Surface Enhanced Raman Scattering (SERS) for Characterisation of Inks for Cultural Heritage

Daniela Iacopino
Tyndall National Institute
University College Cork
Cork, Ireland

daniela.iacopino@tyndall.ie

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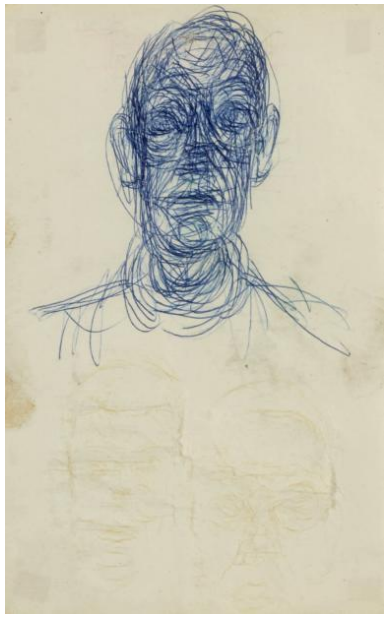
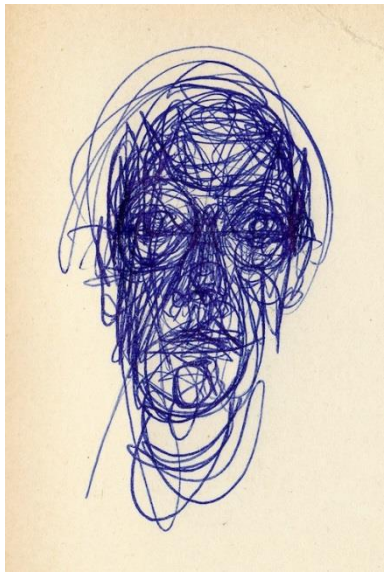
Inks in Works of Art

- Largely used by modern artists (20th – 21st century).
- Suffer from easy degradation.
- Identification of ink composition is a key starting point to appropriate conservative treatment and storage conditions.
- Ink composition identification is difficult:
  - Protected by patent
  - Pens go out of production every few years => Composition changes often
  - Database non existing



Giacometti exposed to light

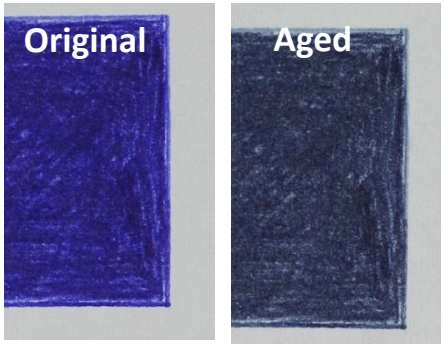


Giacometti not exposed to light

Modern Inks Knowledge Gaps

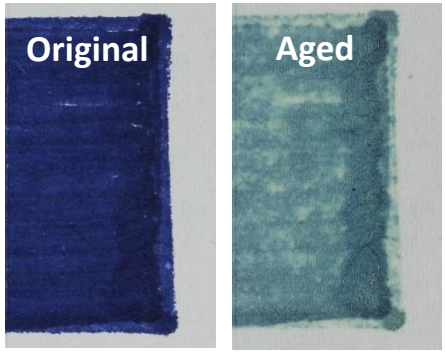
- Composition
- Aging mechanisms

BIC Ballpoint Blue



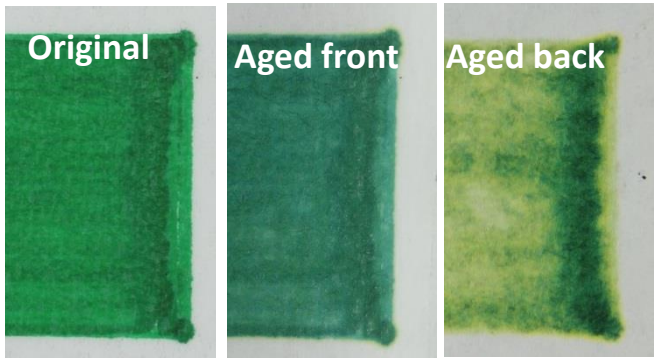
Color change

Stabilo Prussian Blue



Discoloration

Stabilo Green

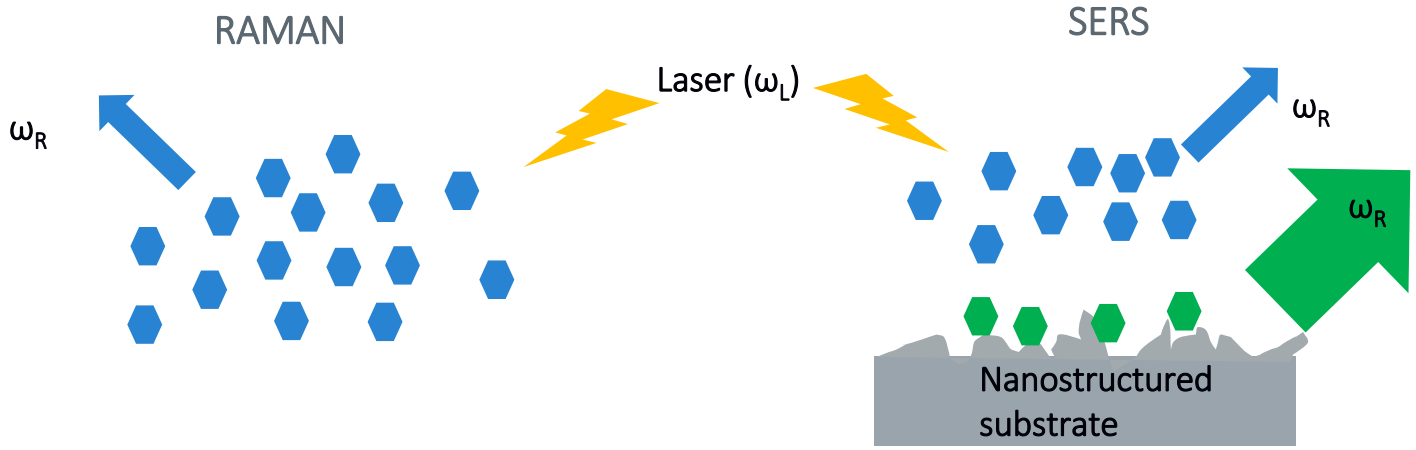


Color migration

Images courtesy of Antonio Mirabile and CSGI

Surface Enhanced Raman Scattering (SERS)

- SERS first observed by M. Fleischman in 1973
- Increase of Raman signals up to 10^{-11} orders of magnitude of analytes in close proximity to metal rough surfaces



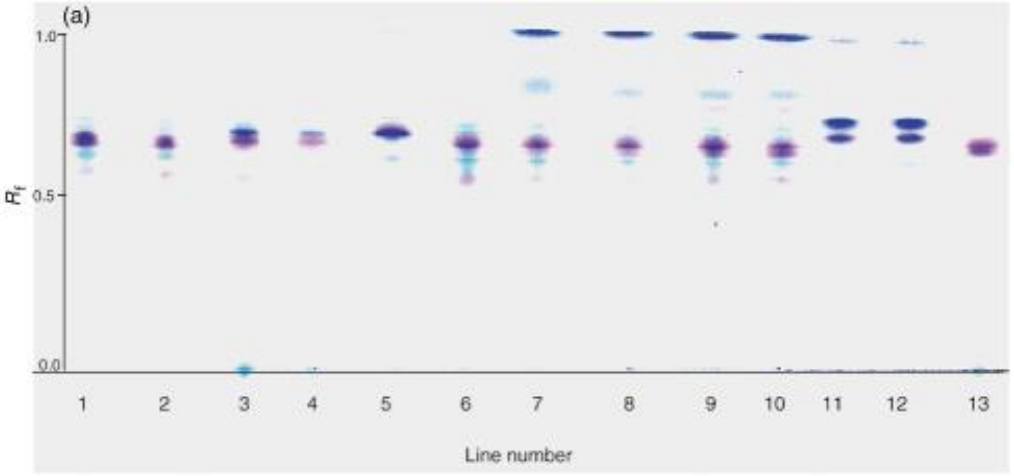
Key characteristics

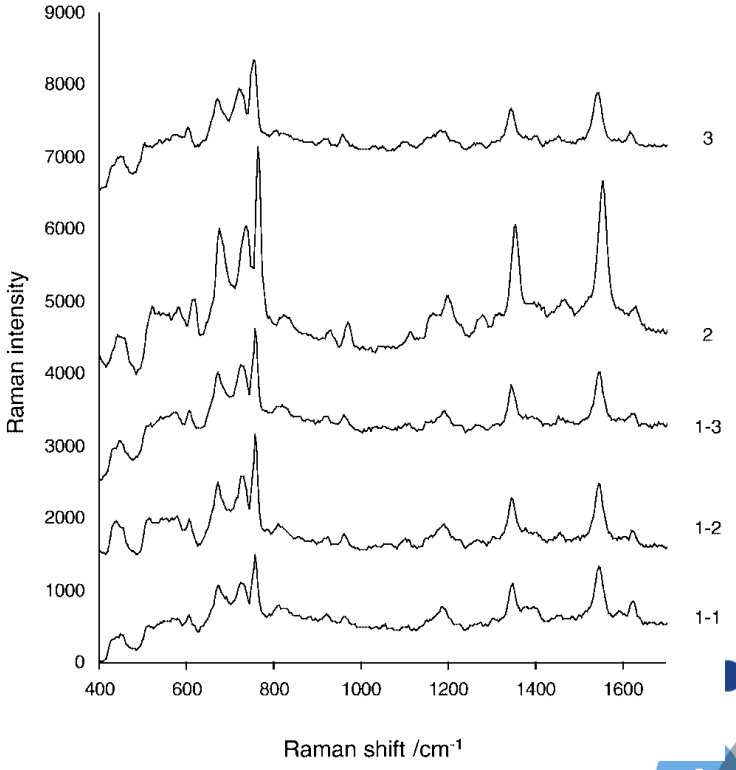
- Fingerprint of analytes
- Non destructive
- In situ and ex-situ analysis
- Minimum sampling or no sampling required
- No sample preparation or extraction required
- Background fluorescence interference

SERS of Modern Inks

Mainly ballpoint pen forensic analysis performed

- Enhancement of Raman signals due to fluorescence background quenching
- Oxidation of Ag observed, fast analysis required
- Poor signal due to the negative charge of both dyes and NPs
- Coffee stain effects in evaporated Ag NP solutions. Not uniform detection
- Ex-situ, extraction required



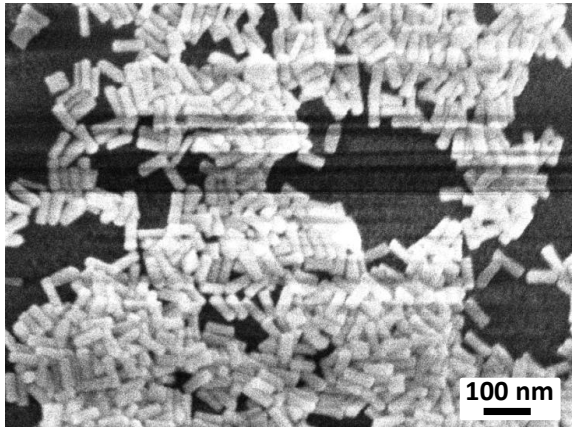


TLC and SERS spectra of blue ballpoint pens

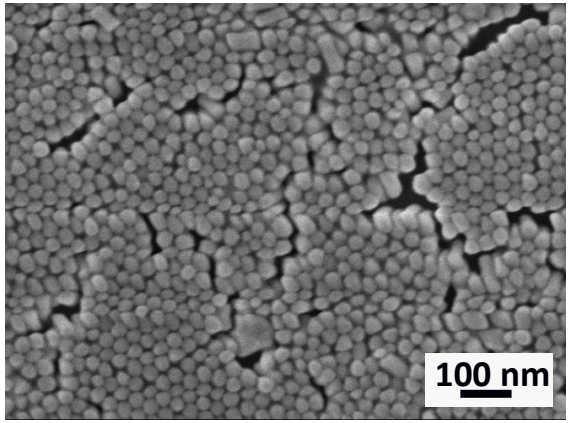
Geirman, I. et al., *J. Forensic Sci.*. 2009, *54*, 947-952

Our Ambition

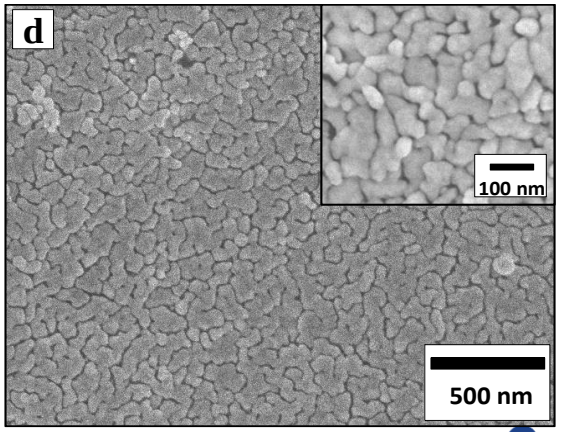
- Widening SERS art application
  - Low cost
  - Tailored plasmonic properties and surface charge
  - Chemical stability and uniformity for repeated analysis
  - In situ and ex situ non invasive analysis
- Understanding compositional information and fading mechanisms



Au Nanorods

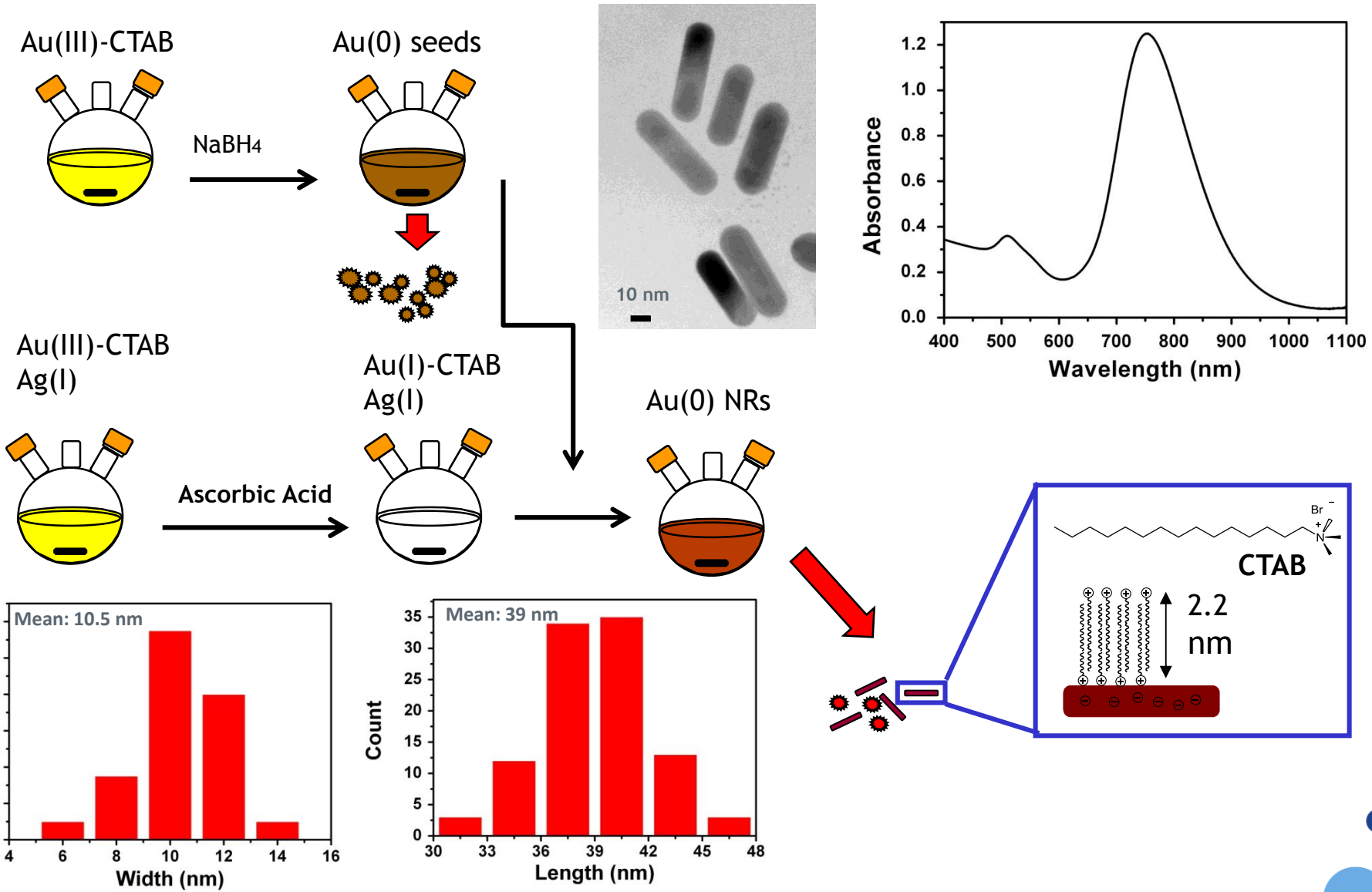


Au NR arrays

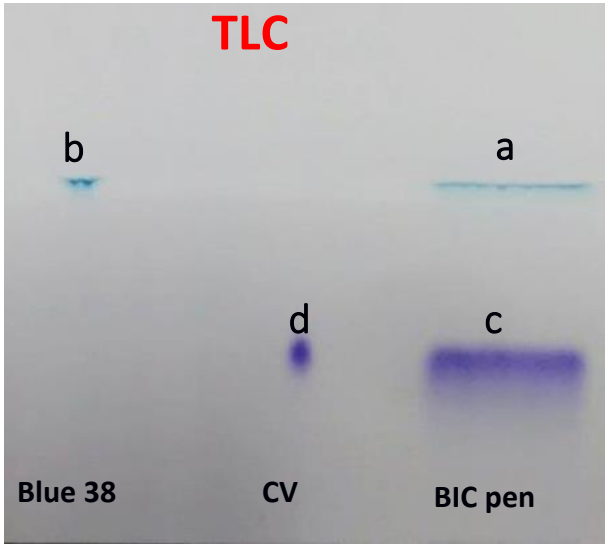


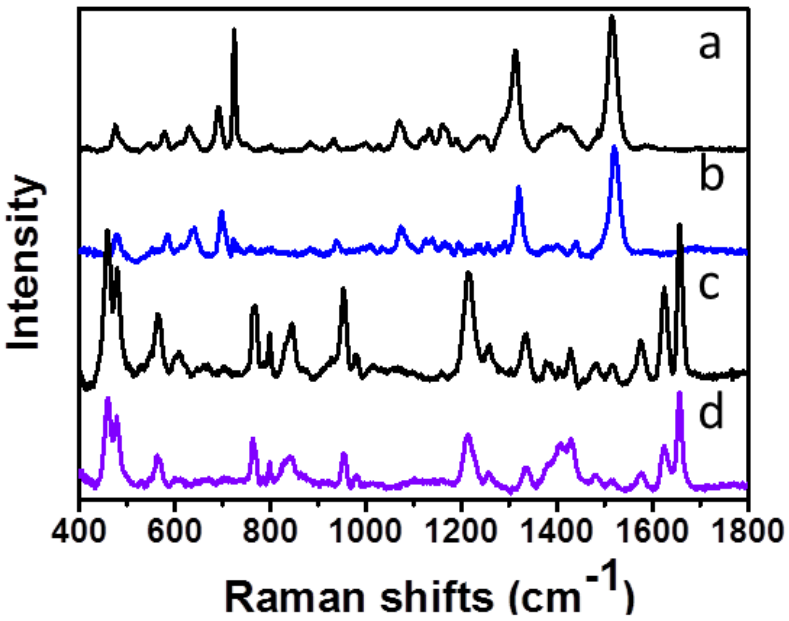
Polymer-Ag substrates

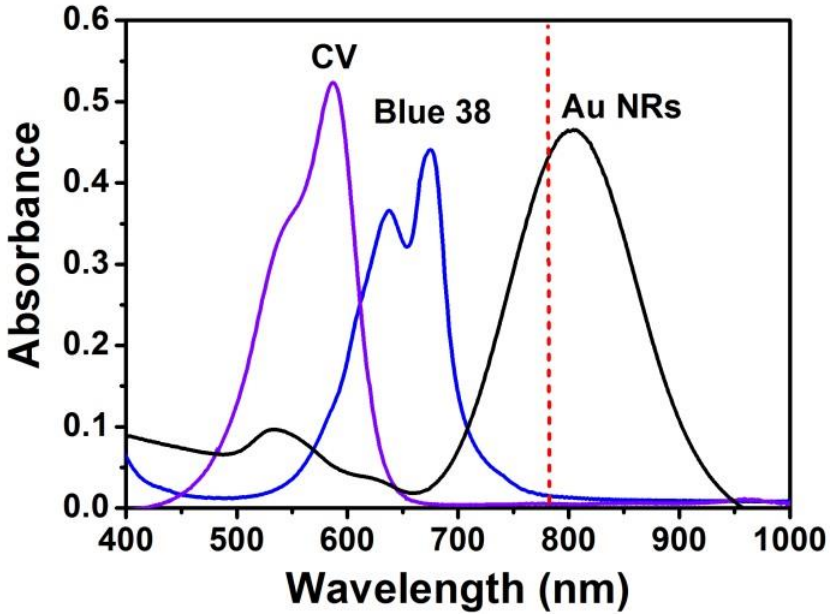
Au NR Seed-Mediated Synthesis



Au NR TLC/Raman Analysis of BIC pen

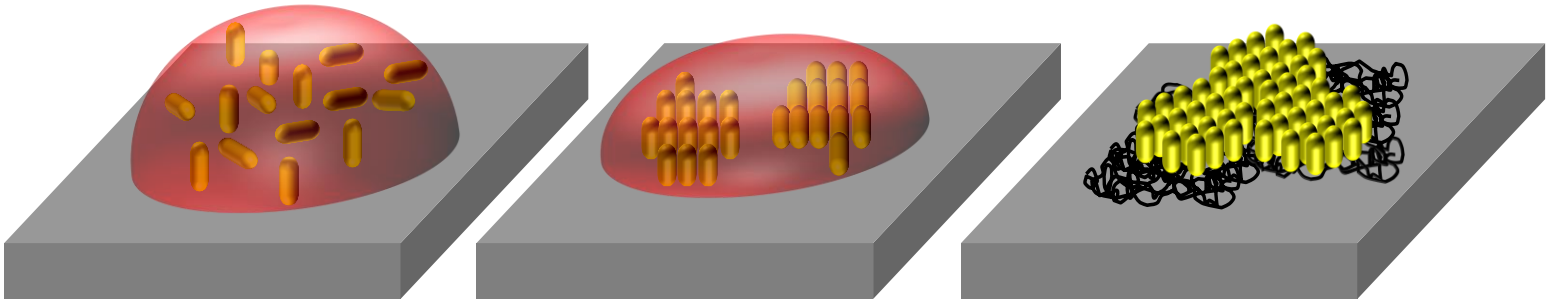




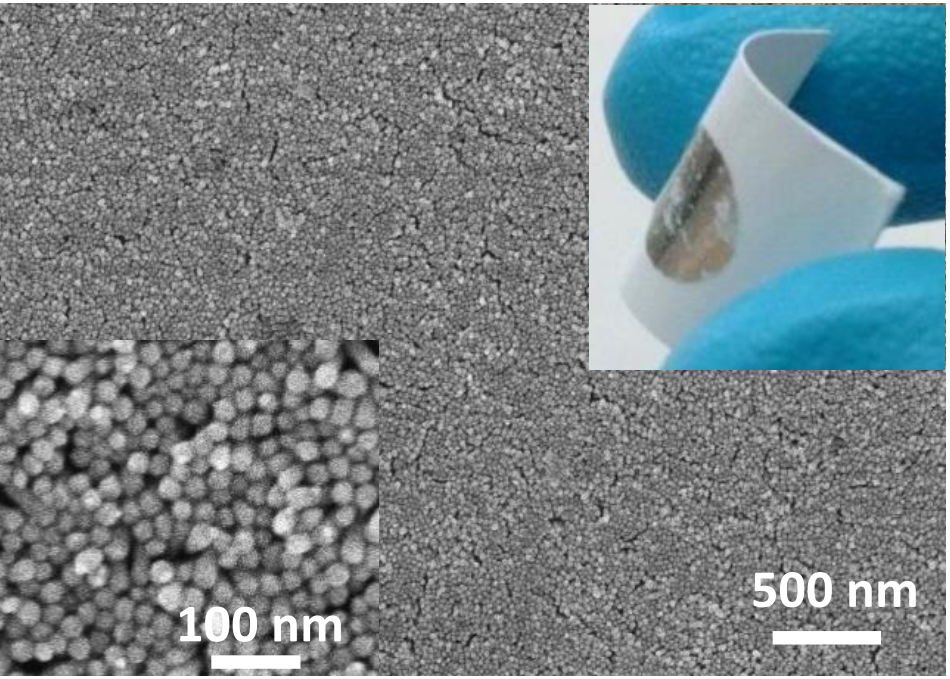


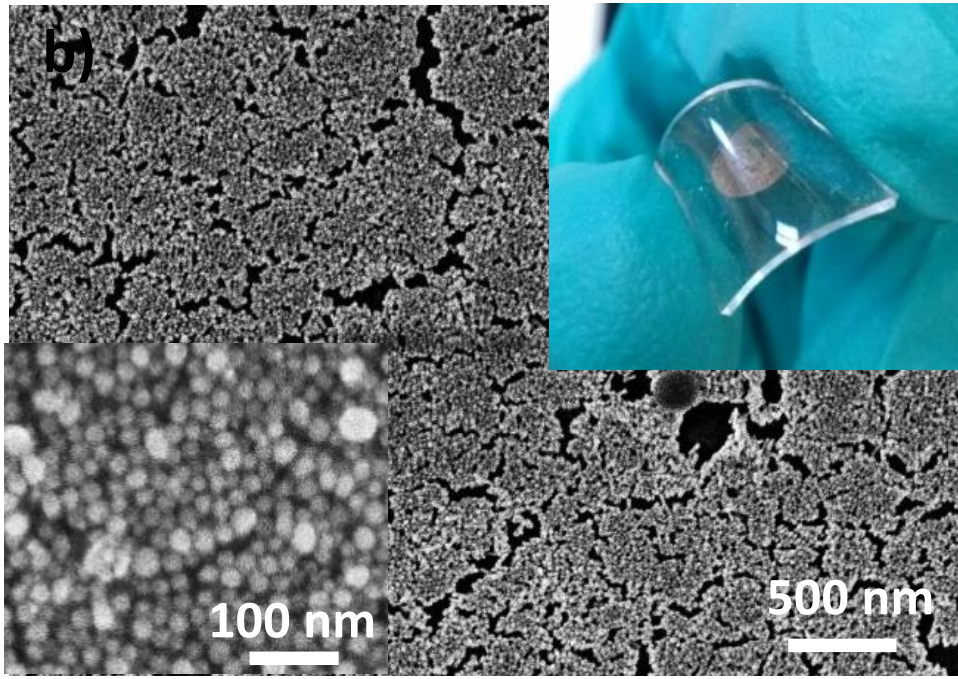
- Attribution of TLC bands made possible by Raman enhancement provided by Au NRs
- Enhancement due to the overlap of Au NR plasmon band to the excitation wavelength

Synthesis of NR Arrays



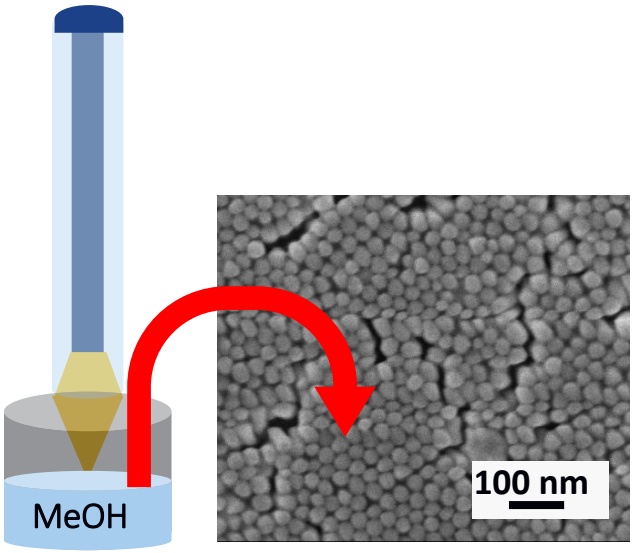
Evaporation of Au NR organic solutions followed by stamping on substrates

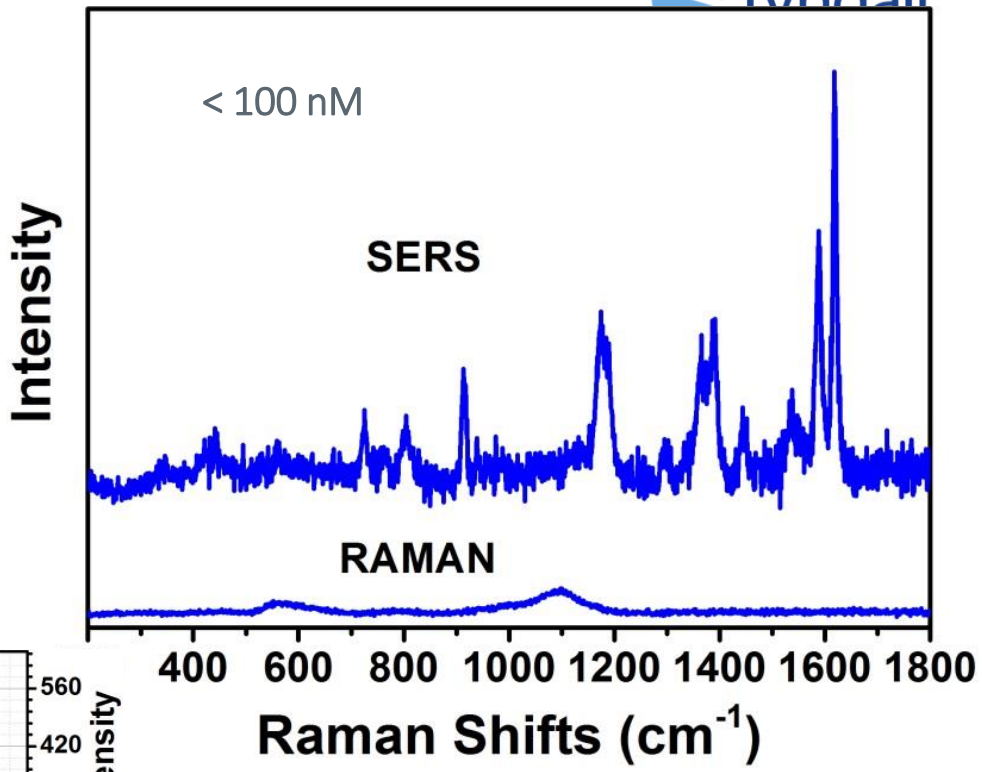


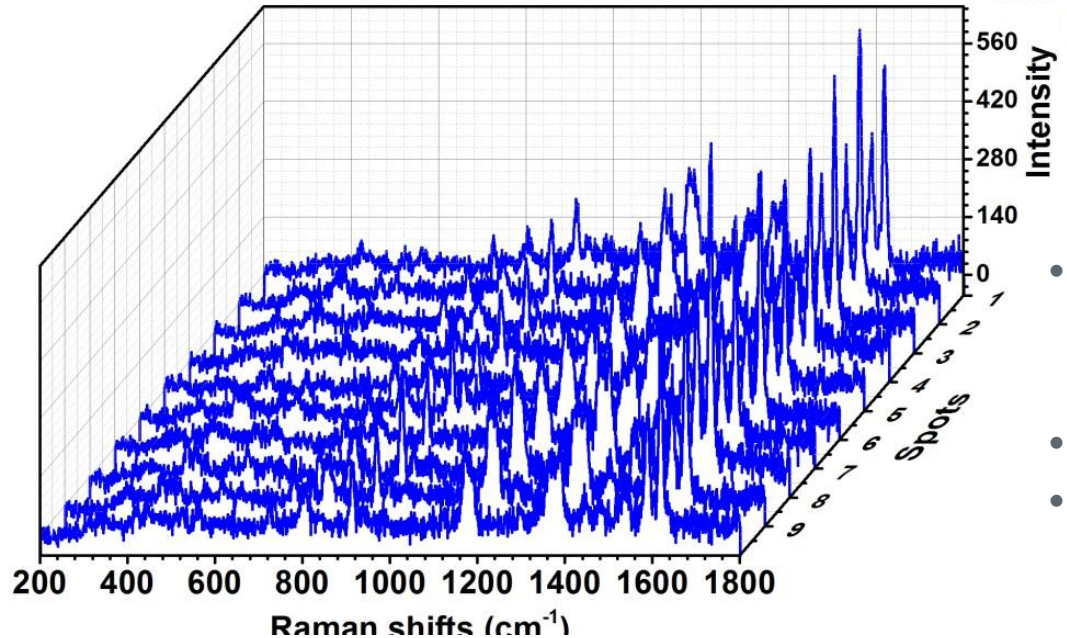


- Uniform arrays from self-assembly of Au NR solutions
- Low-cost SERS substrates

SERS Trace Analysis BIC pen

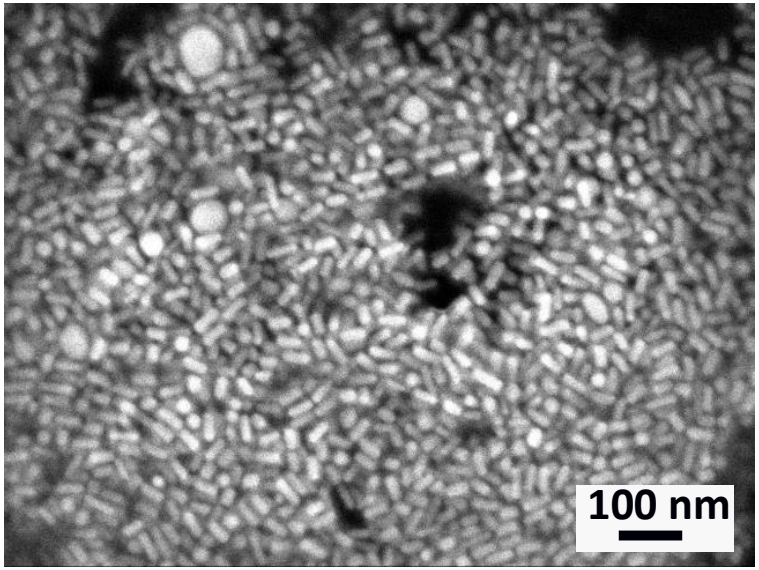




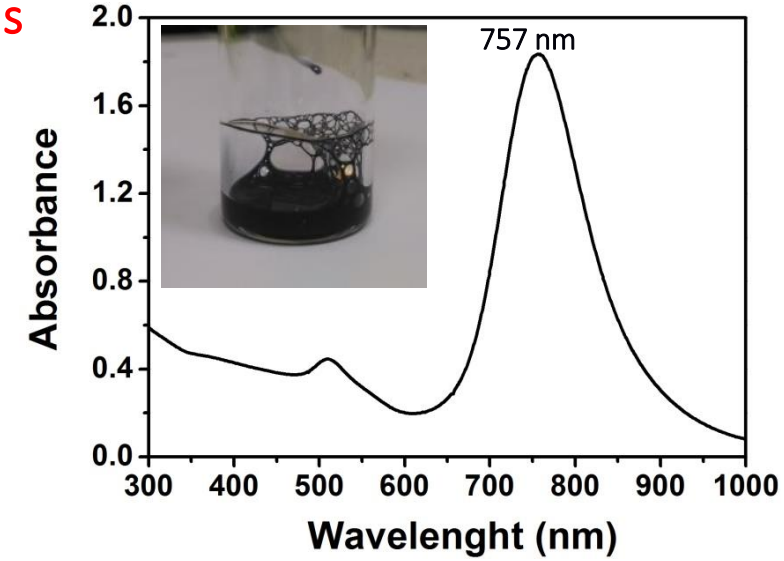


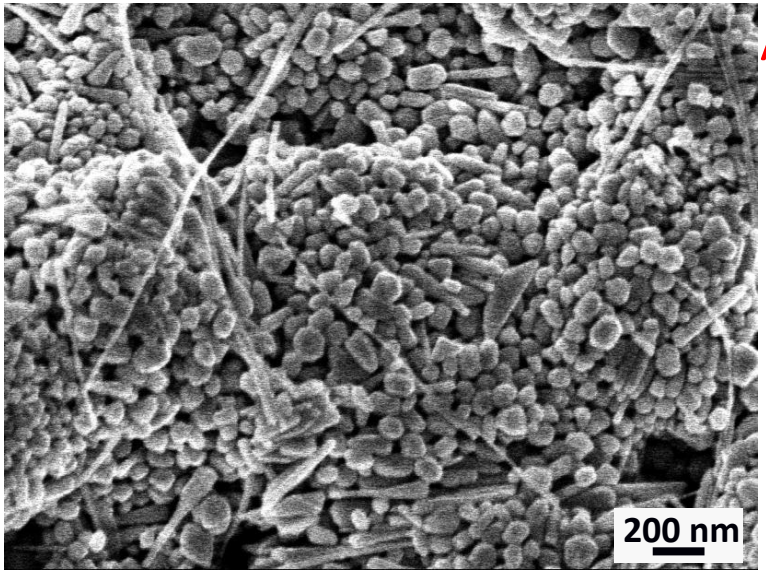
- Trace analysis enabled by the strong enhancement due to strong coupling between adjacent NRs
- Standard deviation 8%
- Potential for quantitative analysis

Metal Nanoinks

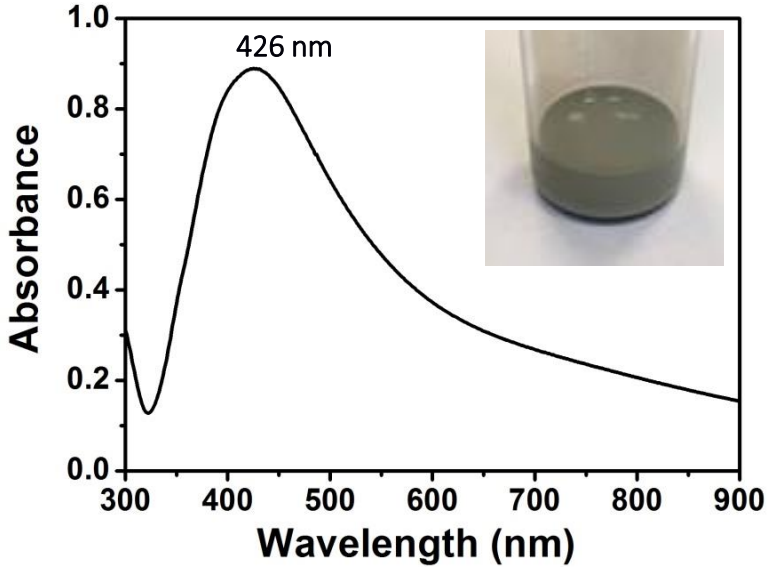


Au NIs

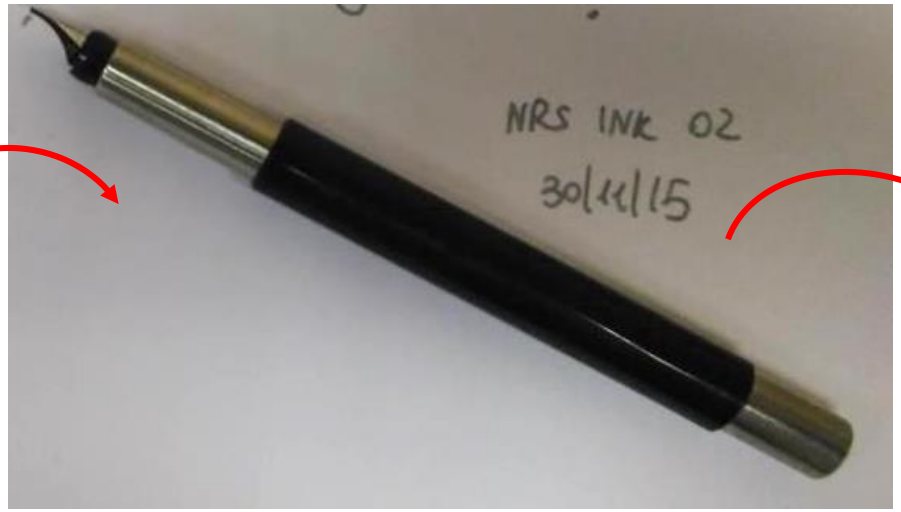


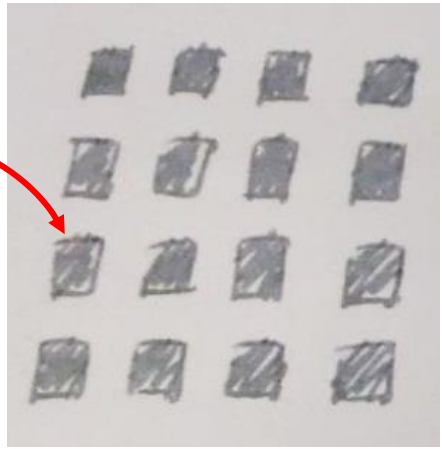


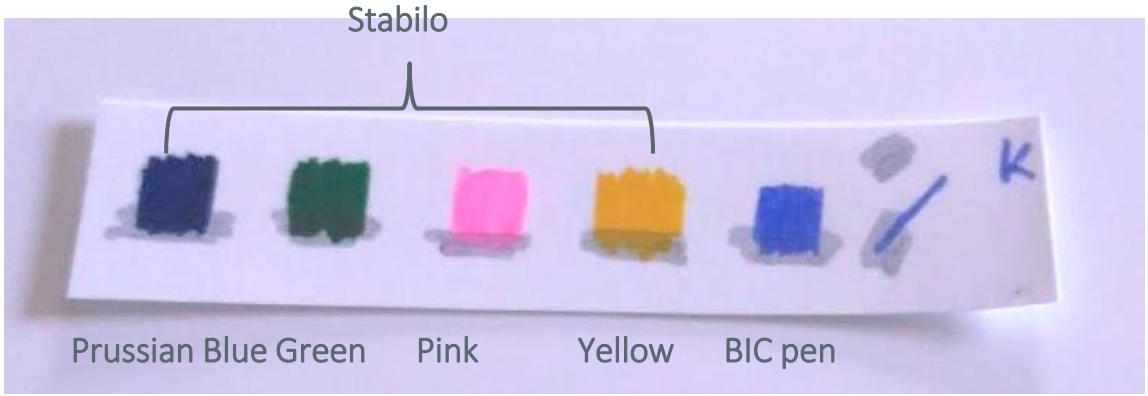
Ag NIs



Plasmonic Calligraphy

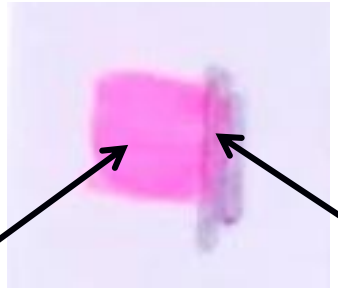




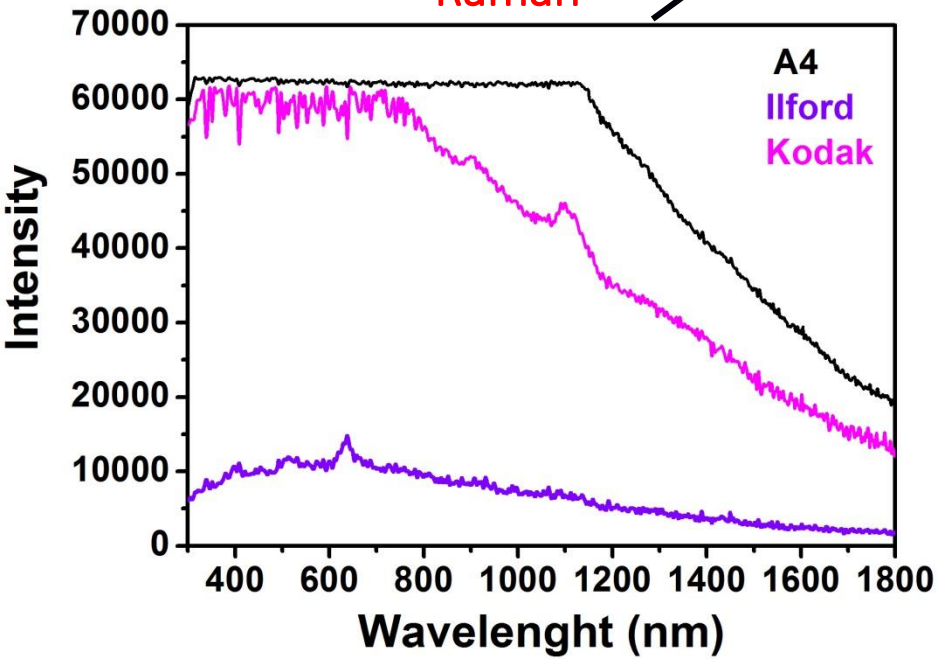


In situ, portable instrumentation

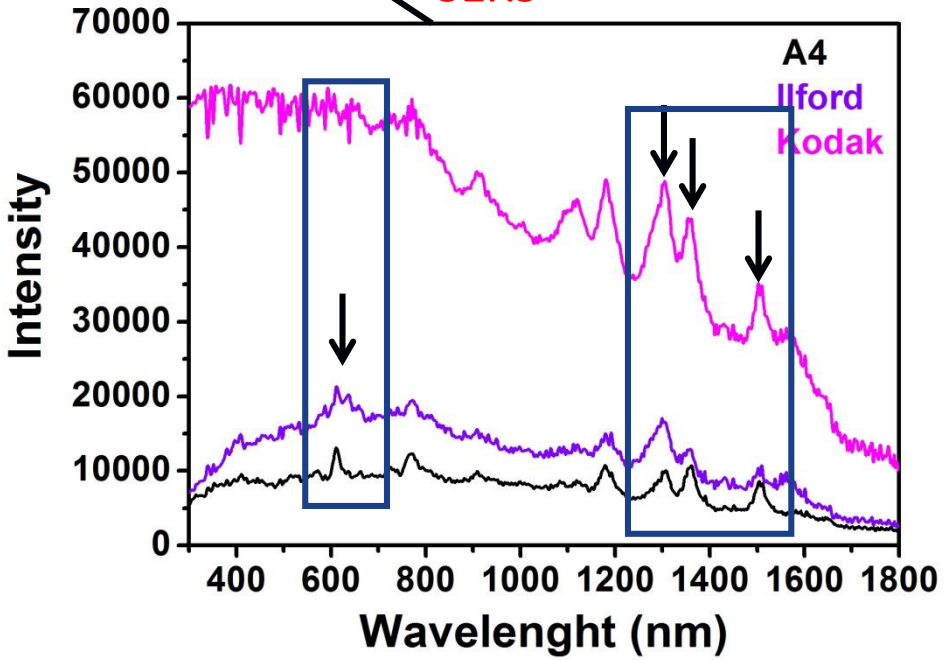
In-situ Analysis of Pink Stabilo with Au Nanoink



Raman



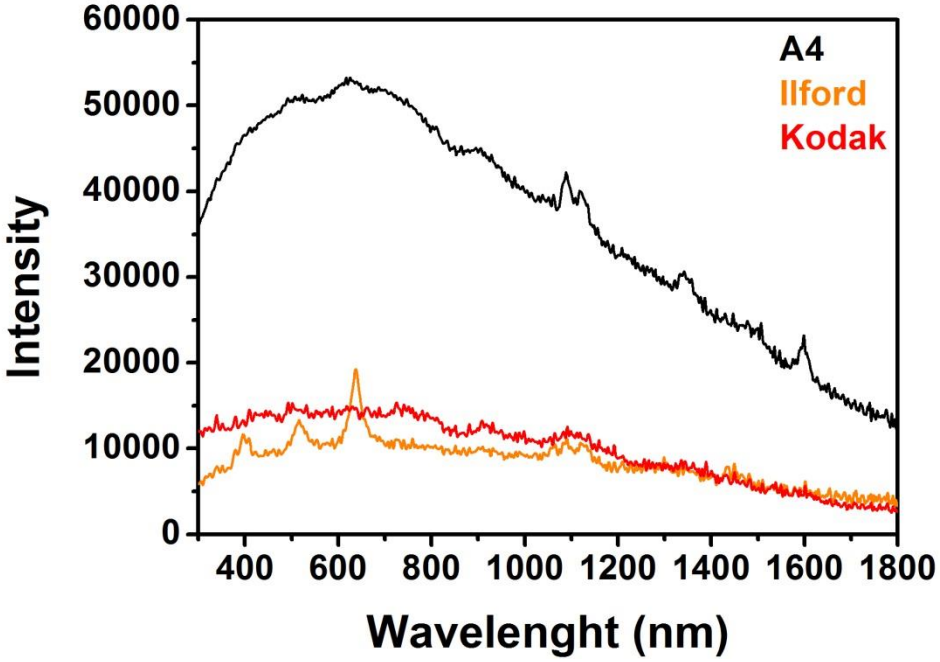
SERS



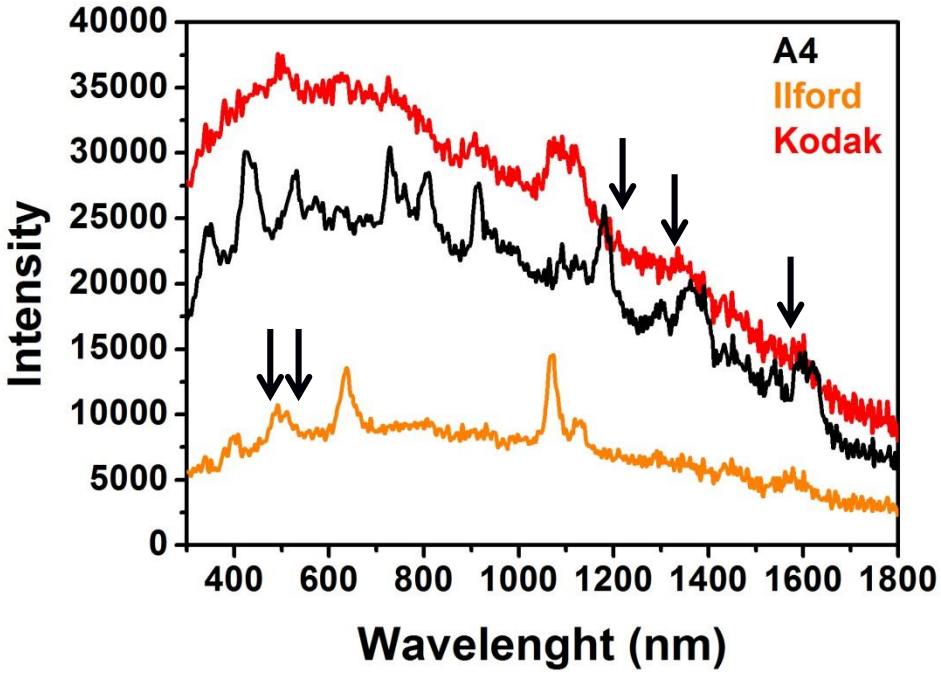
- R6G identified with use of portable instrumentation

In-situ Analysis of Yellow Stabilo with Au Nanoink

Raman

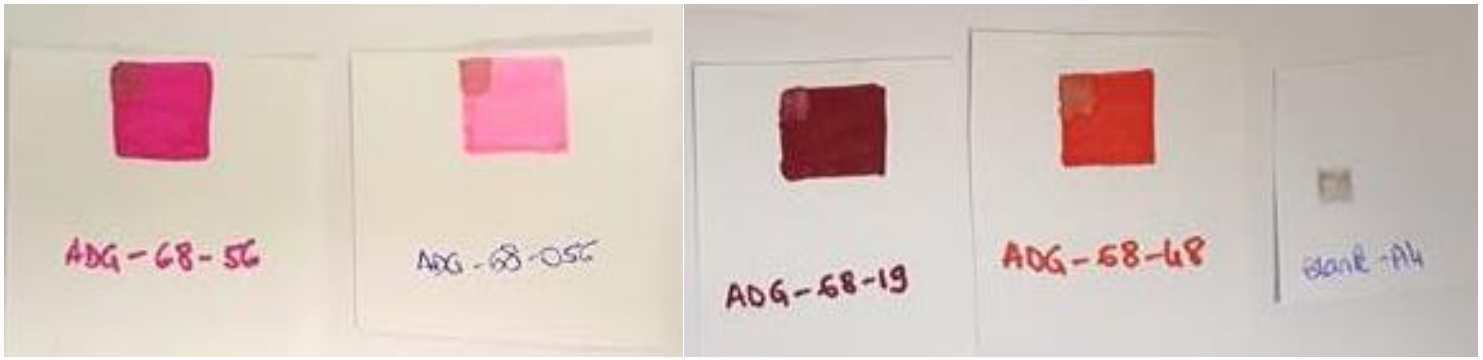


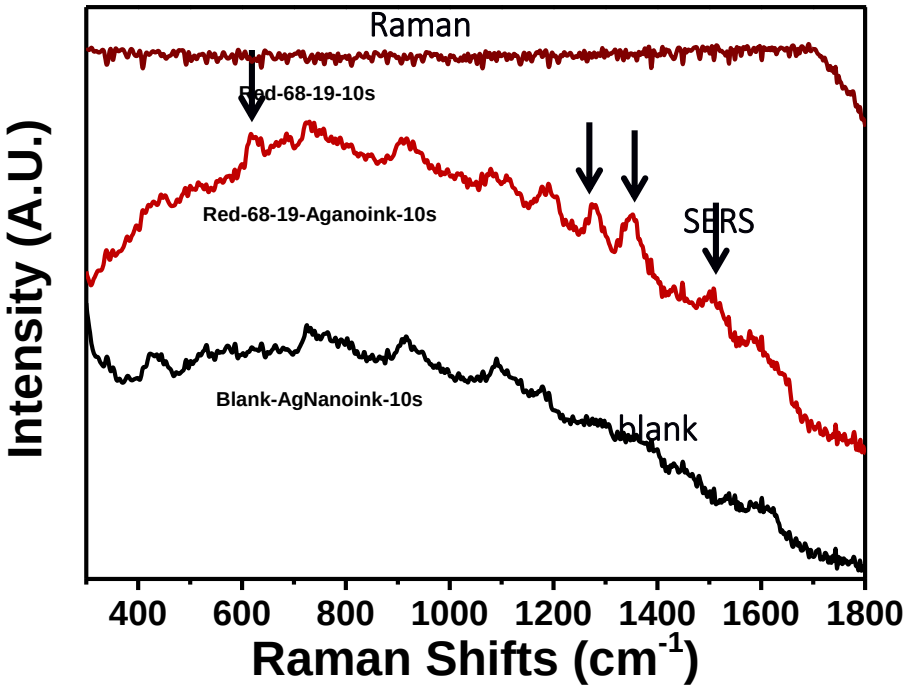
SERS



- Handheld Raman 785 nm excitation
- Tartrazine identified with use of portable instrumentation

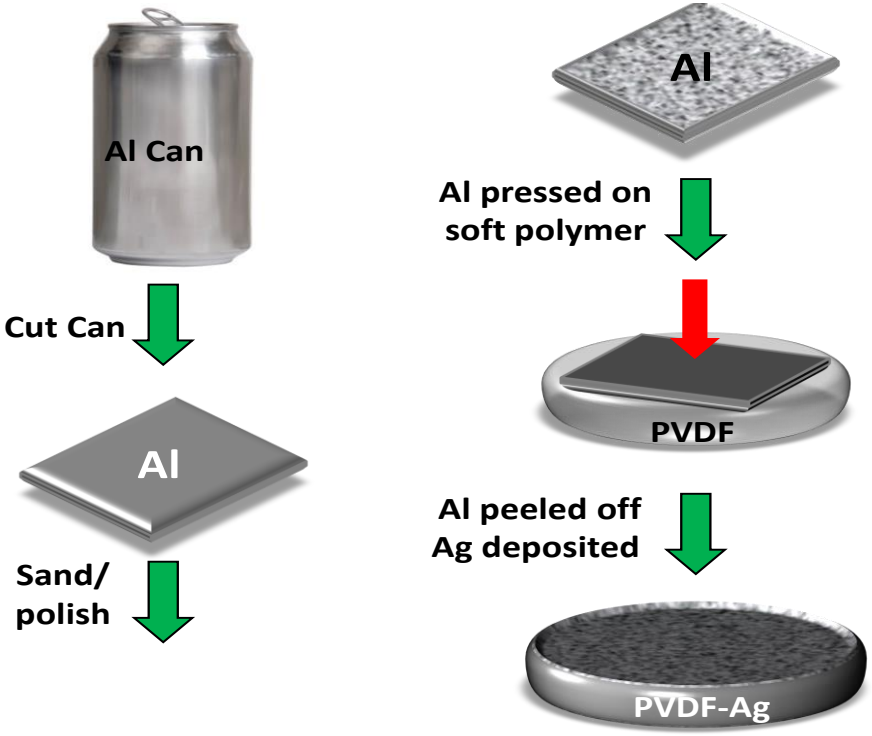
In-situ Analysis of Red Stabilo with Ag Nanoink

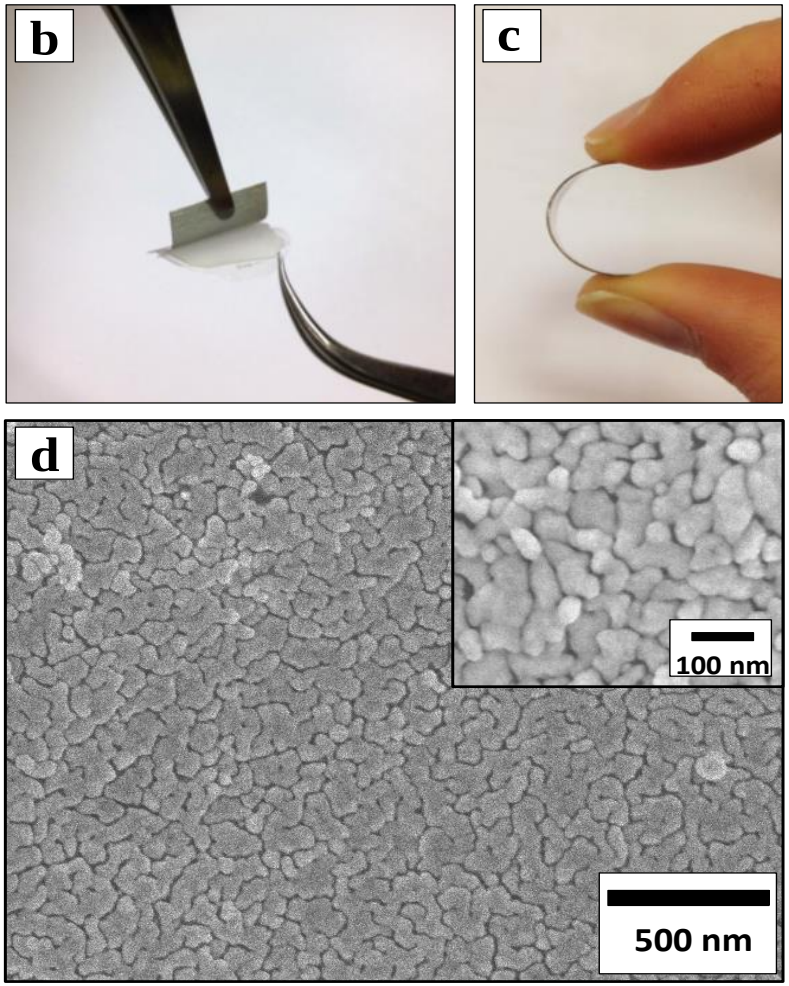




- R6G identified with use of portable instrumentation
- All red and pink colors showed presence of R6G

SERS Substrates from Coke Cans



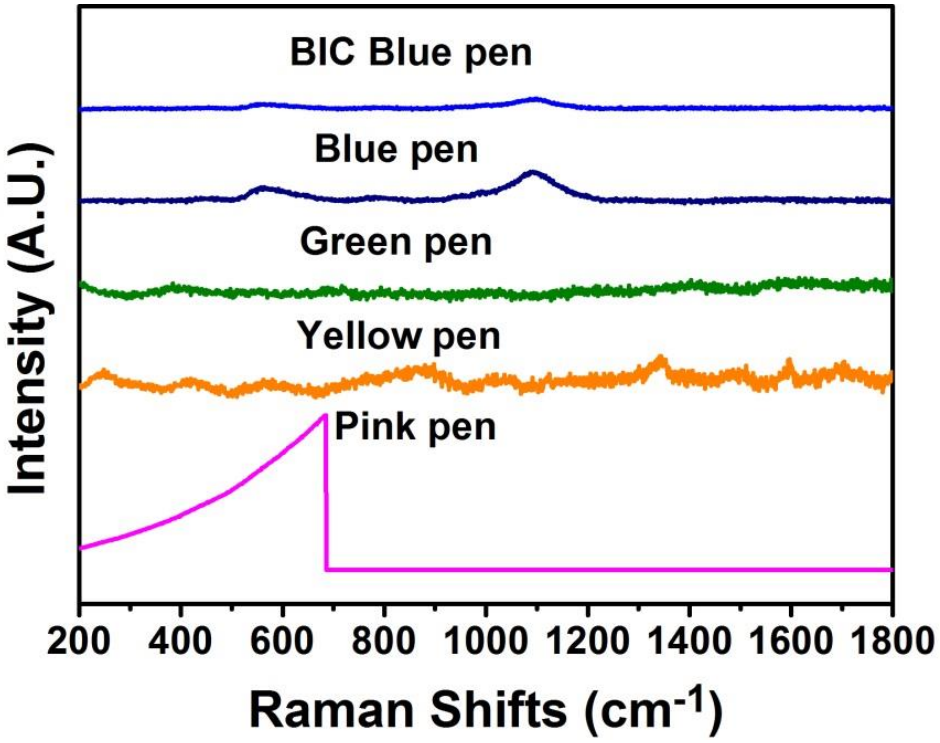


Pen MeOH solution dropped and dried on PVDF-Ag substrates

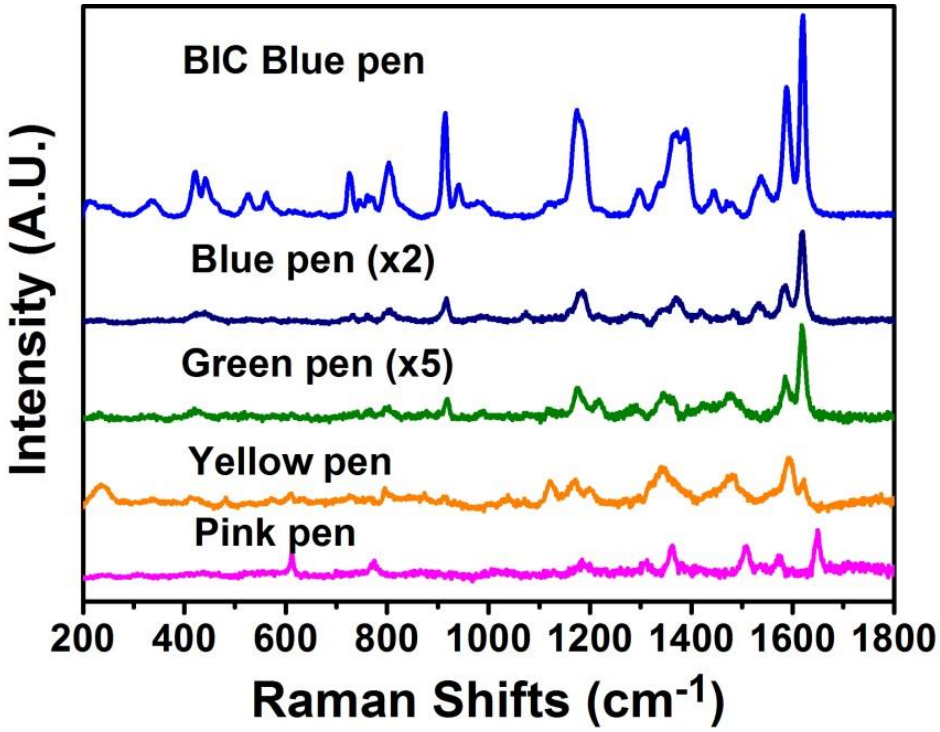
- Drop and dry analysis
- SERS signals highly enhanced
- 514 nm excitation wavelength

PVDF-Ag SERS

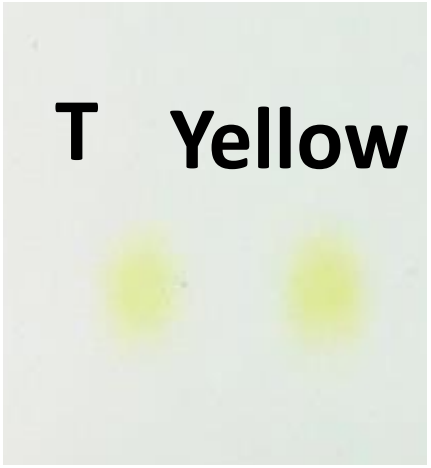
Normal Raman

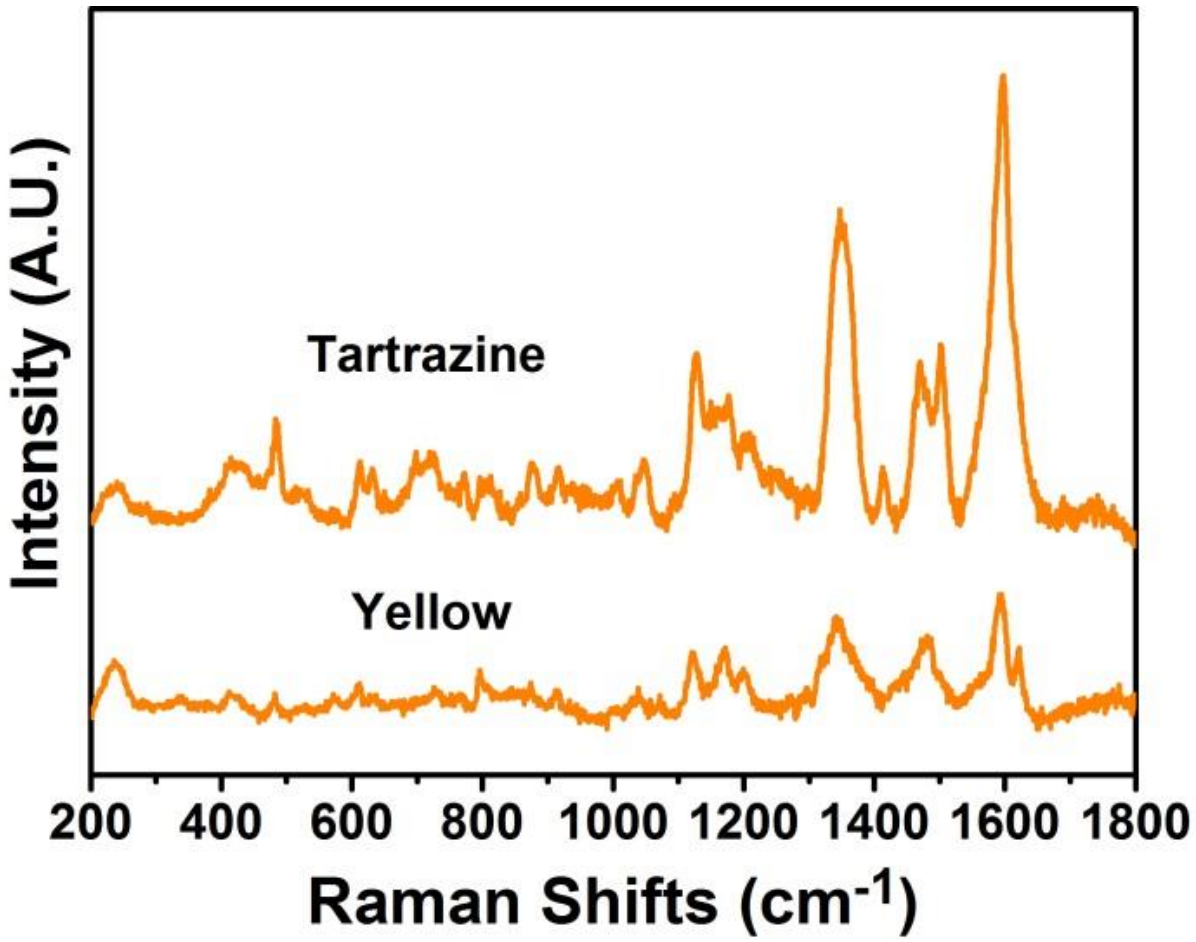


SERS

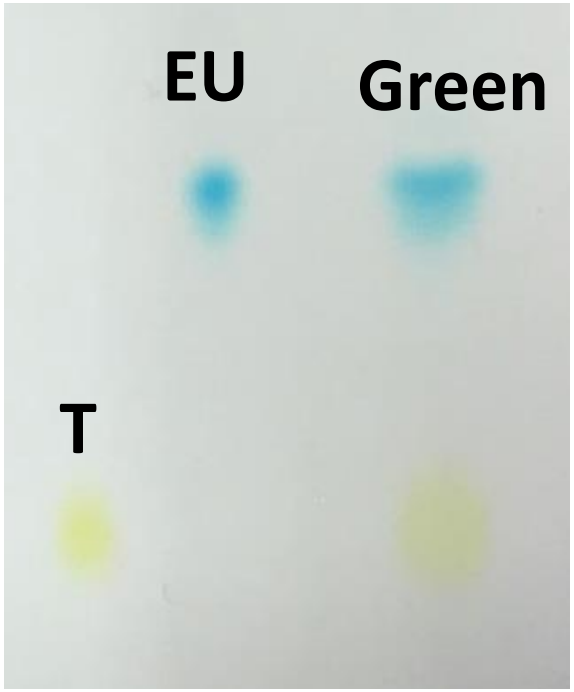


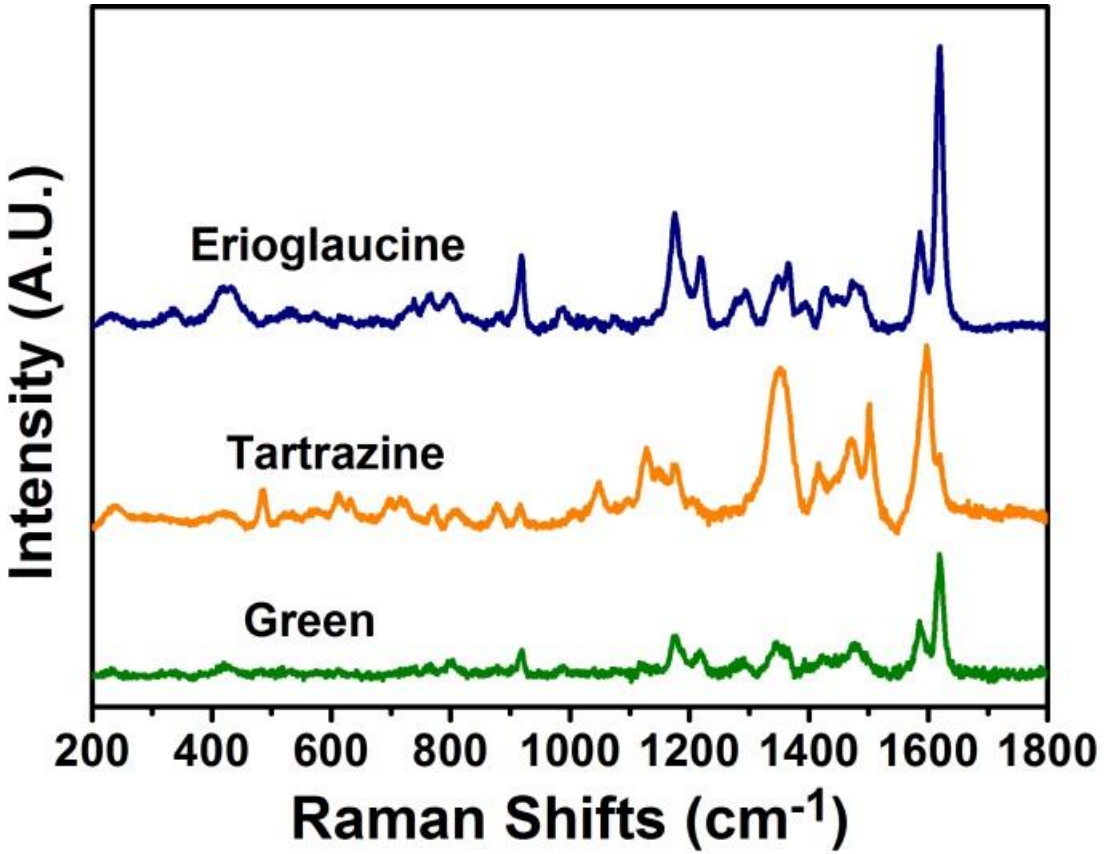
PVDF-Ag Ink Yellow identification



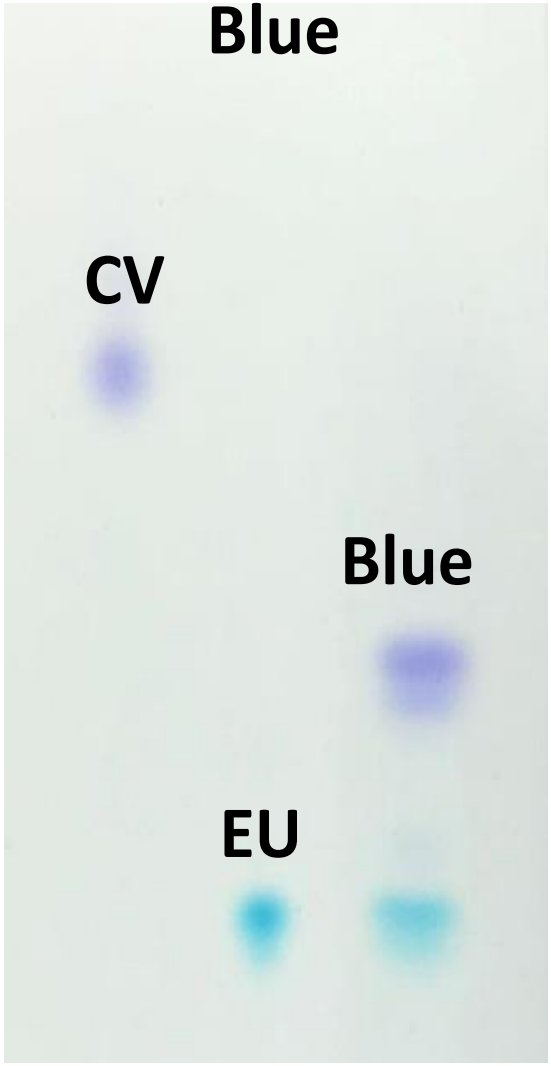


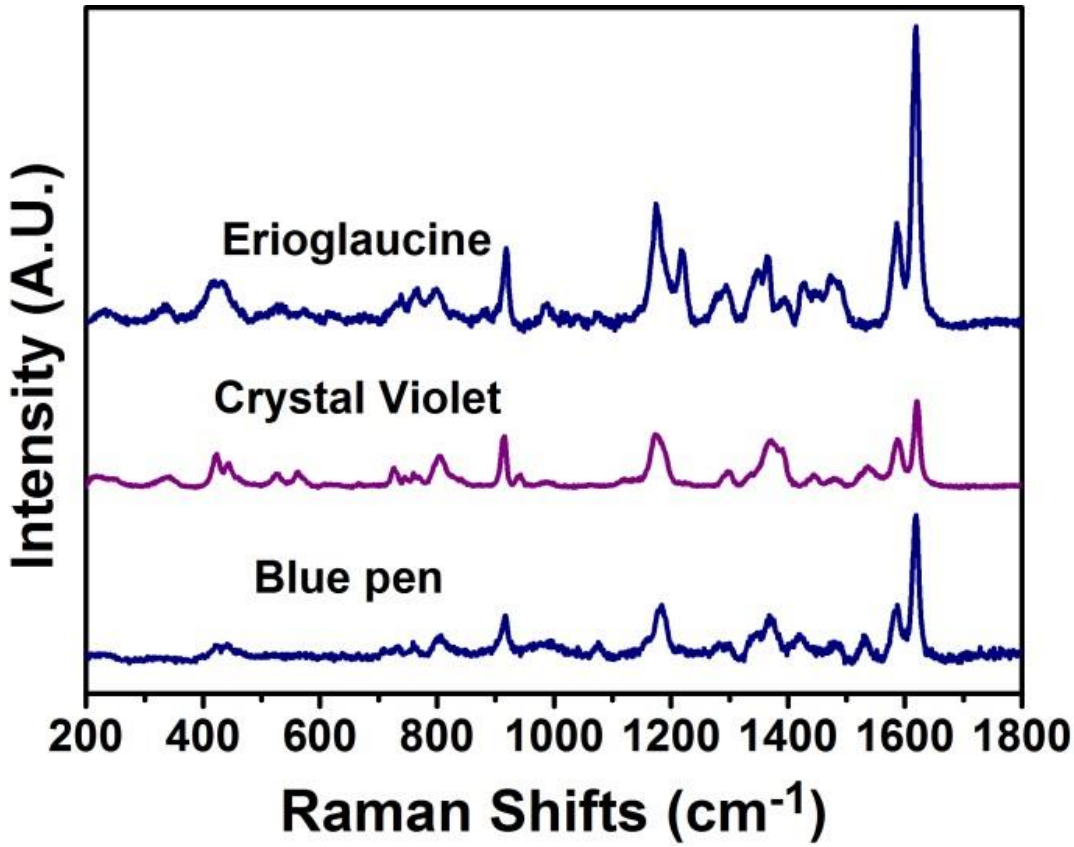
PVDF-Ag Ink Green identification



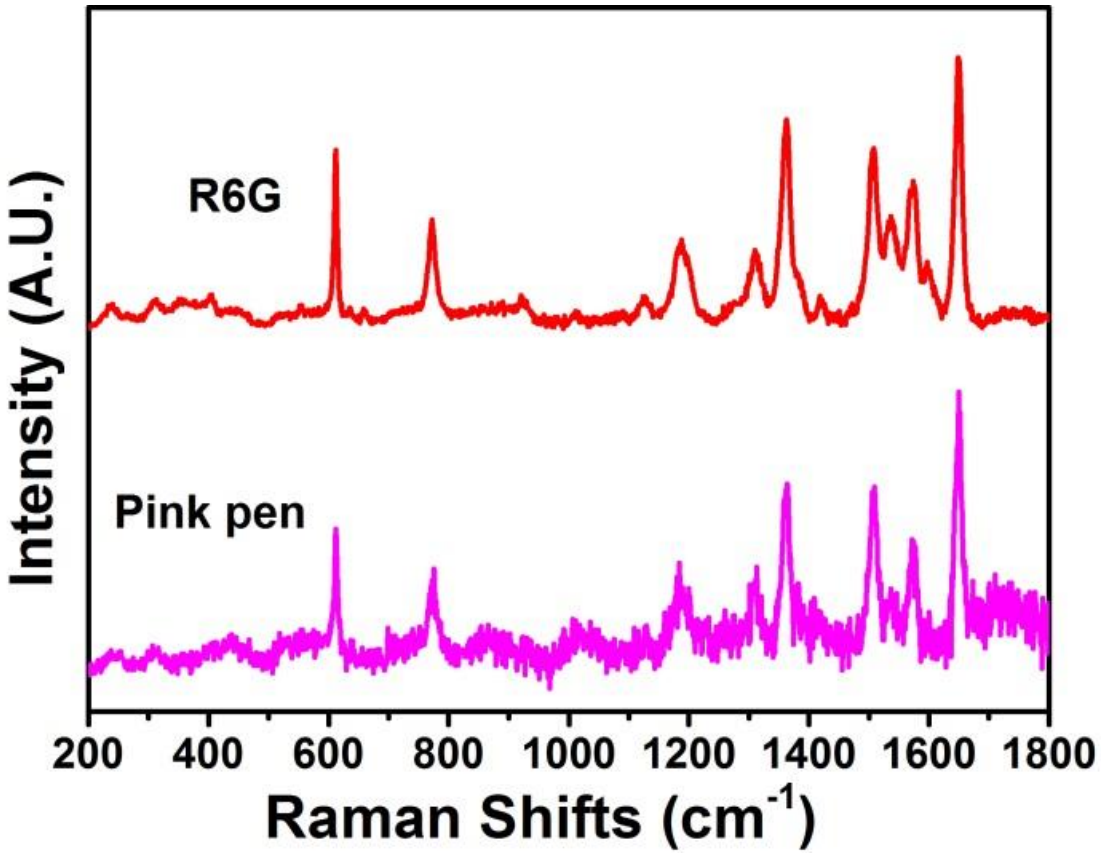


PVDF-Ag Ink Prussian Blue Identification





PVDF-Ag Ink Pink Identification



Conclusions

- Not one universal SERS substrate can be used
- Fabrication of chemically stable SERS probes for in situ and ex situ analysis
- Identification of BIC pen ink mixture with Au NRs SERS/TLC method
- Detection of BIC pen traces signals (< 0.1 μM) with Au NR arrays
- Felt-tip pens analyses in situ with metal nanoinks
- Ex situ analysis of felt tip pens with PVDF-Ag substrates

Acknowledgements

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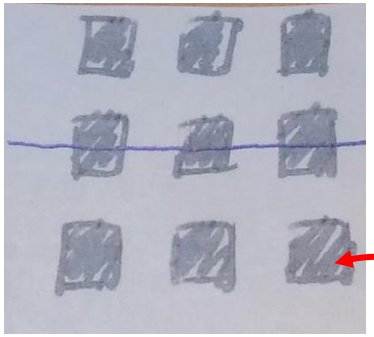
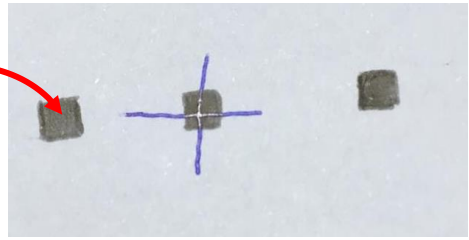
- Centre For Advanced Photonics and Process Analysis, CAPPA
  - Dr. Liam Lewis
  - Dr. Micheal McAuliffe

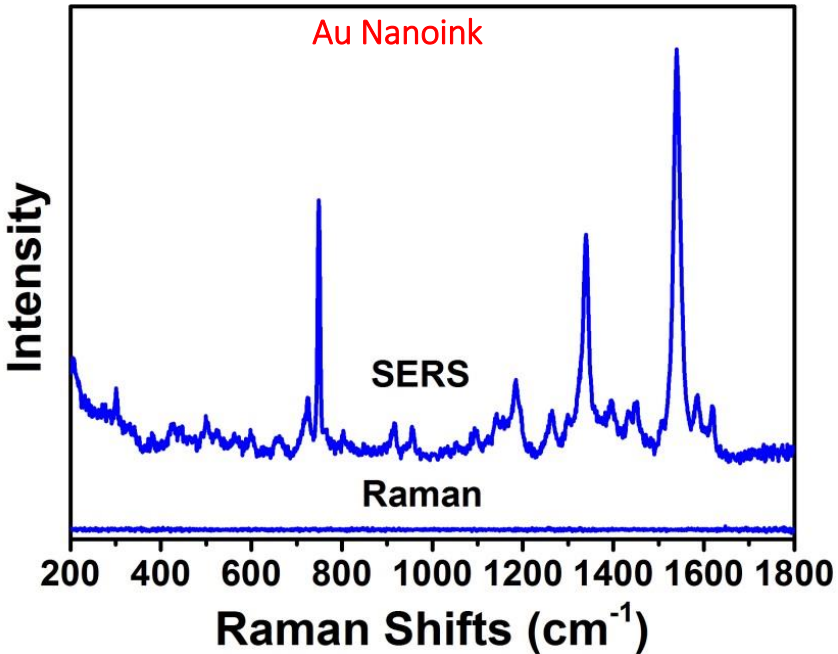
Analysis of BIC Pen Lines with Metal Nanoink

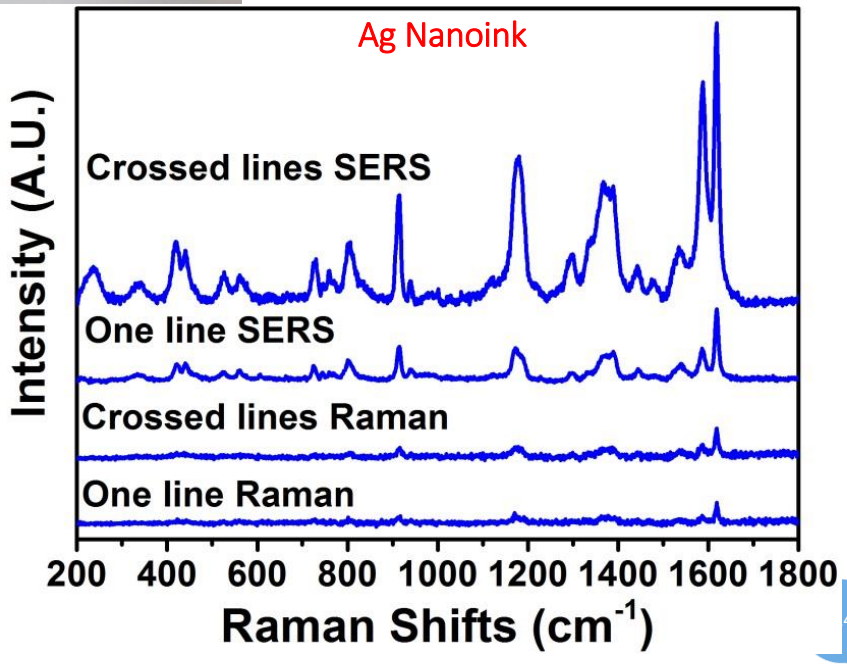


Au Nanoink



Ag Nanoink

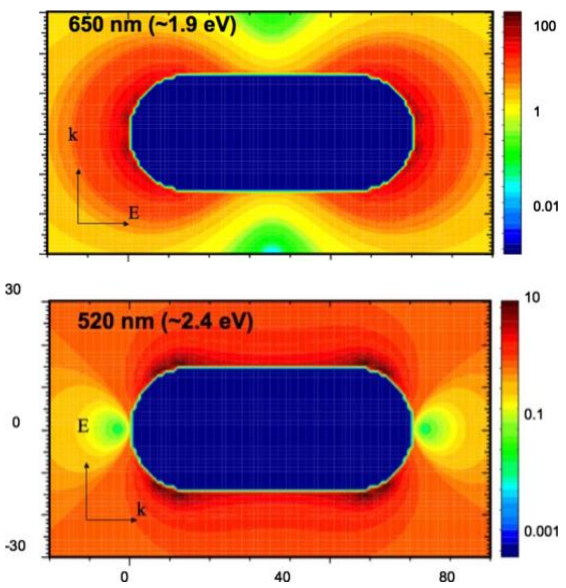




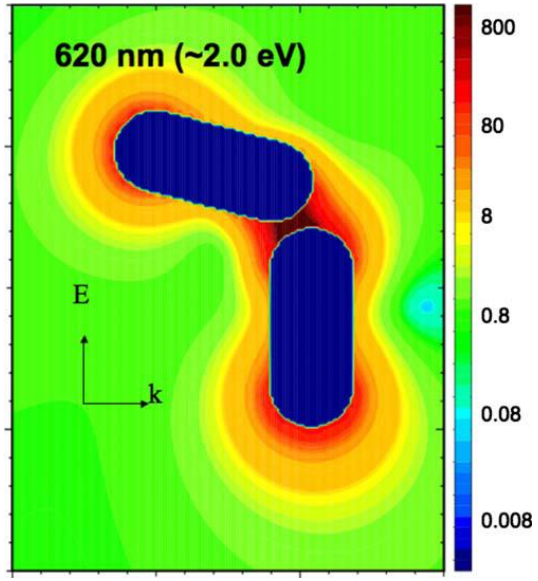
SERS with Nanorods and Nanorod Arrays

- Increased electromagnetic field => enhancement of radiative properties (scattering, absorption)
- Coupling of EM fields in closely spaced nanorod lattices => HOT SPOT FORMATION
- Enhanced optical effects (SERS, fluorescence, antenna…)

Isolated NR



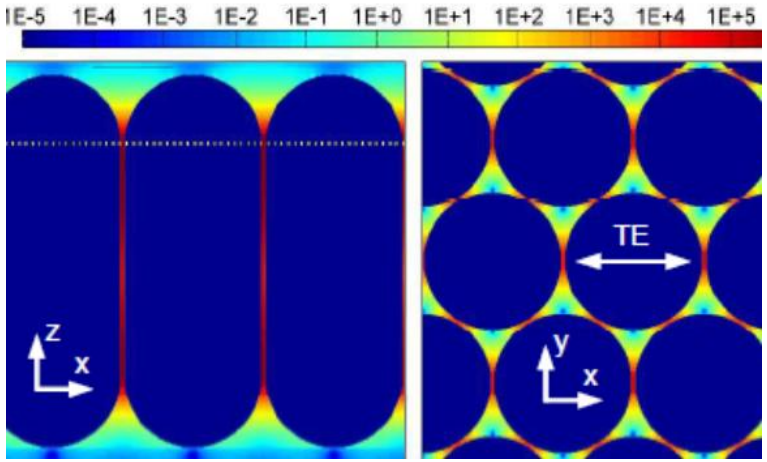
Coupled NR



EM field distribution at given energy

M. N'Gom *et al. Phys.Rev. B* 2009, 80, *113411*

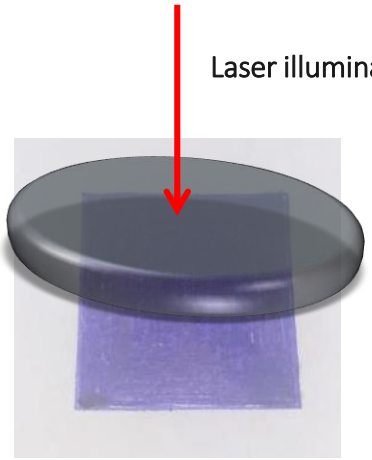
NR arrays



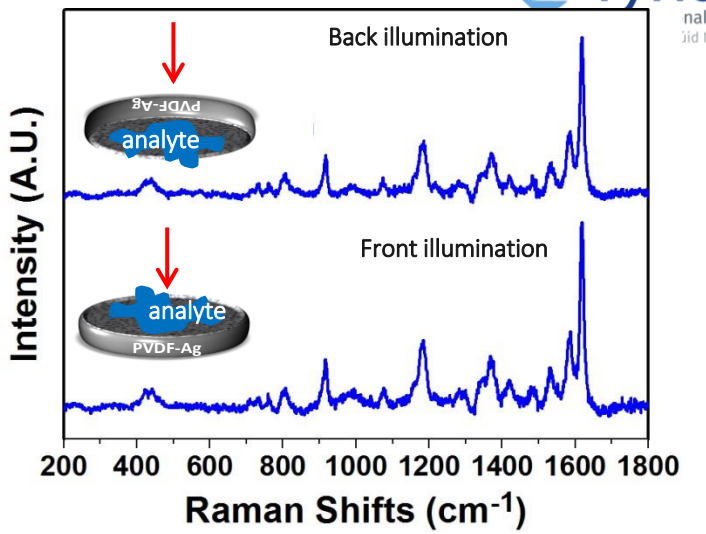
EM field distribution in closely spaced arrays

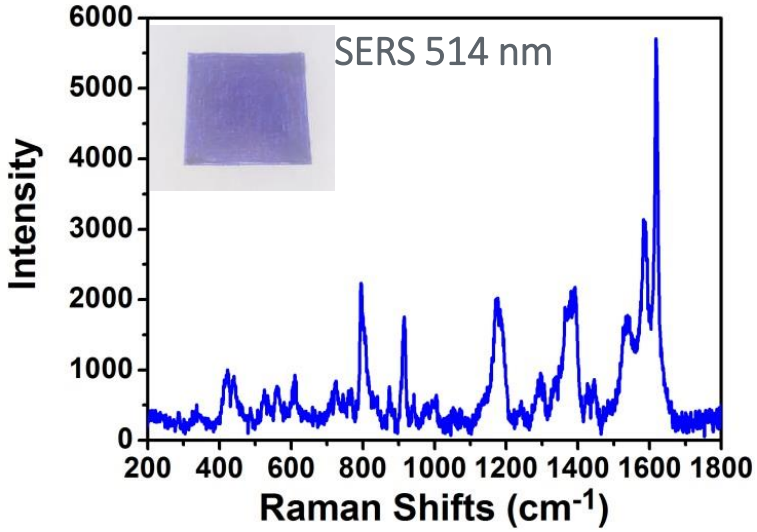
Q. Xiong *et al. ACS Nano*, 2013, 7, 5993-6000

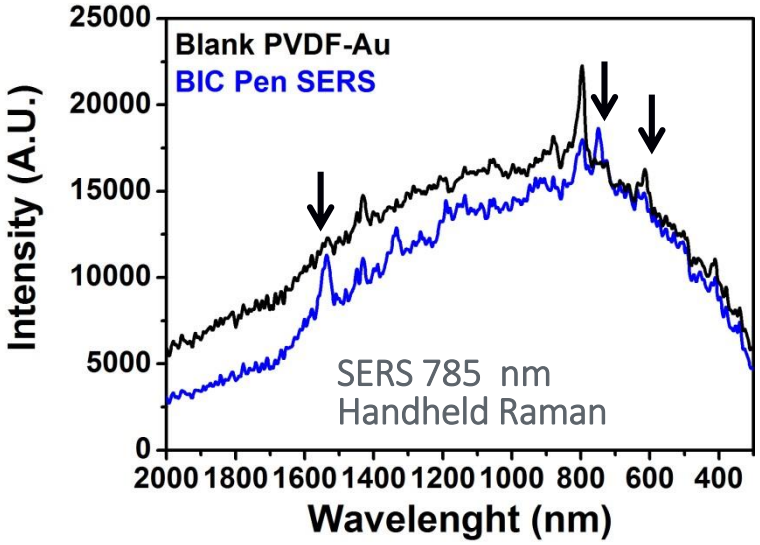
Non-invasive Analysis on Paper



PVDF-Ag substrates on paper.
Back illlumination







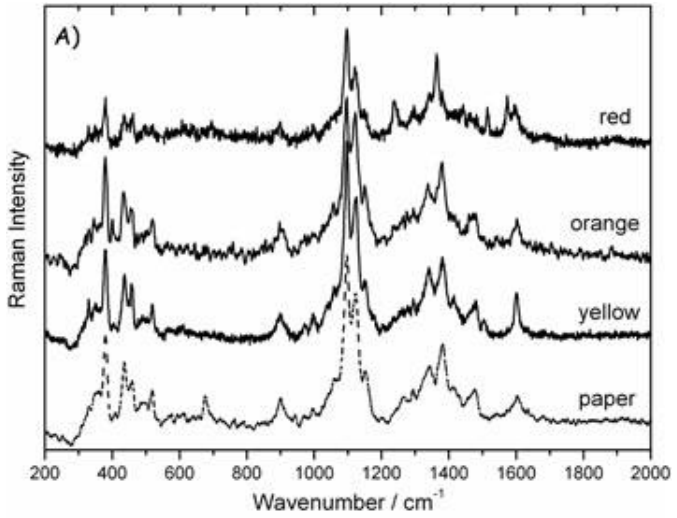
- Possible illumination from the back
- SERS spectra obtained under dry conditions

Raman Investigations of Inks

- Raman spectroscopy provides a fingerprint by which molecules can be identified
- Excitation light interacts with molecular vibrations resulting in the energy of the laser photons being shifted up or down. ONLY inelastic scattered light collected
- Identification of inks in ancient manuscripts

Key characteristics

- Non destructive
- In situ and ex-situ analysis
- Minimum sampling or no sampling required
- No sample preparation or extraction required
- Fingerprint of analytes
- Weak signals
- Background fluorescence interference

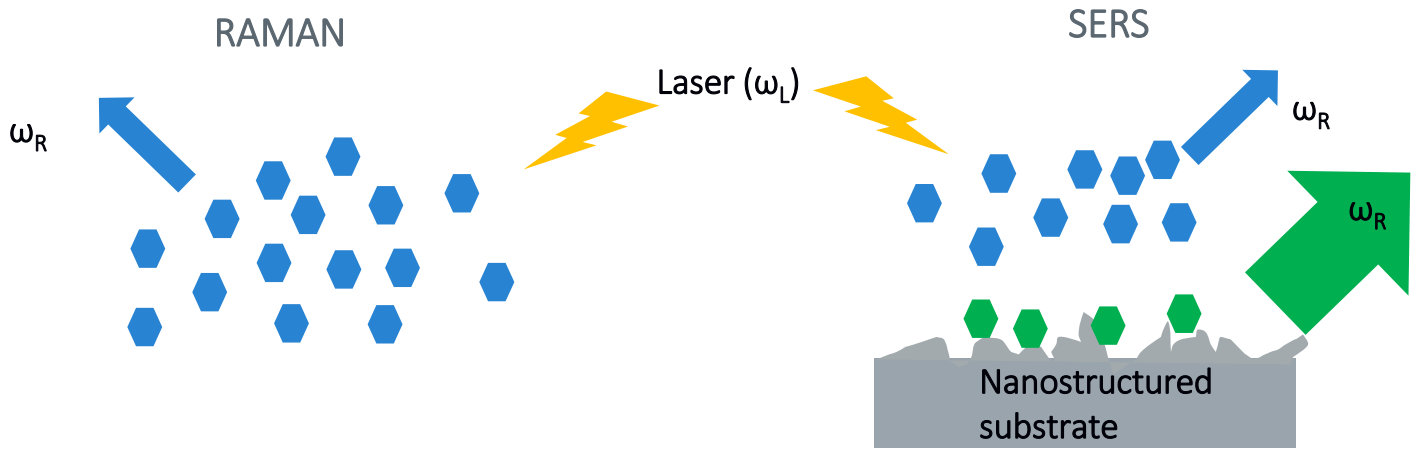


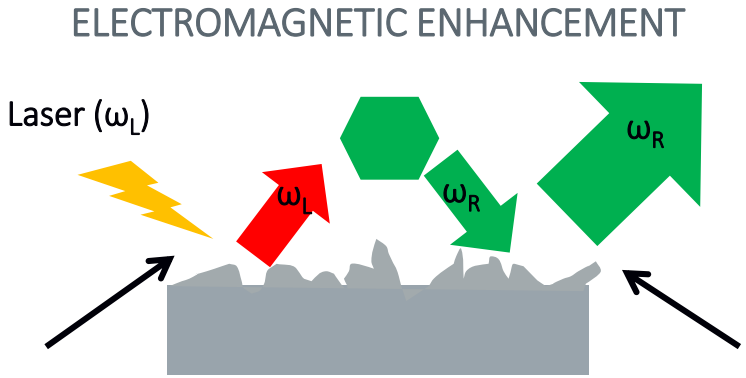
Raman spectra of Fellini's drawing

Sodo, A. *et al., J. Raman Spectrosc.* 2012, *43*, 1781-1787

Surface Enhanced Raman Scattering (SERS)

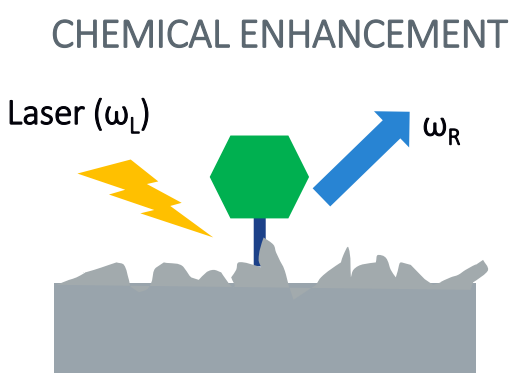
- SERS first observed by M. Fleischman in 1973
- Increase of Raman signals up to 10-11 orders of magnitude of analytes in close proximity to metal rough surfaces
- Electromagnetic and chemical enhancements





Enhancement of the local incident field on the analyte

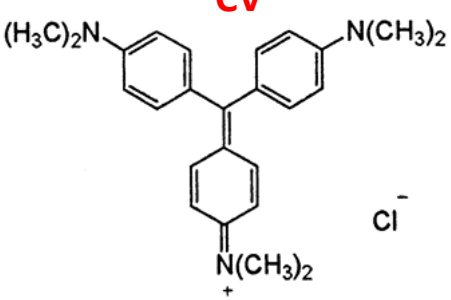
Enhancement of the re-emitted Raman scattering from the analyte



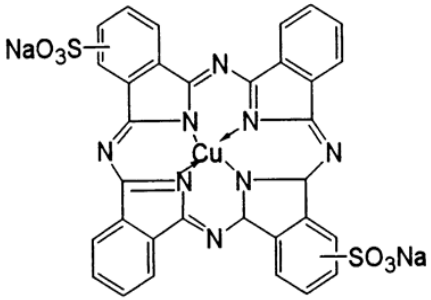
Analyte-substrate charge transfer

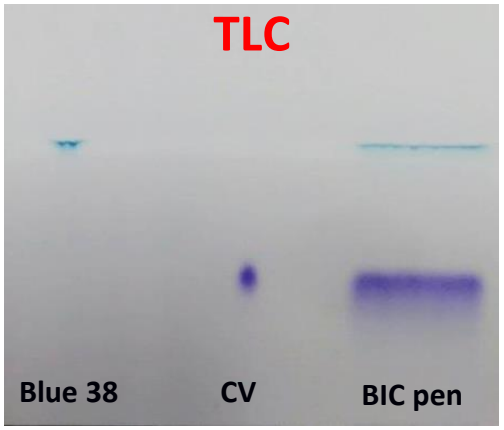
Au NR TLC/Raman Analysis of BIC pen

CV



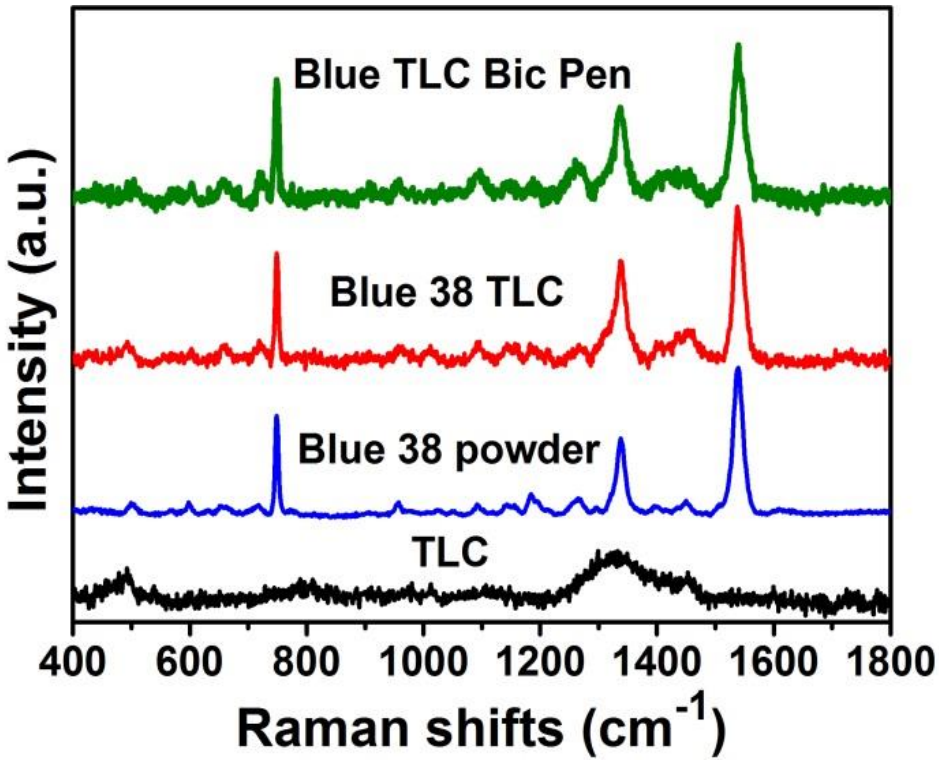
Blue 38

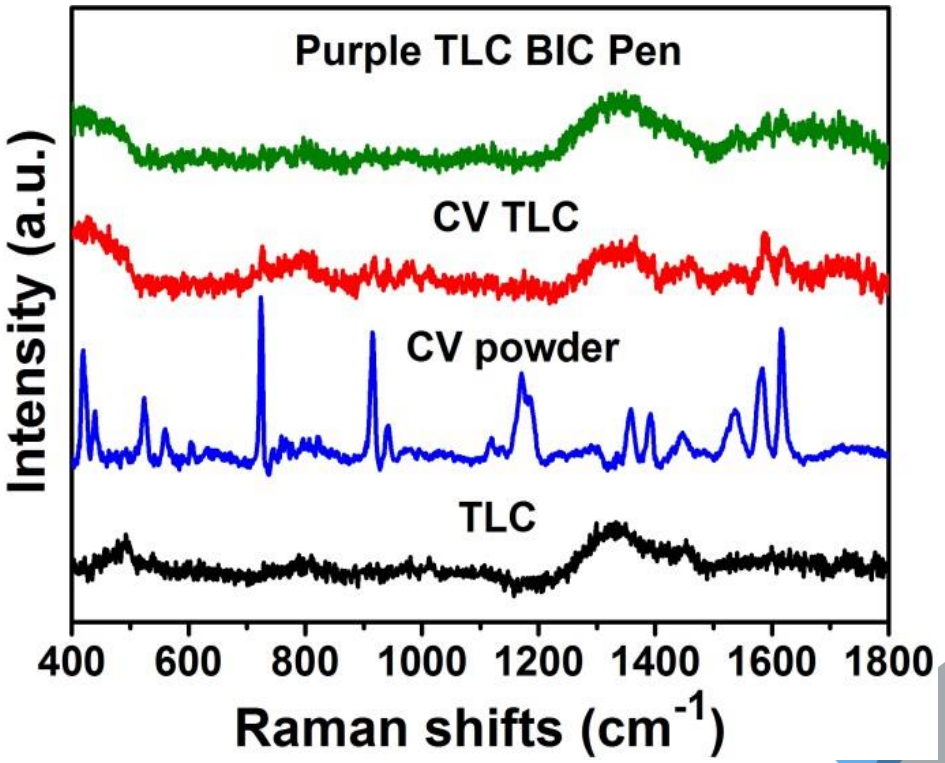




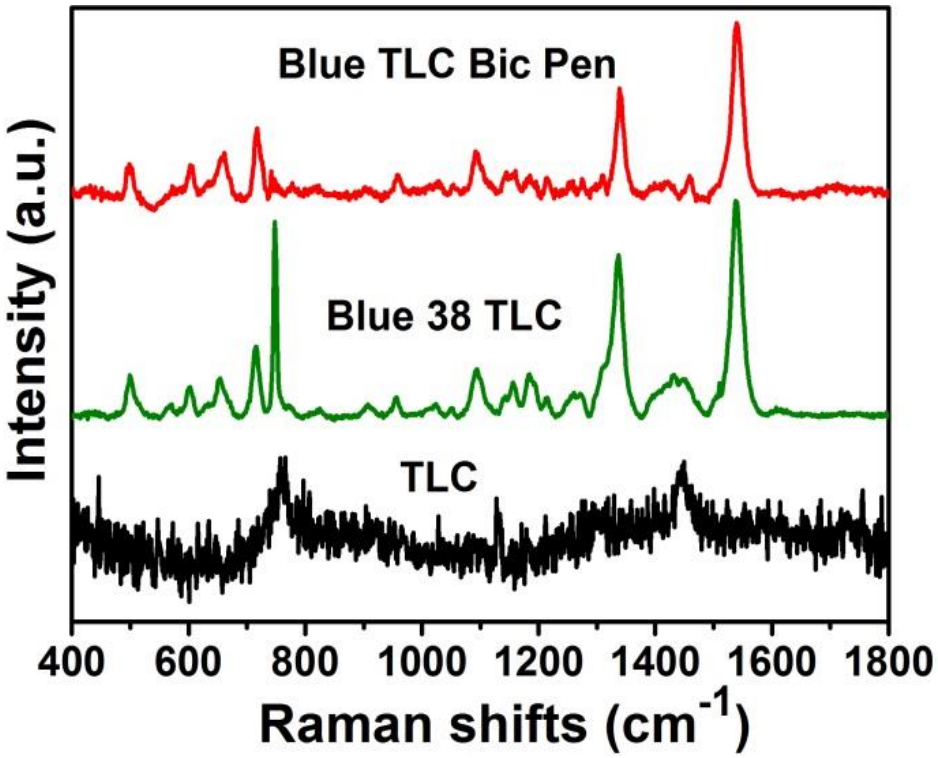
Pen lines on TLC

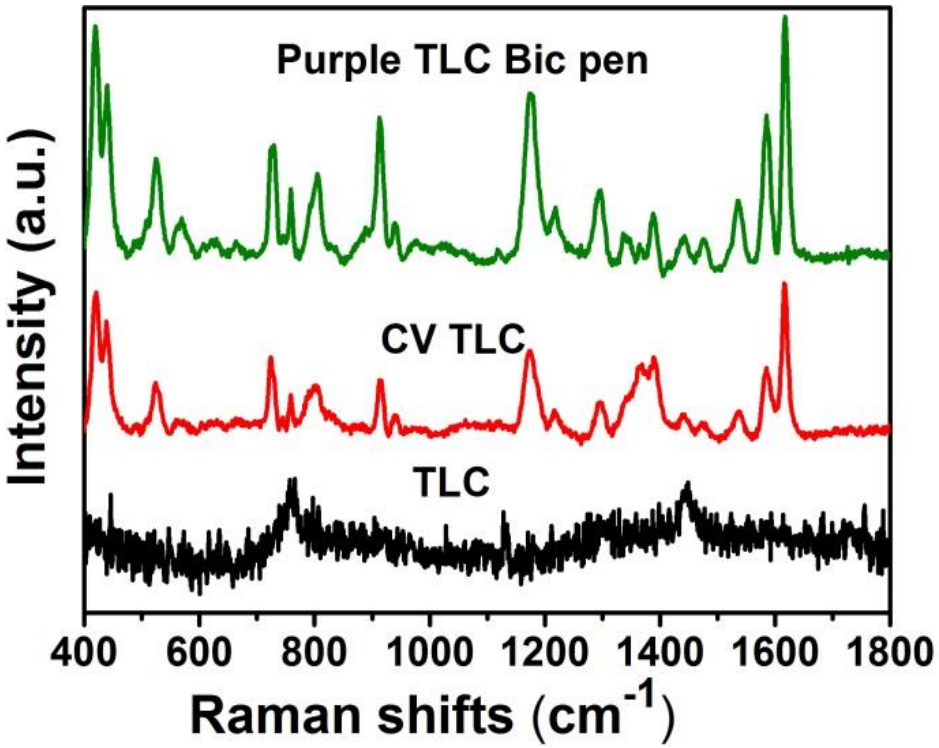
Normal Raman





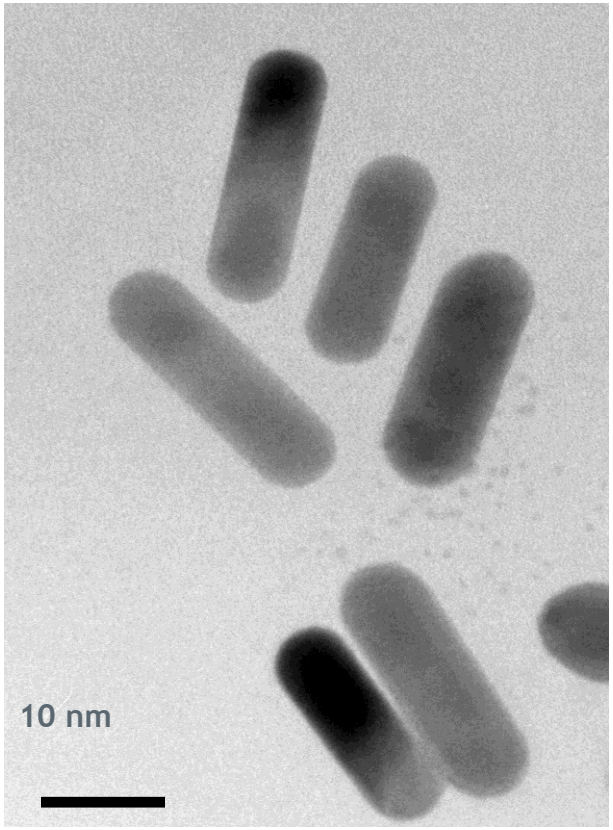
Au NR TLC/SERS Analysis of BIC pen

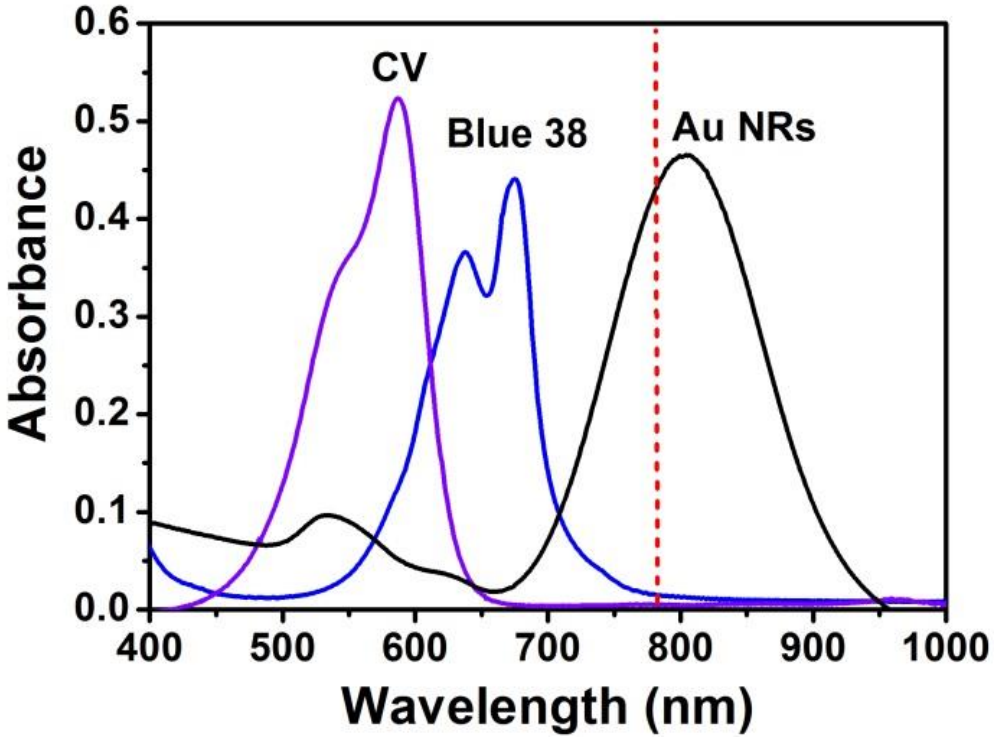




- Possible attribution of spots
- Purple spot => CV, blue spot => phtalocyanine

SERS Enhancement





- Overlap between nanorod plasmon resonance and laser excitation wavelenght