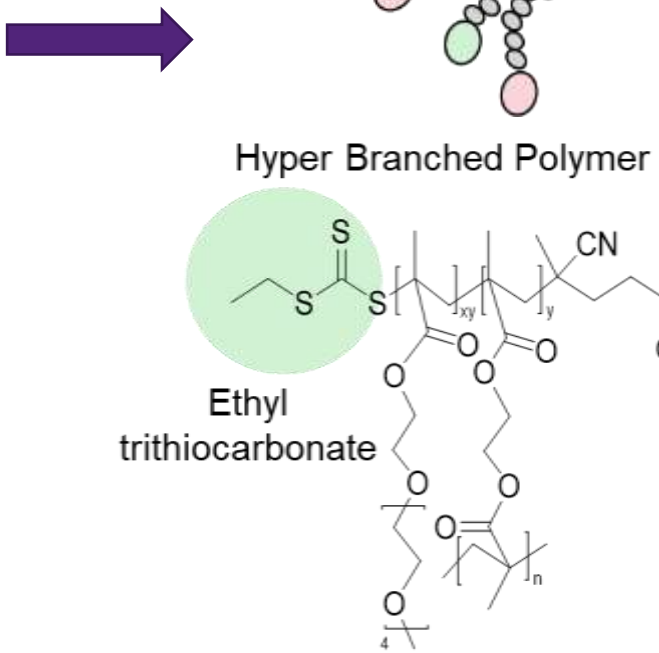
AuNP core

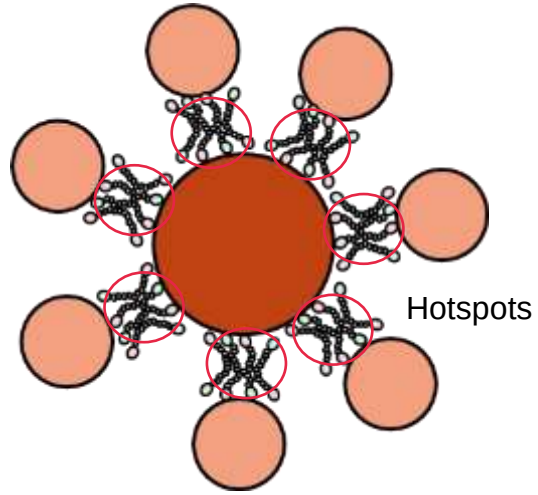
40 nm



AuNP satellite

20 nm

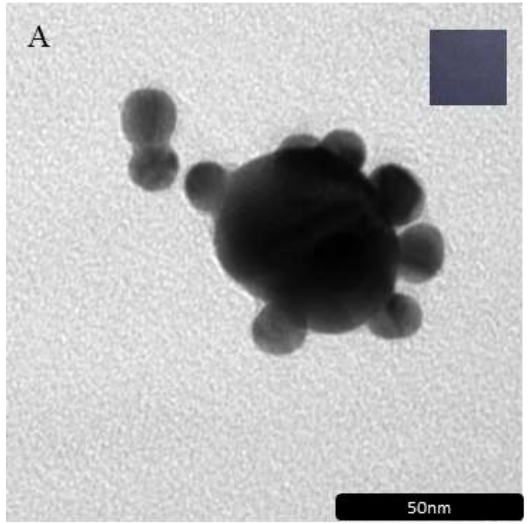


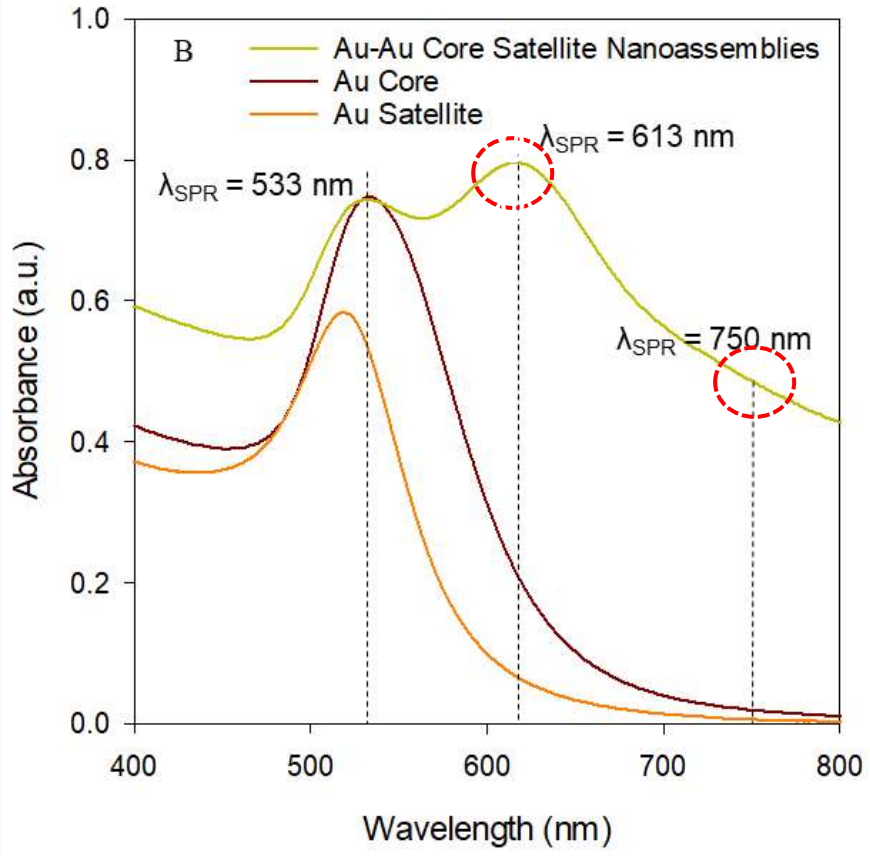


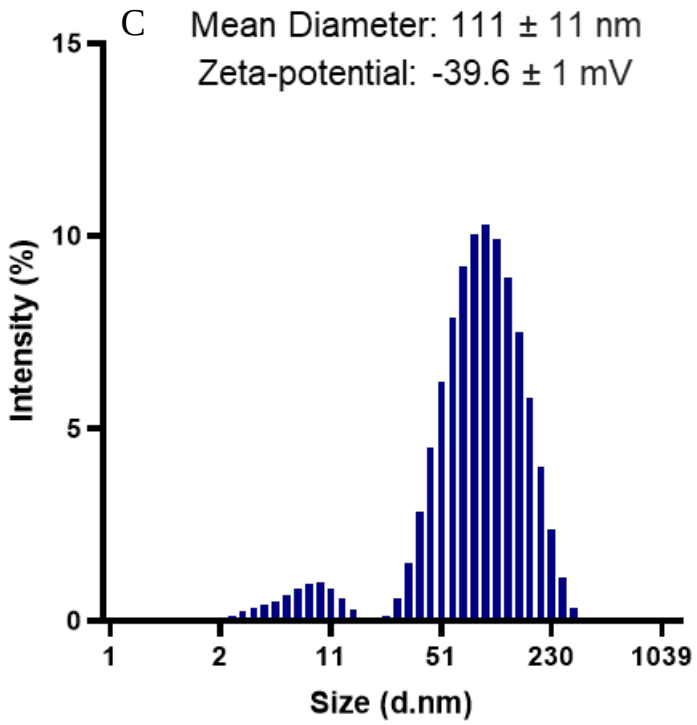
Core-satellite nanoassemblies

Dey, P.; SERS-based detection of barcoded gold nanoparticle assemblies from within animal tissue. 2013

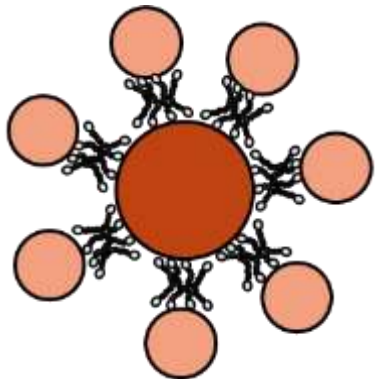
TEM, UV-Vis and DLS results of Luminol-Functionalised Au Core-Satellite Nanoassemblies



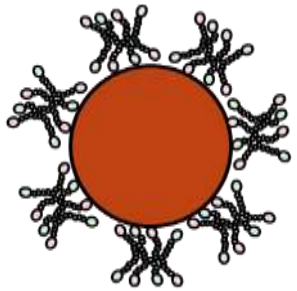




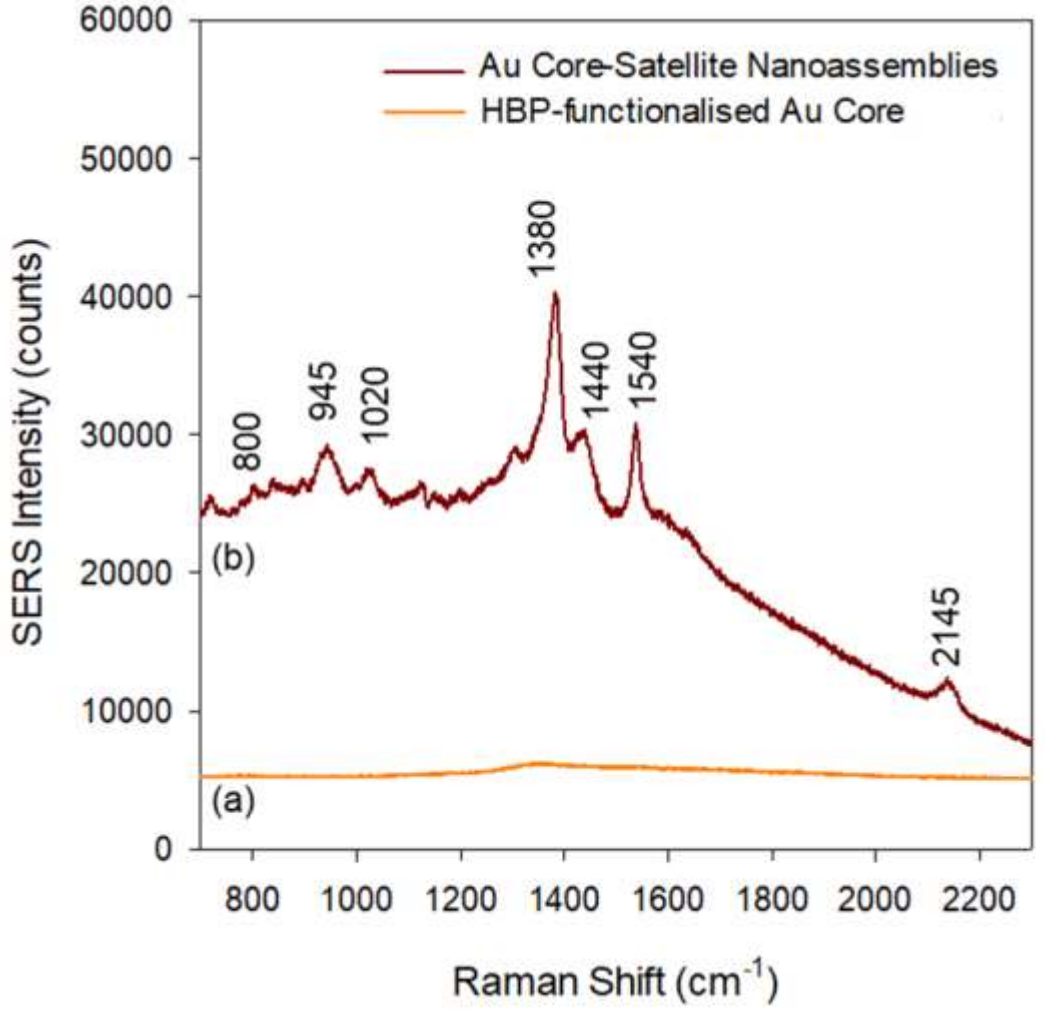
SERS Enhancements due to Hotspots



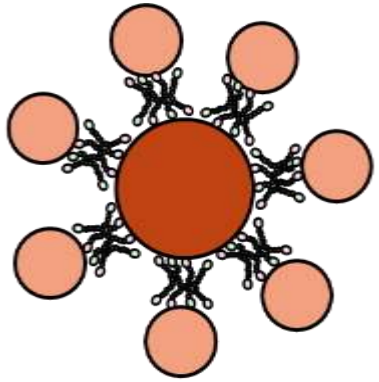
Au-Au Core-Satellite Nanoassemblies



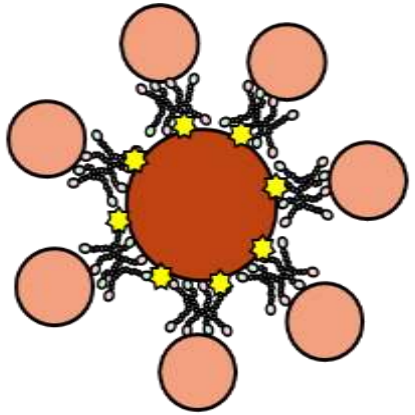
HBP-Functionalised AuNP Core



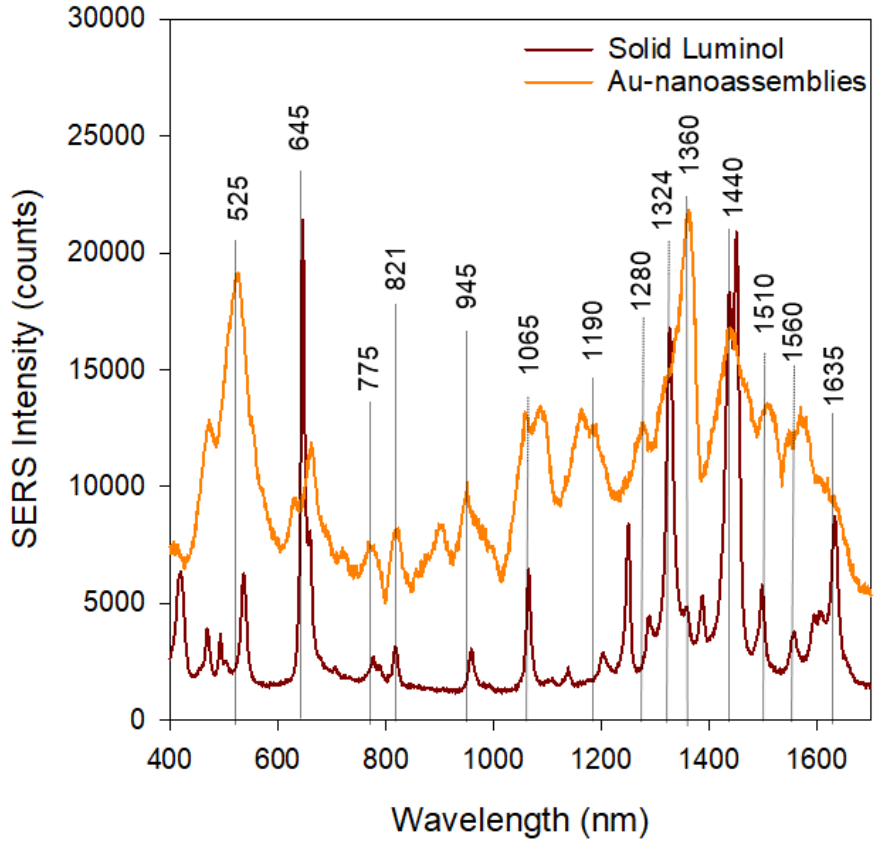
Validation of Luminol Functionalisation on the Core by SERS



Core-Satellite Nanoassemblies

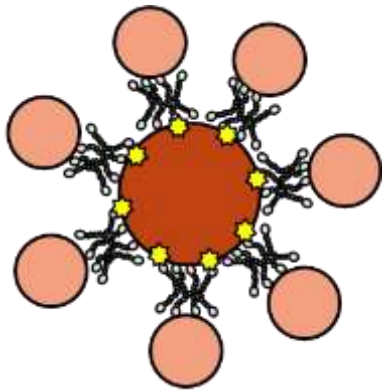


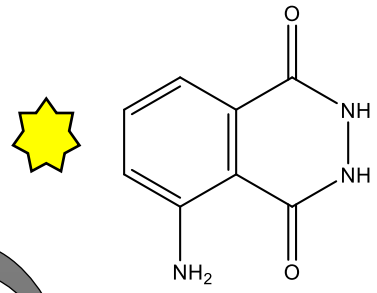
Luminol-Functionalised Core-Satellite Nanoassemblies



SERS (cm^{-1})	Assignment
1635_s	C=O stretching
1560_w	C=C stretching,
1510_w	N-H in-plane bending
1434_s	C-C stretching,
1360_{vw}	C-C stretching
1324_s	N-N stretching
1280_v	C-NH_2 stretching
1190_w	C-N stretching
1065_m	NH_2 rocking
945_m	Trigonal bending
821_w	C-H out-of-plane bending / ring breathing
775_{vw}	NH_2 wagging, C-H out-of-plane bending / NH_2 twisting
645_s	CCC in-plane bending / N-H out-of-plane bending
525_m	C=O in-plane bending / CCC out-of-plane bending

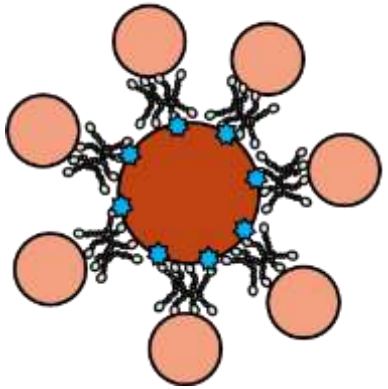
SERS of Nanoassemblies in the presence of H_2O_2

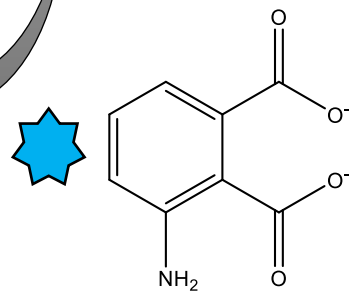




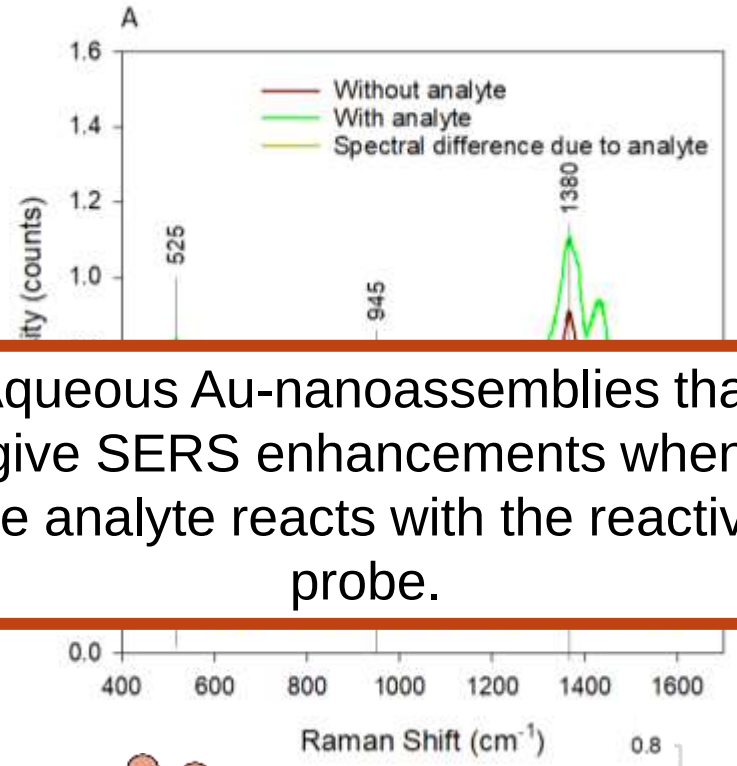
Luminol

H_2O_2

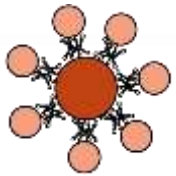




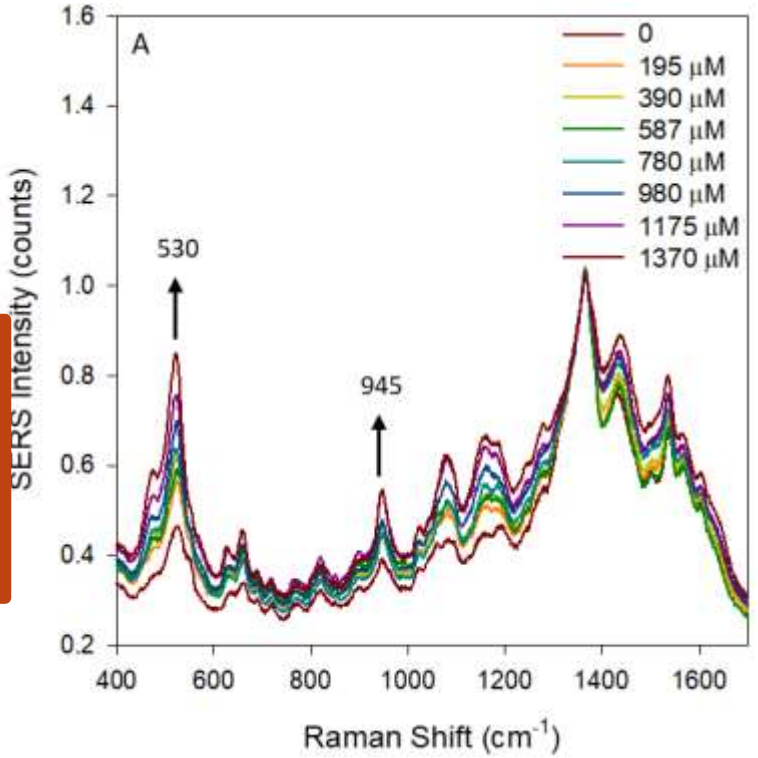
3-Aminophthalate

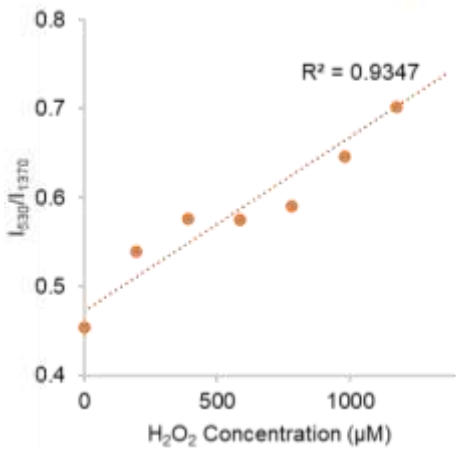


Aqueous Au-nanoassemblies that give SERS enhancements when the analyte reacts with the reactive probe.

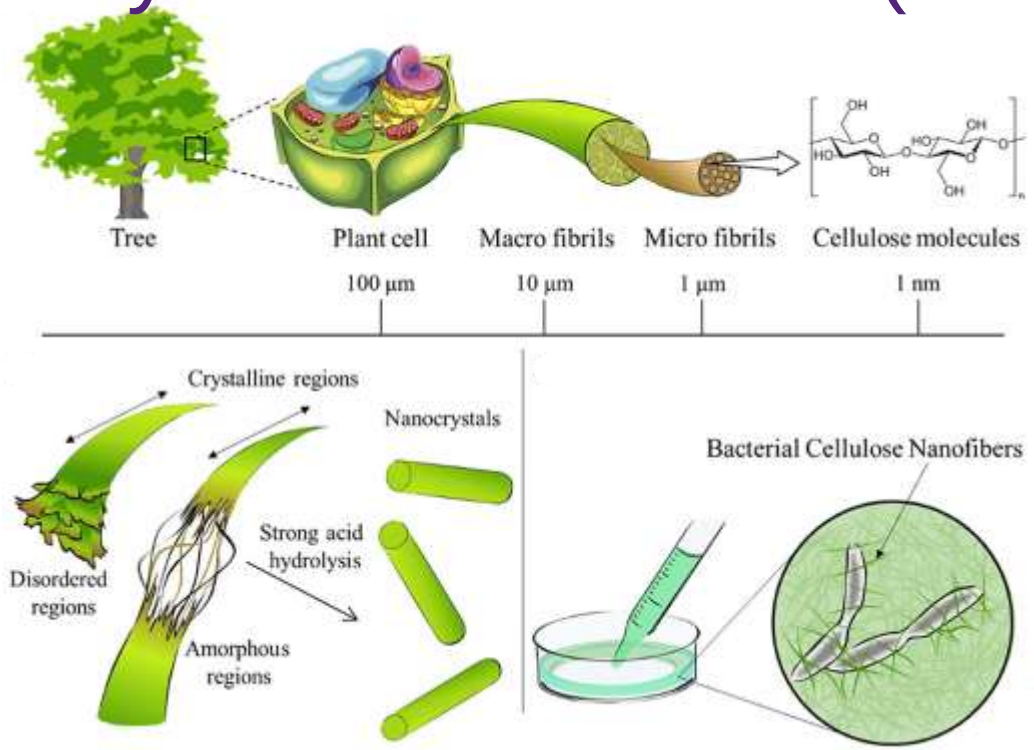


Au-Nanoassemblies





Nanocrystalline Cellulose (NCC) as a Scaffold



Rod-like particles, 100-1000 nm by 5-50 nm

Biocompatibilty

Tailorable parameters; mechanical and optical properties

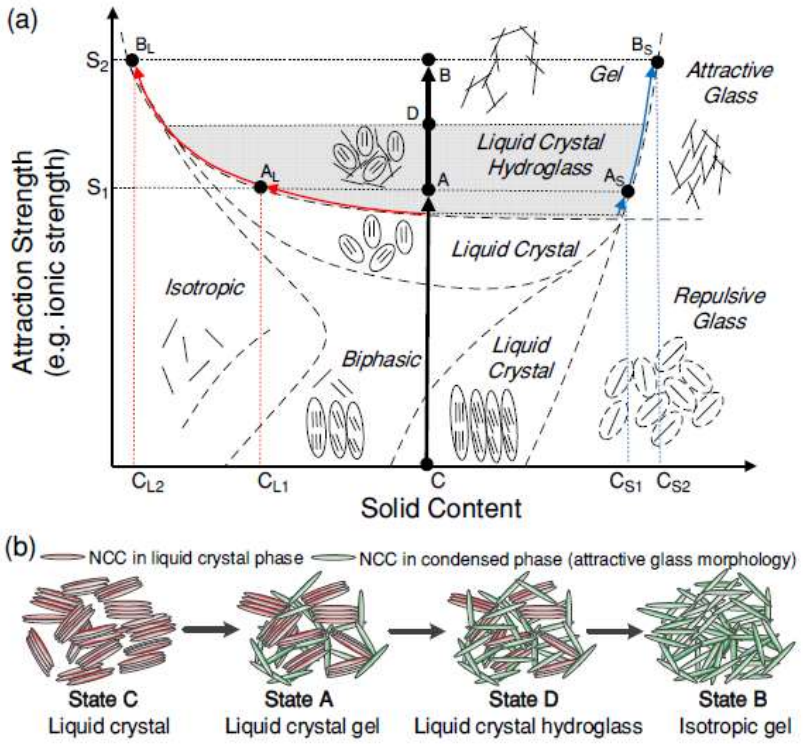
Inherent scattering nature

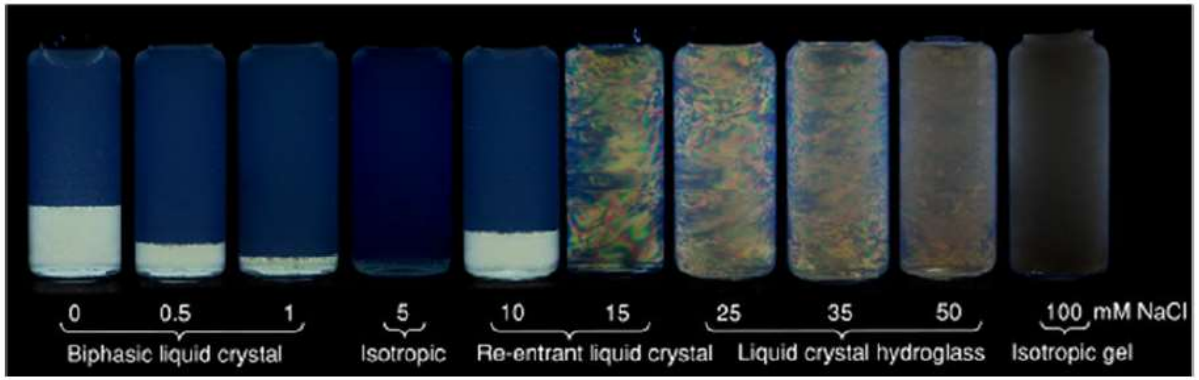
NCC Hydrogel

- Increased stability of SERS signals
- Controllability over diffusion rate
- Allows for pH control to optimize sensing reaction
- Adsorb wound exudates and allow oxygen diffusion for healing
- Load with therapeutic drug molecules

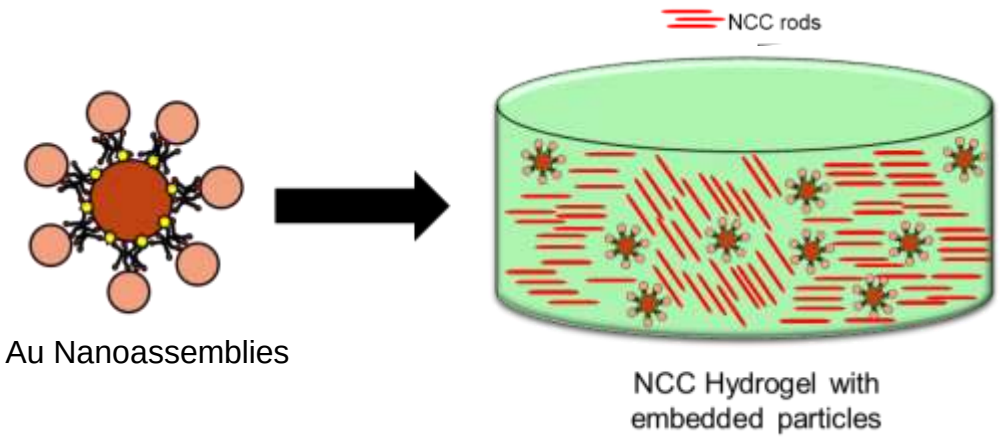
Miyashiro, D., Hamano, R., and Umemura, K. (2020). A review of applications using mixed materials of cellulose, nanocellulose and carbon nanotubes.

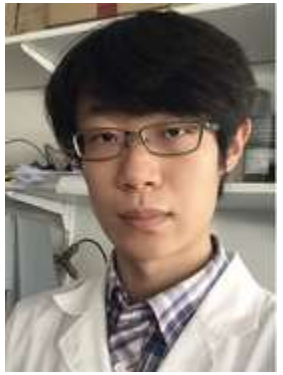
Phase Diagrams of NCC Suspensions





Cross-polarized photographs of 5wt% NCC suspensions

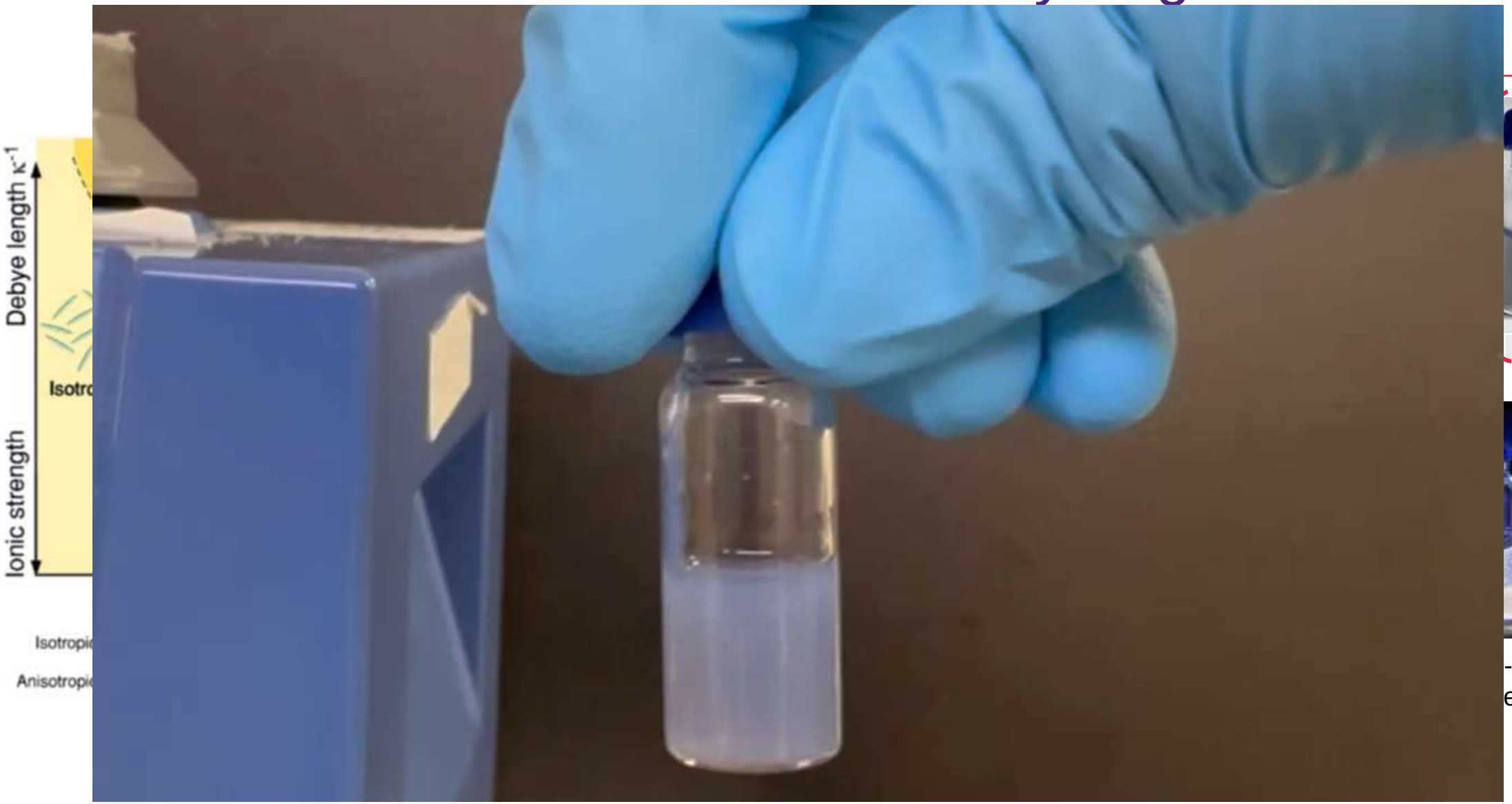




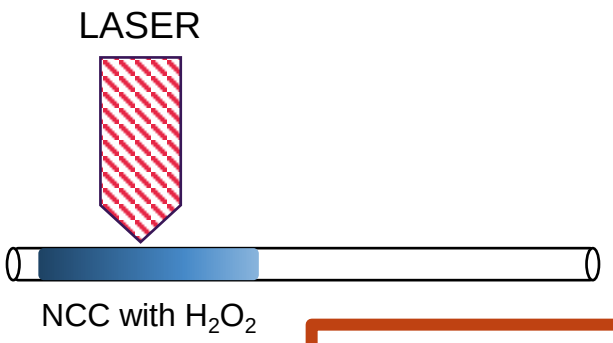
Dr Yuan Xu
Stokes Group
School of Chemical Engineering

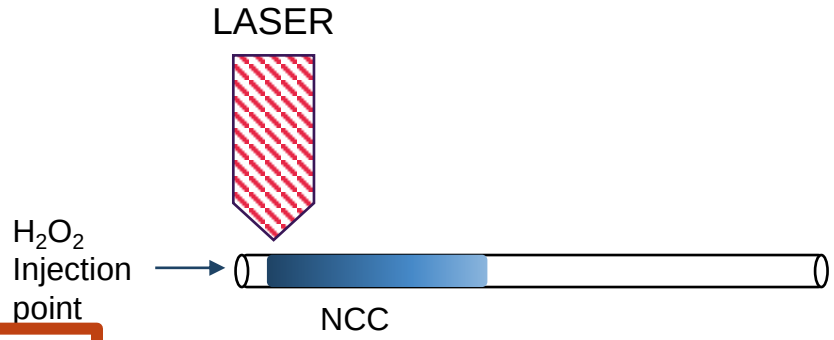
Xu, Y.; Atrens, A.; Stokes, J. R., Structure and rheology of liquid crystal hydroglass formed in aqueous nanocrystalline cellulose suspensions. J Colloid Interface Sci 2019, 555, 702-713.

Nanoassemblies embedded in NCC hydrogel

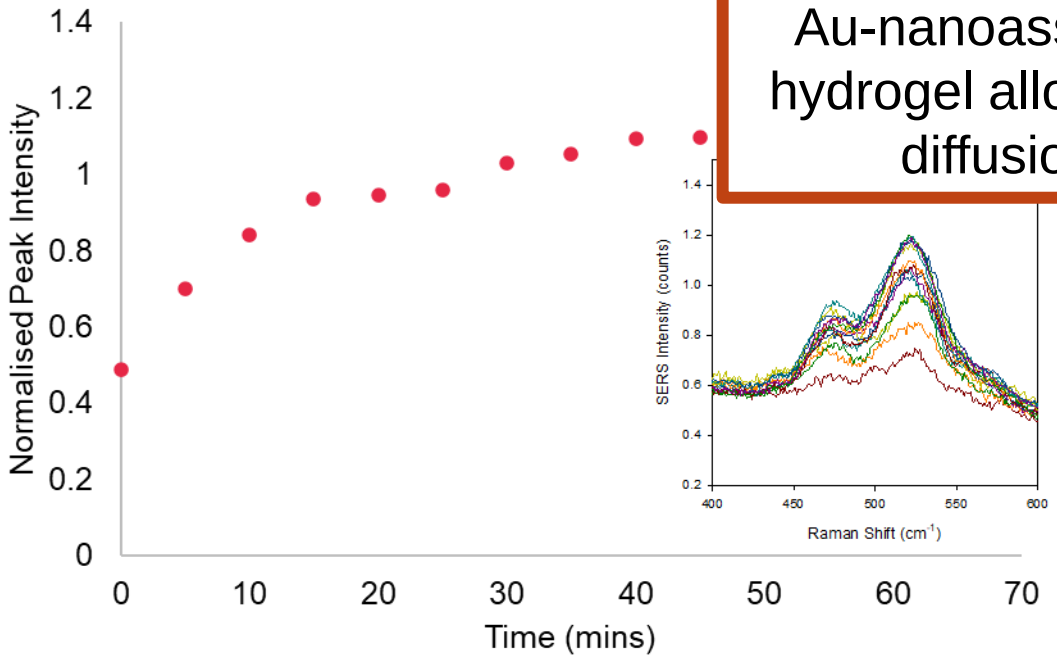


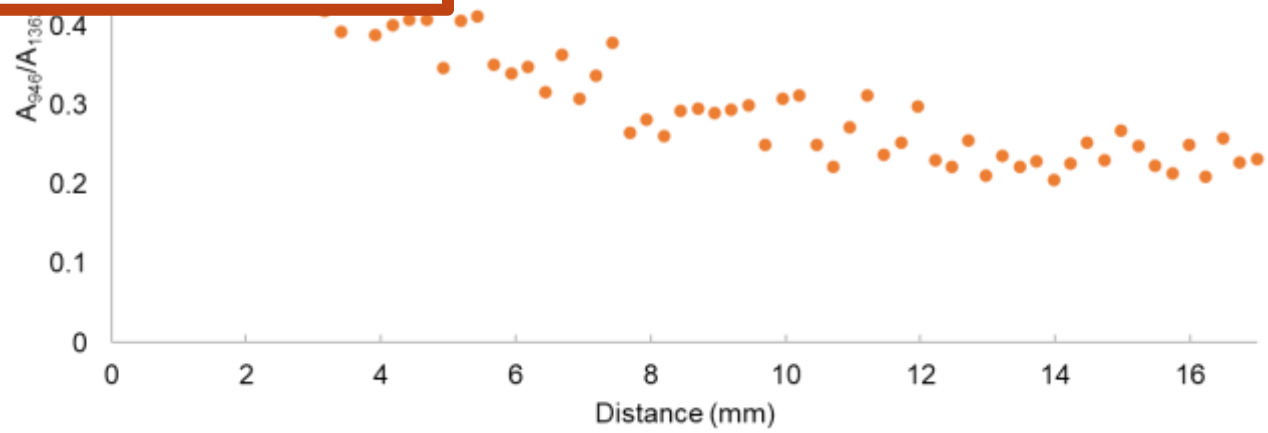
Time and Distance-based SERS of NCC-Nanoassemblies





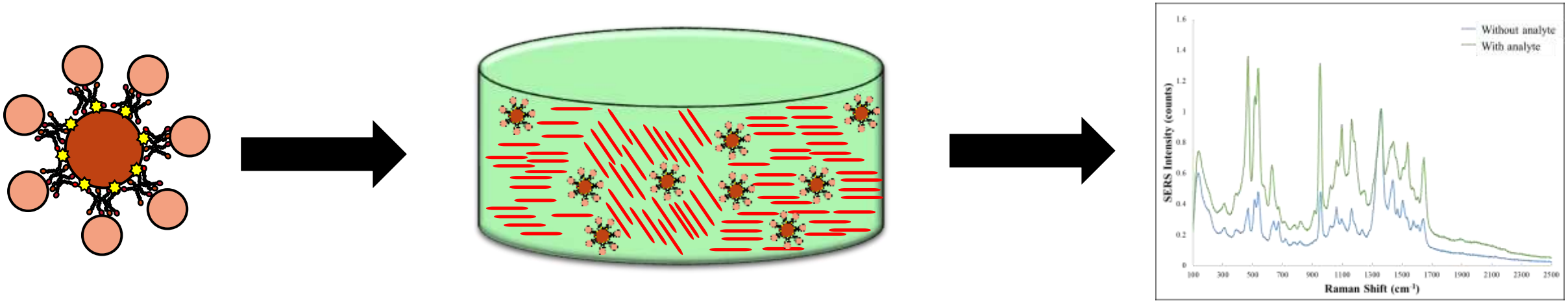
Maintain SERS enhancements of Au-nanoassemblies in the NCC hydrogel allowing control over the diffusion of the analyte





Conclusion

- Synthesis of Au nanoassemblies that enhances Raman signals.
- Functionalisation with a molecular reporter that makes the sensing specific
- Embedding of nanoassemblies in the NCC hydrogel allowing analyte diffusion and maintaining SERS enhancements.



Thank you

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Paul
nman

Dr Yuan Xu

Dr Josua Markus