Functional nanoparticle superlattices: New materials for diagnostics

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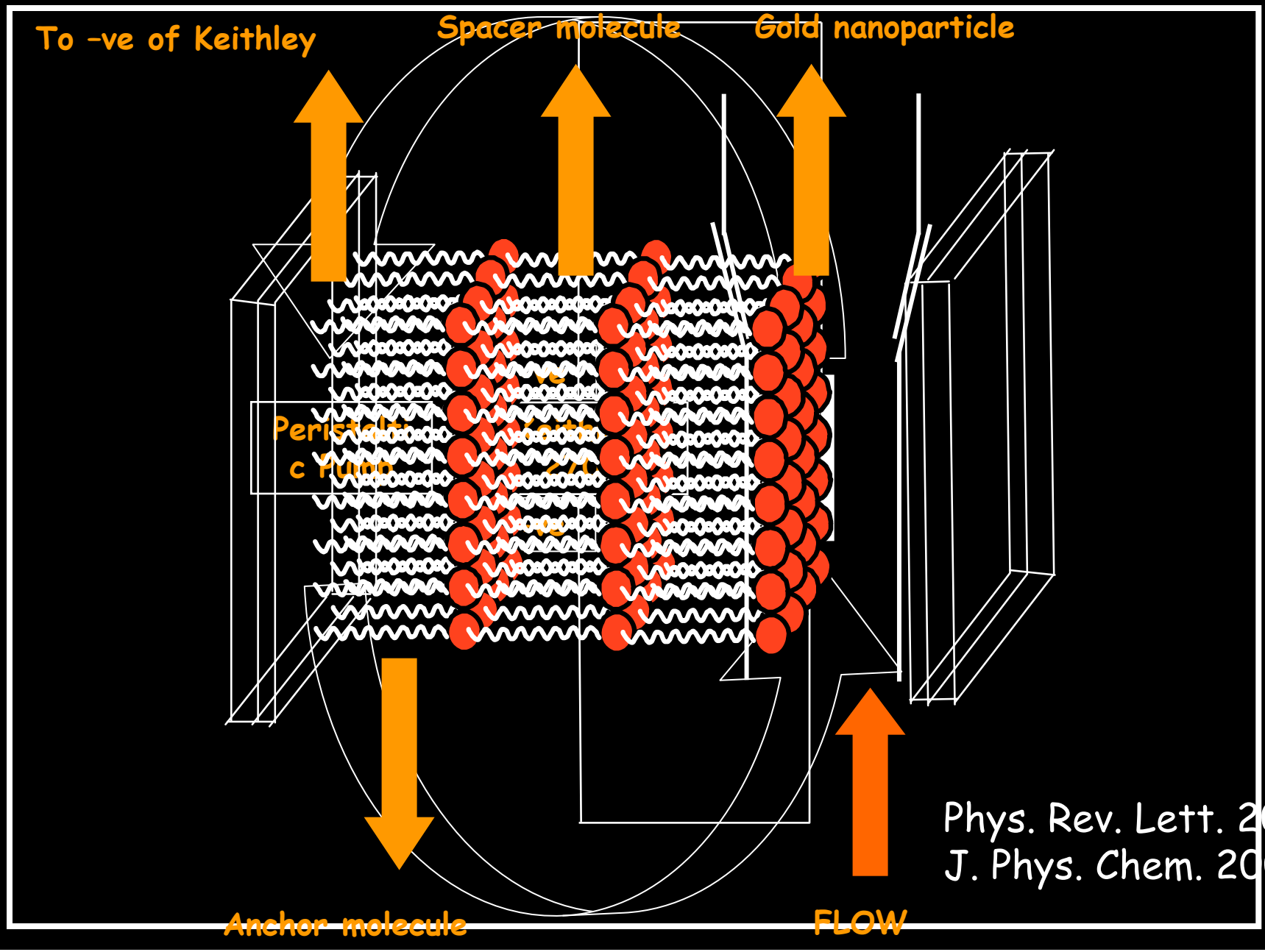
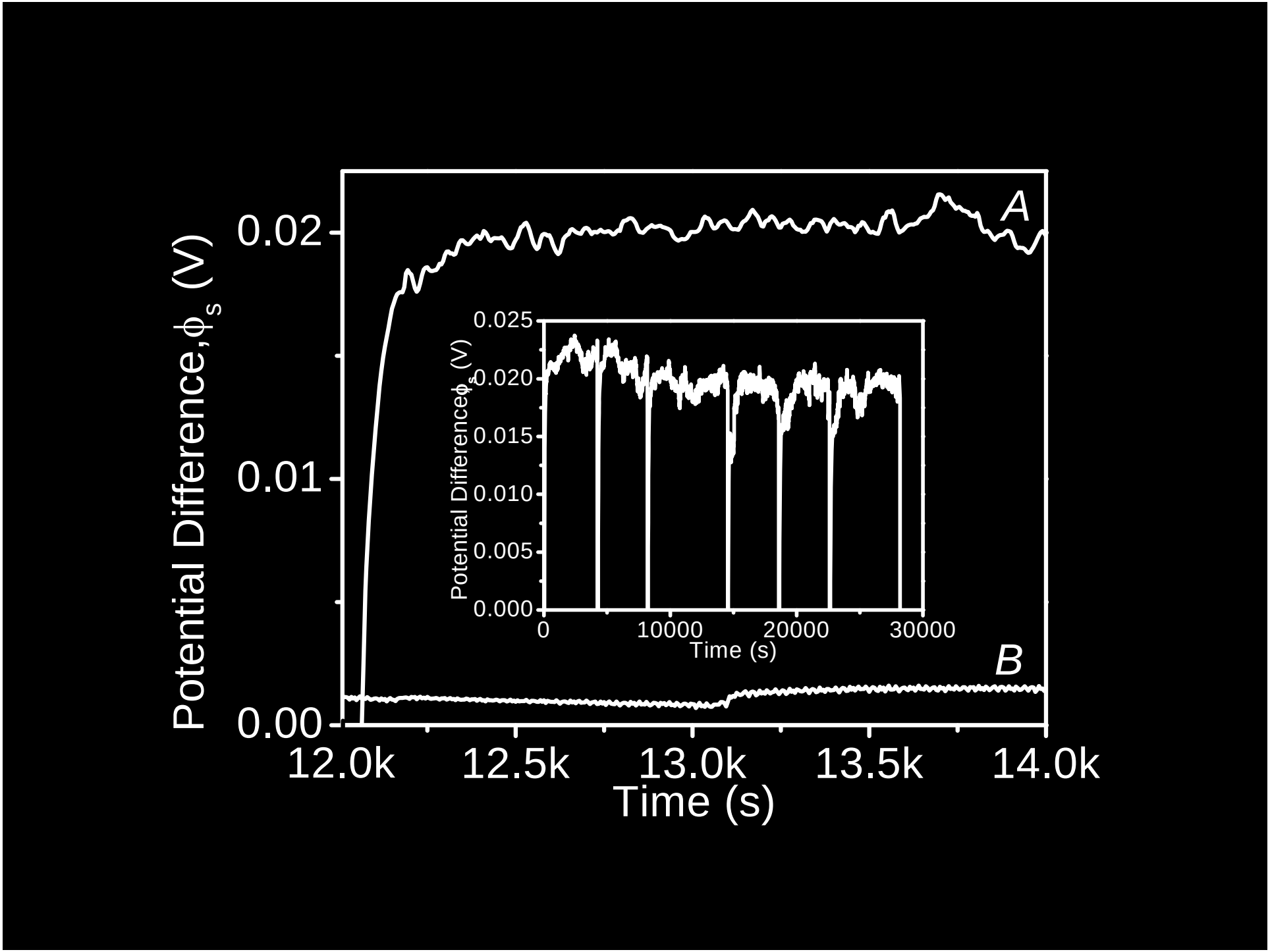
NANOBIO-2009, AIMS, Cochin, February 17-19, 2009

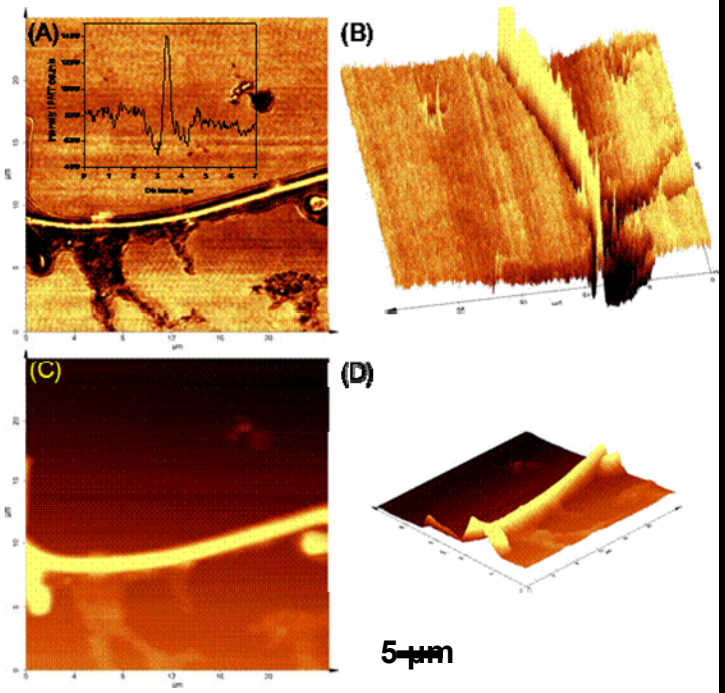
Group-2008

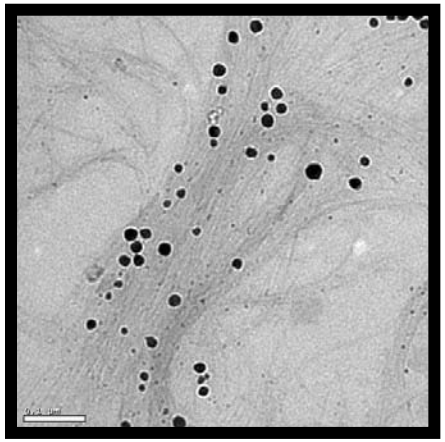
New phenomenon - Flow induced potential in nanoparticle assemblies

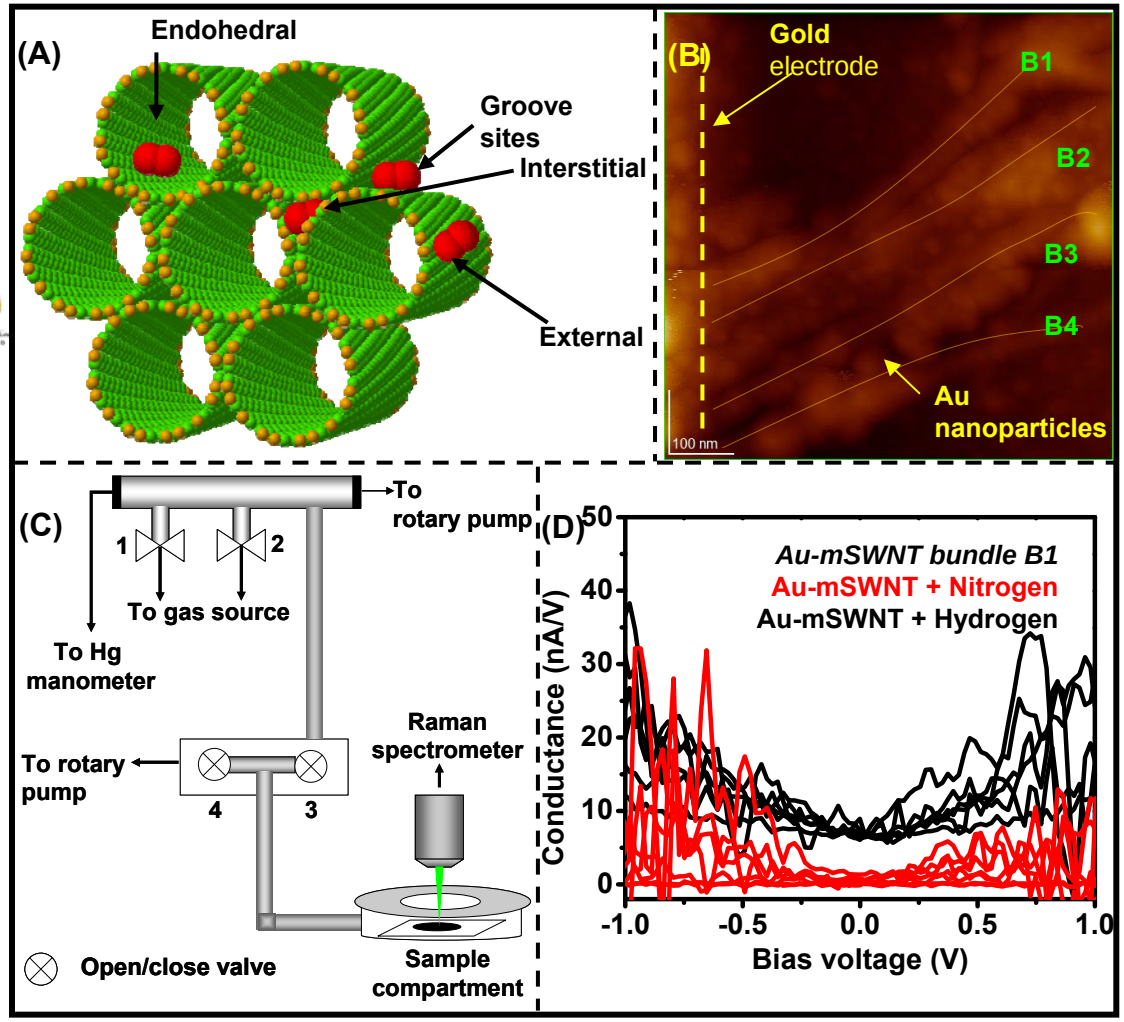



Potential Difference, ϕ_s (V)
0.02
0.01
0.00
12.0k
12.5k
13.0k
13.5k
14.0k
Time (s)
A
B
Potential Difference ϕ_s (V)
0.025
0.020
0.015
0.010
0.005
0.000
0
10000
20000
30000
Time (s)

New phenomenon - Visible fluorescence from SWNT composites

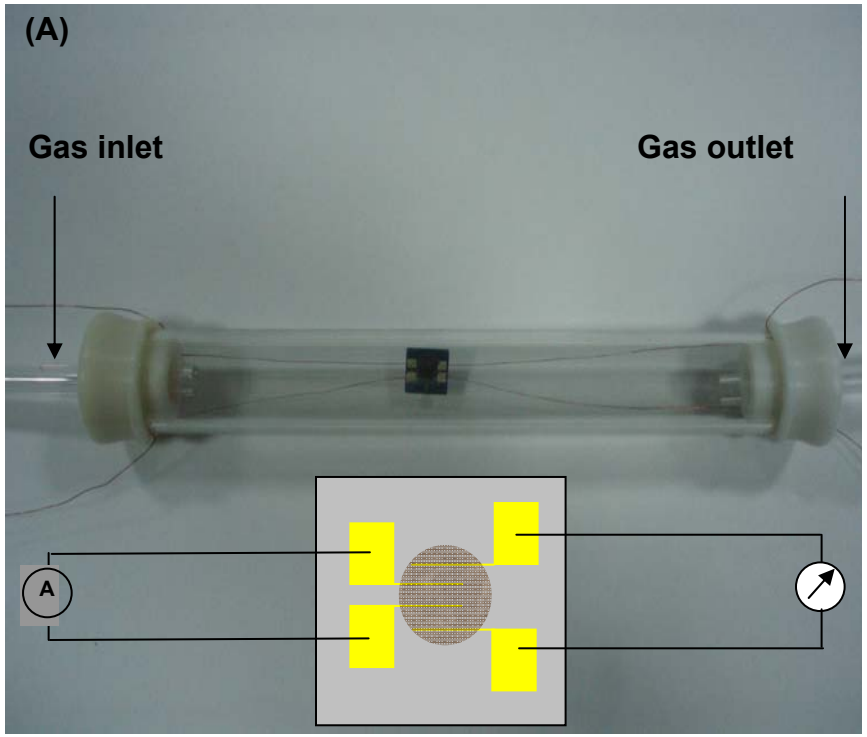




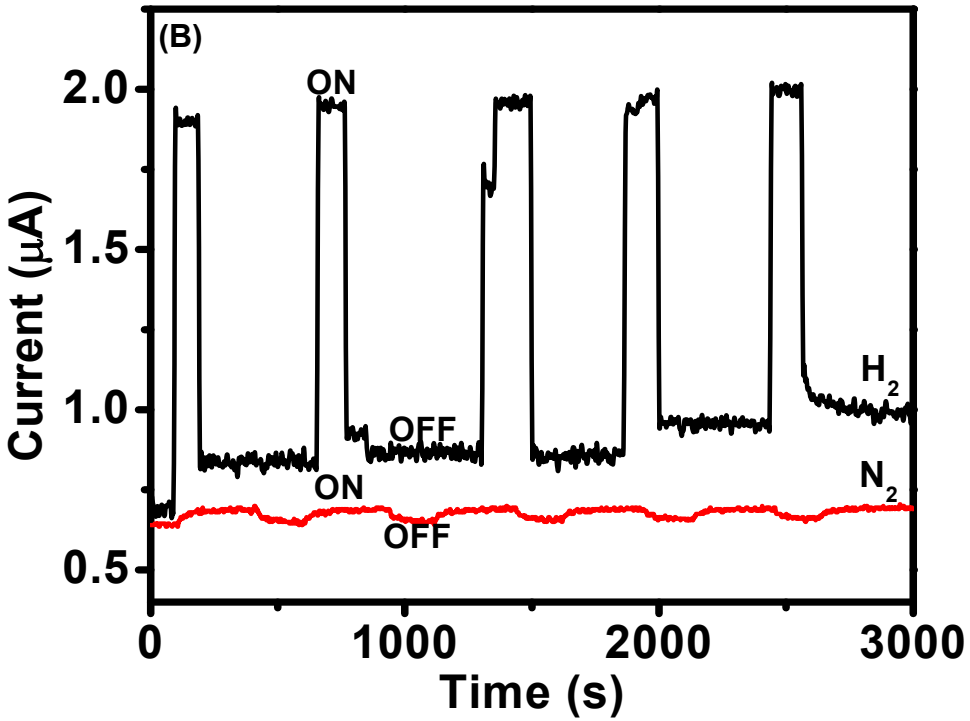


Phys. Rev. Lett. 2007
APL 2009 (submitted)
Indian and PCT patent applications 2007. 2008

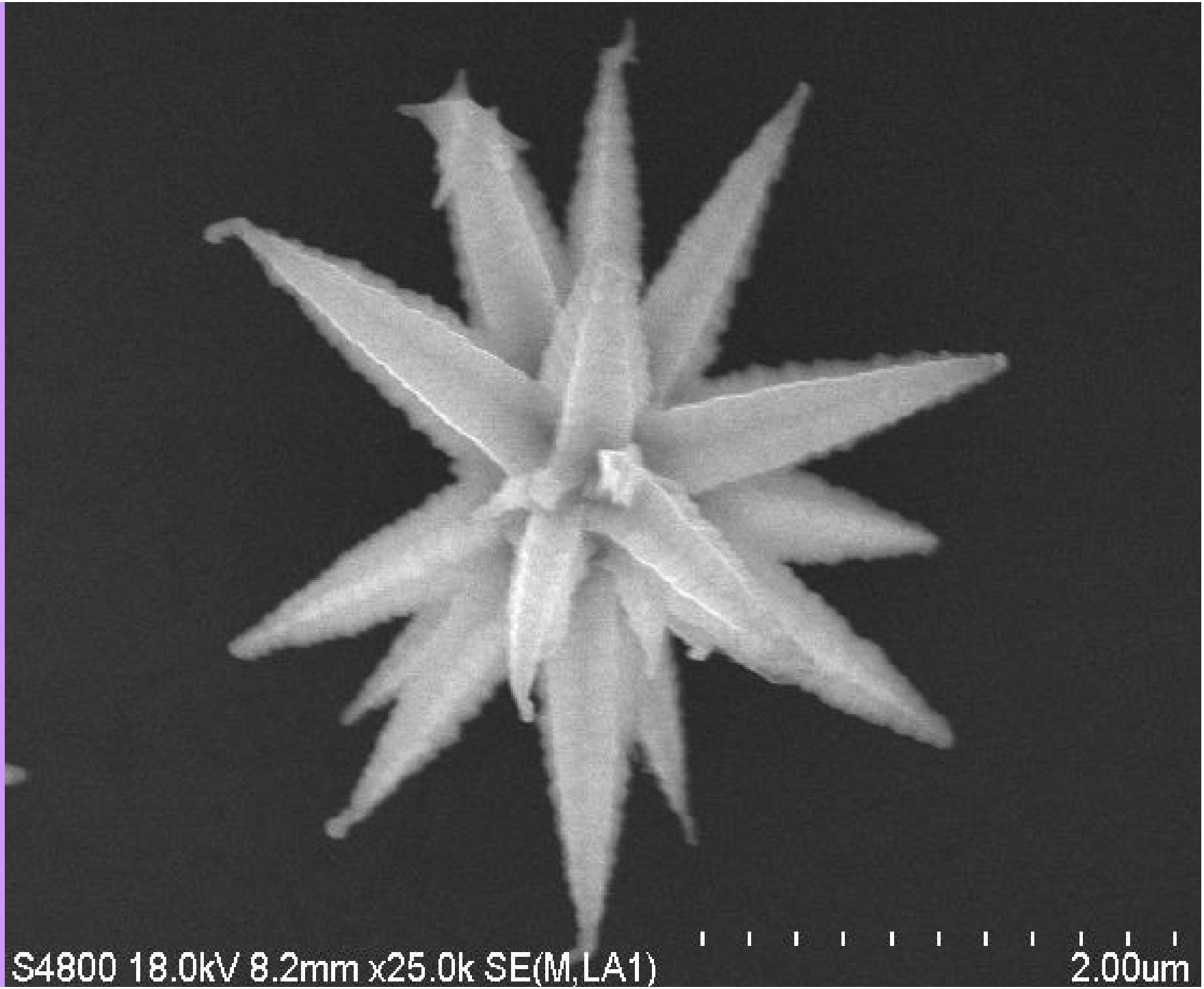
New phenomenon - Visible fluorescence from SWNT composites - Device



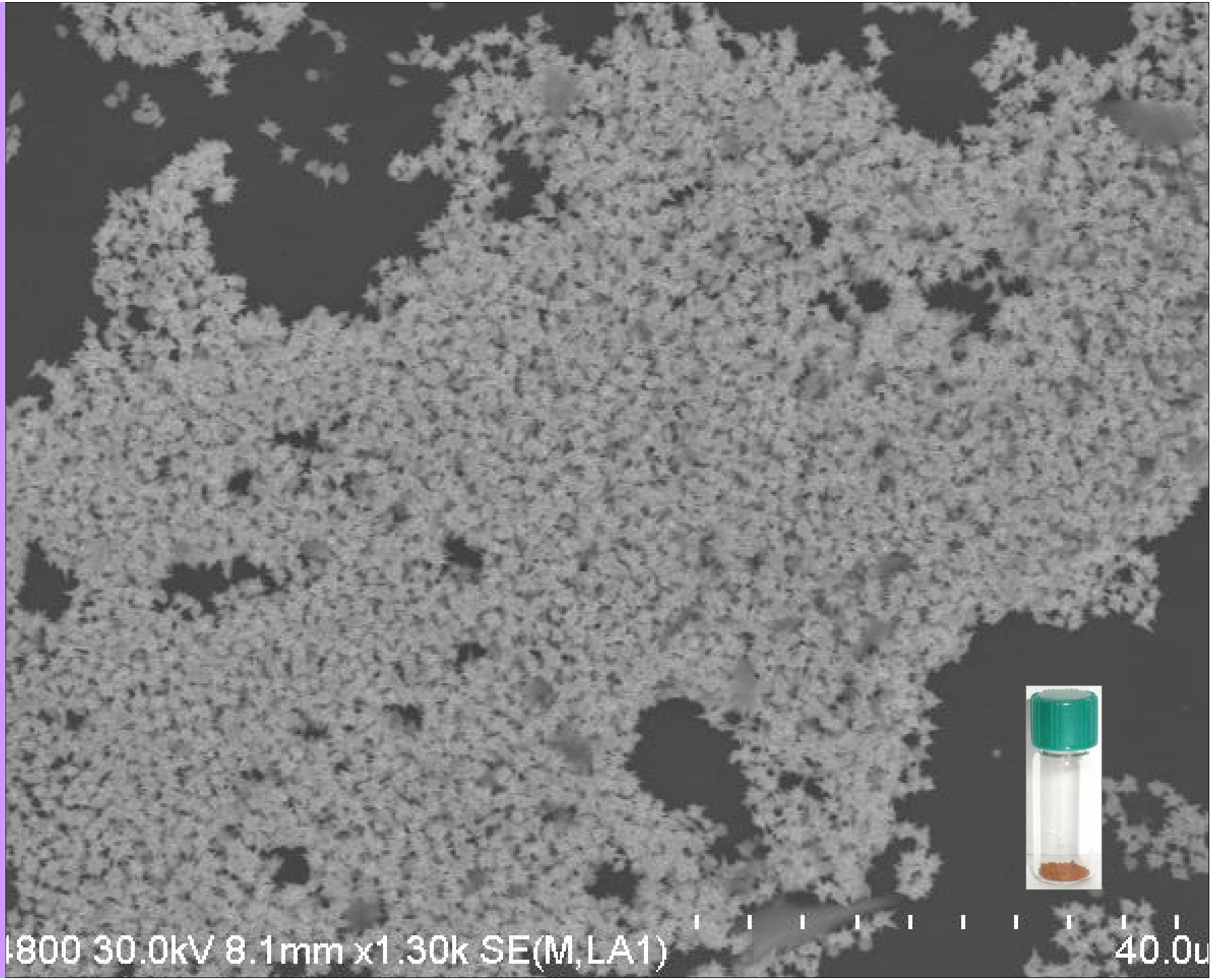
Switch



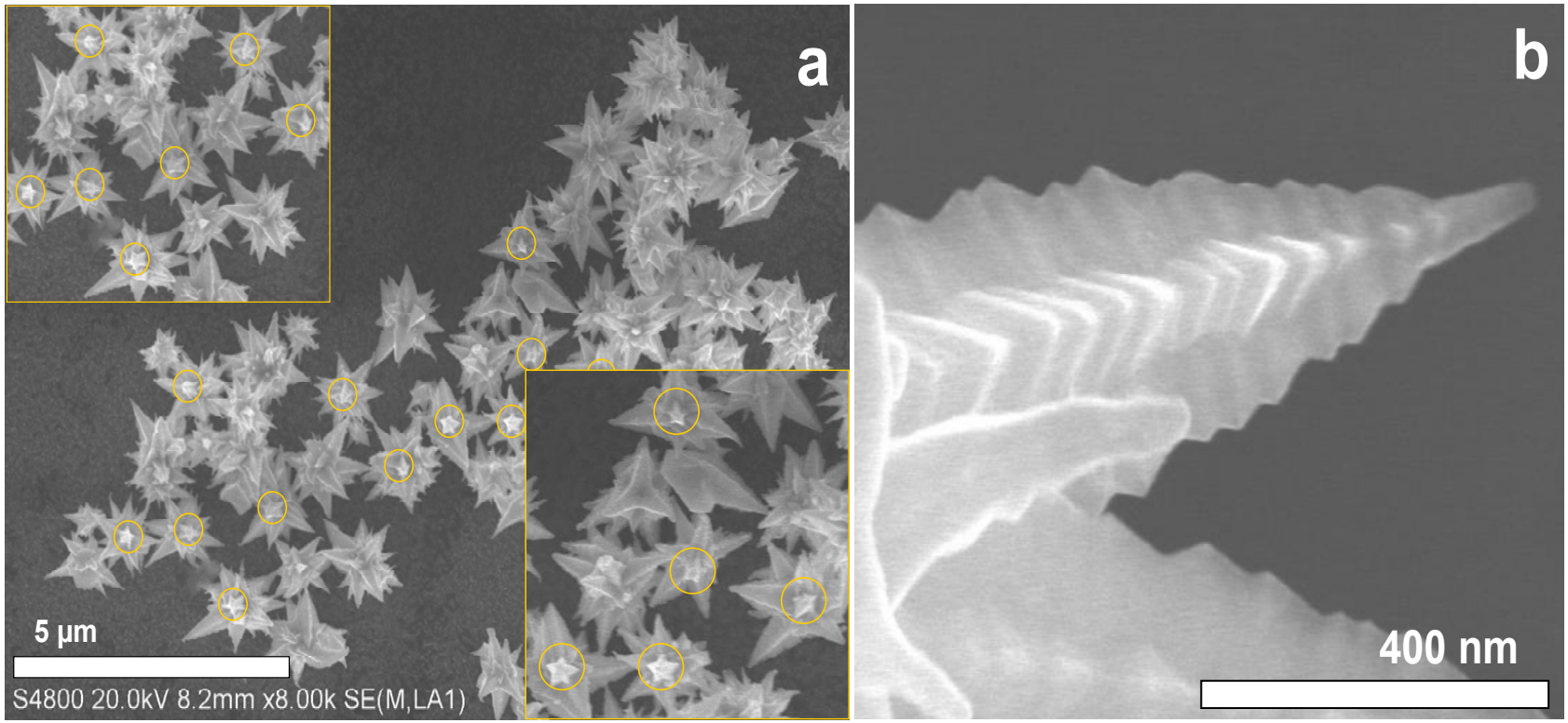
NEW MATERIALS



LARGE AREA SEM

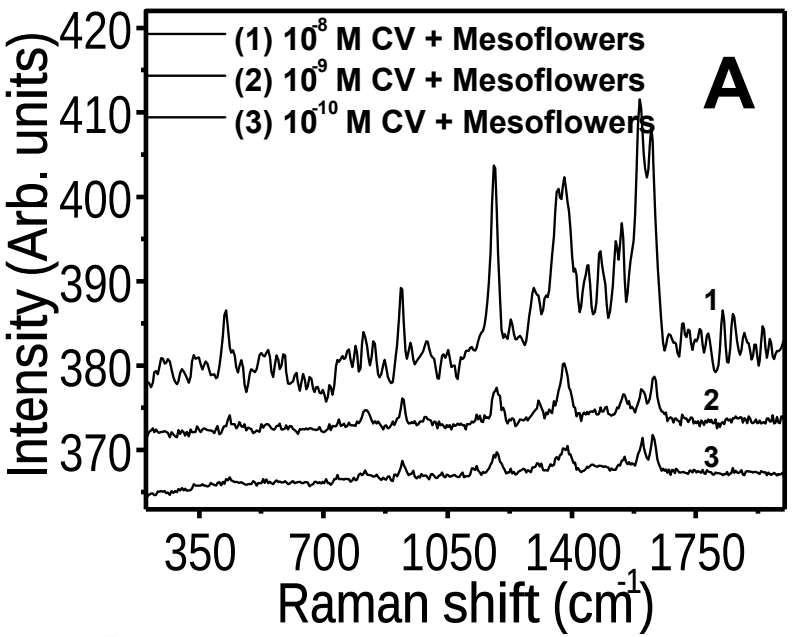


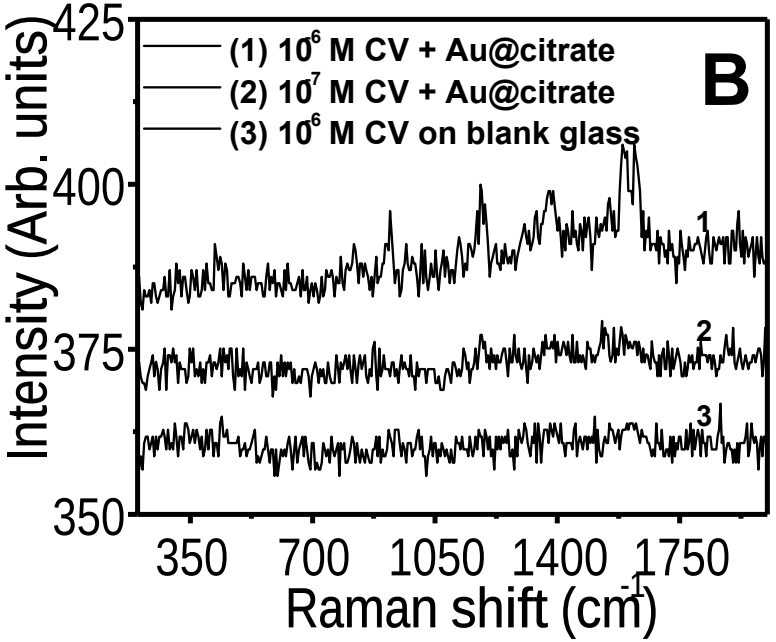
MESOFLOWERS

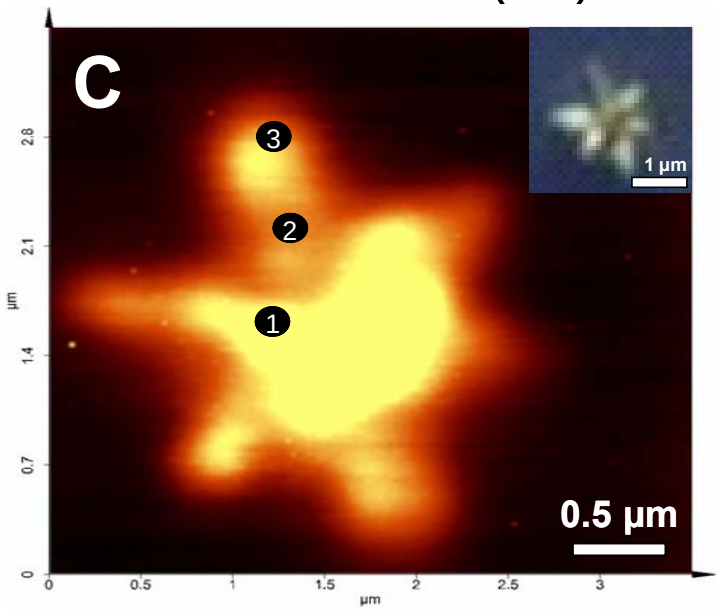


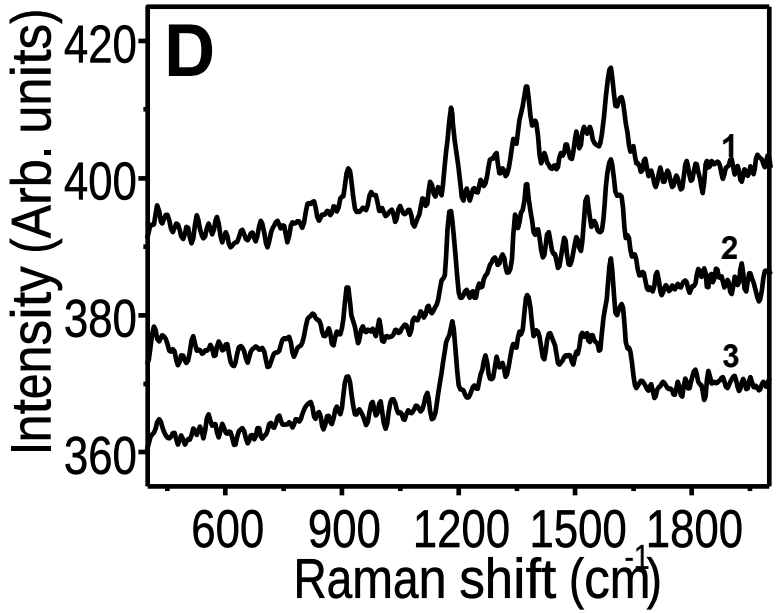
P. R. Sajanlal and T. Pradeep, Nano Res. 2009

SERS & RAMAN IMAGING



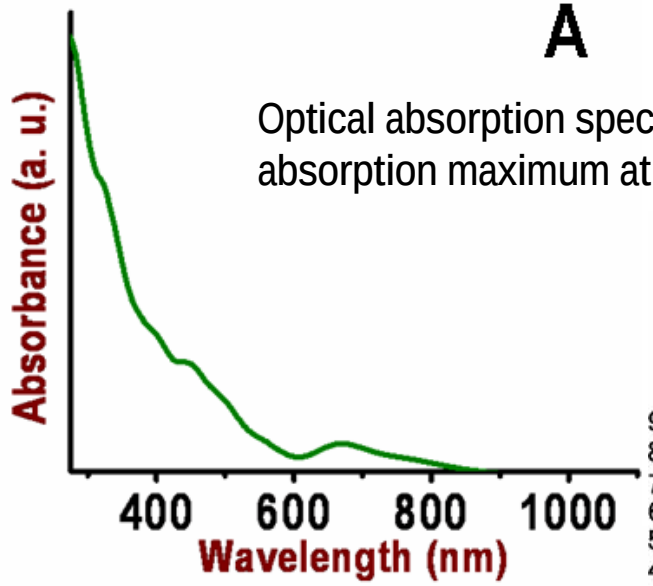




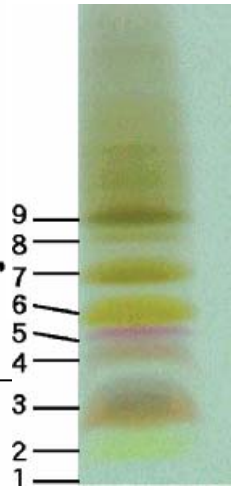


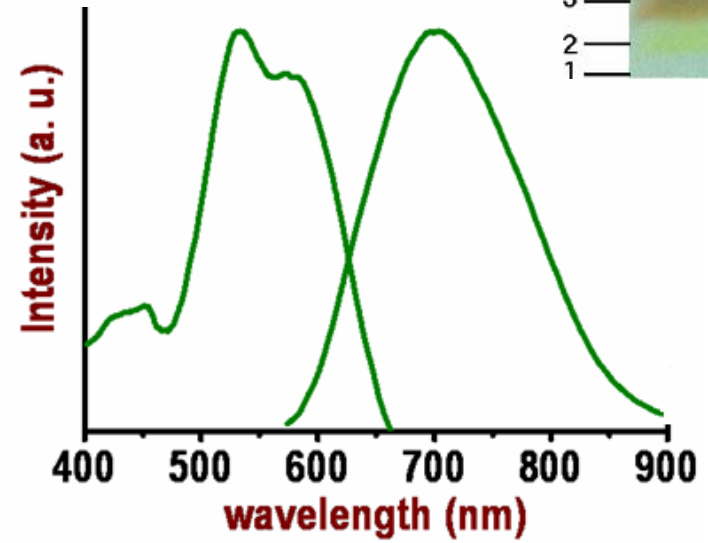
Fluorescent clusters of gold and silver

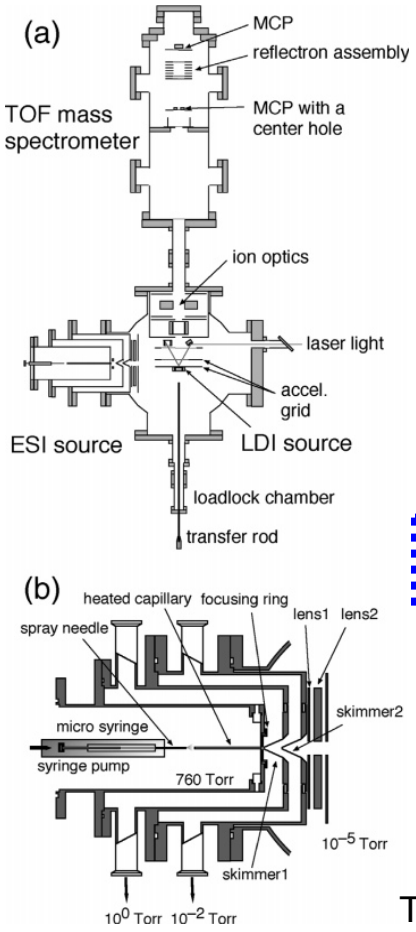
Characterization of $Au_{25}SG_{18}$

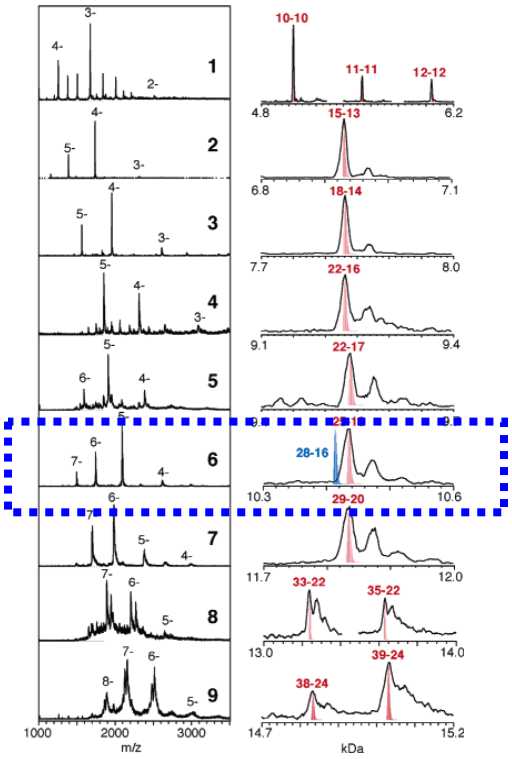


Optical absorption spectrum with an absorption maximum at 672 nm.









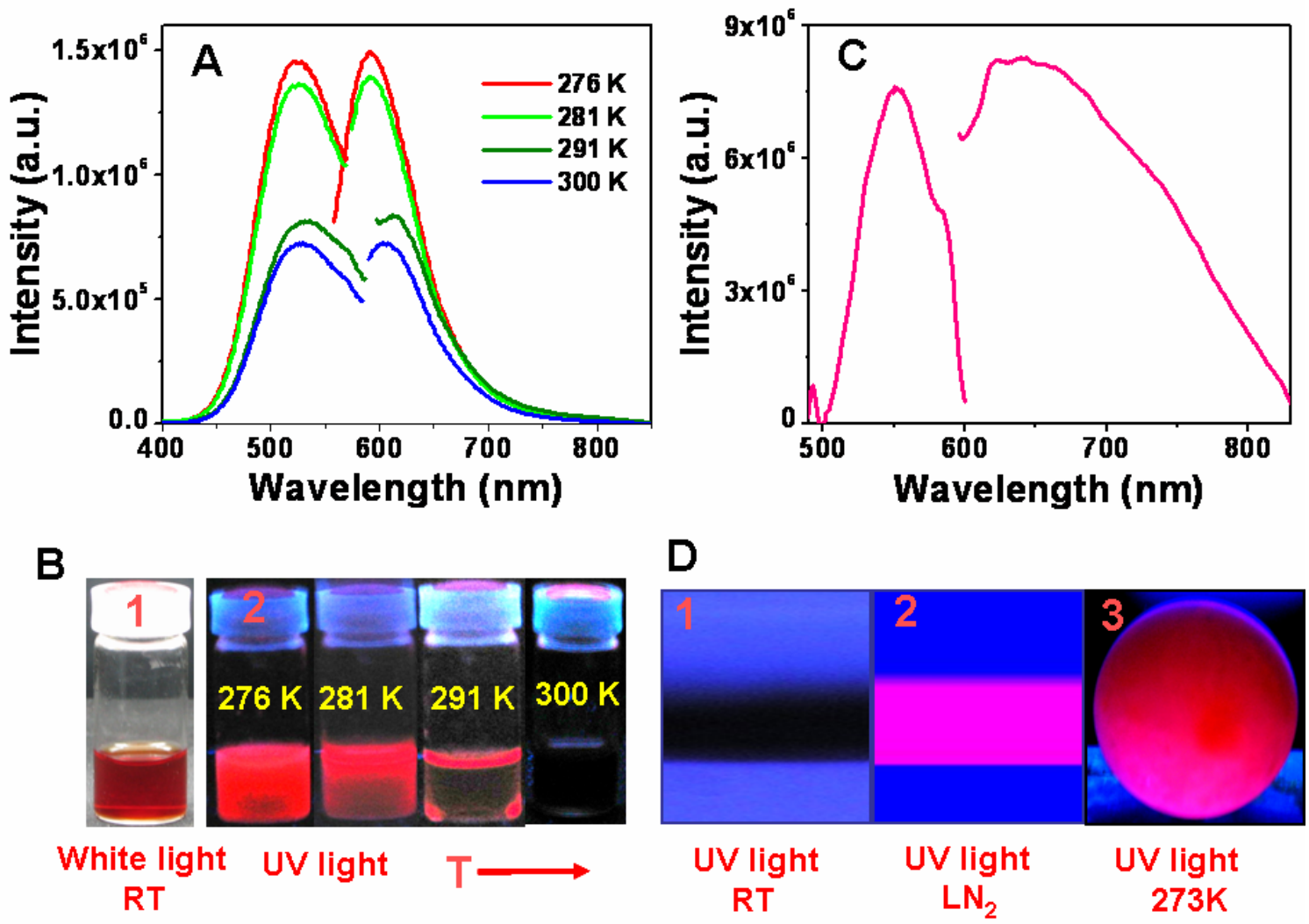
Tsukuda et. al. JACS 2005

Photoluminescence profile with excitation and emission maxima at 535 and 700 nm, respectively.

Shibu, Habeeb, et al. J. Phys. Chem. C 2008

Fluorescent clusters of gold and silver

Ag_4 clusters

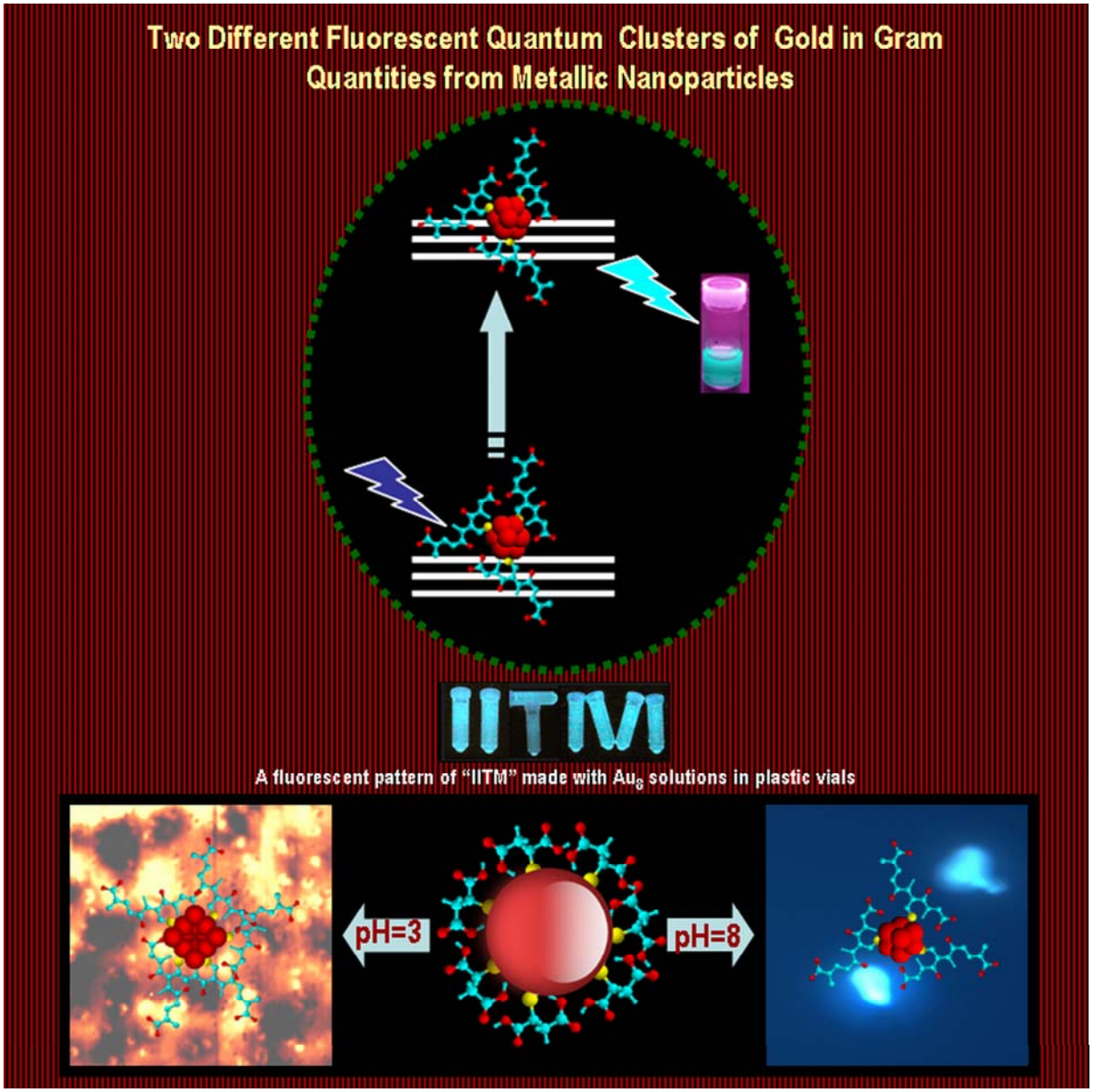


Udaya Bhaskara Rao and Pradeep, Submitted

K.V. Mrudula, et al. J. Mat. Chem. 2009

Au_8 clusters

Cover art ⟶



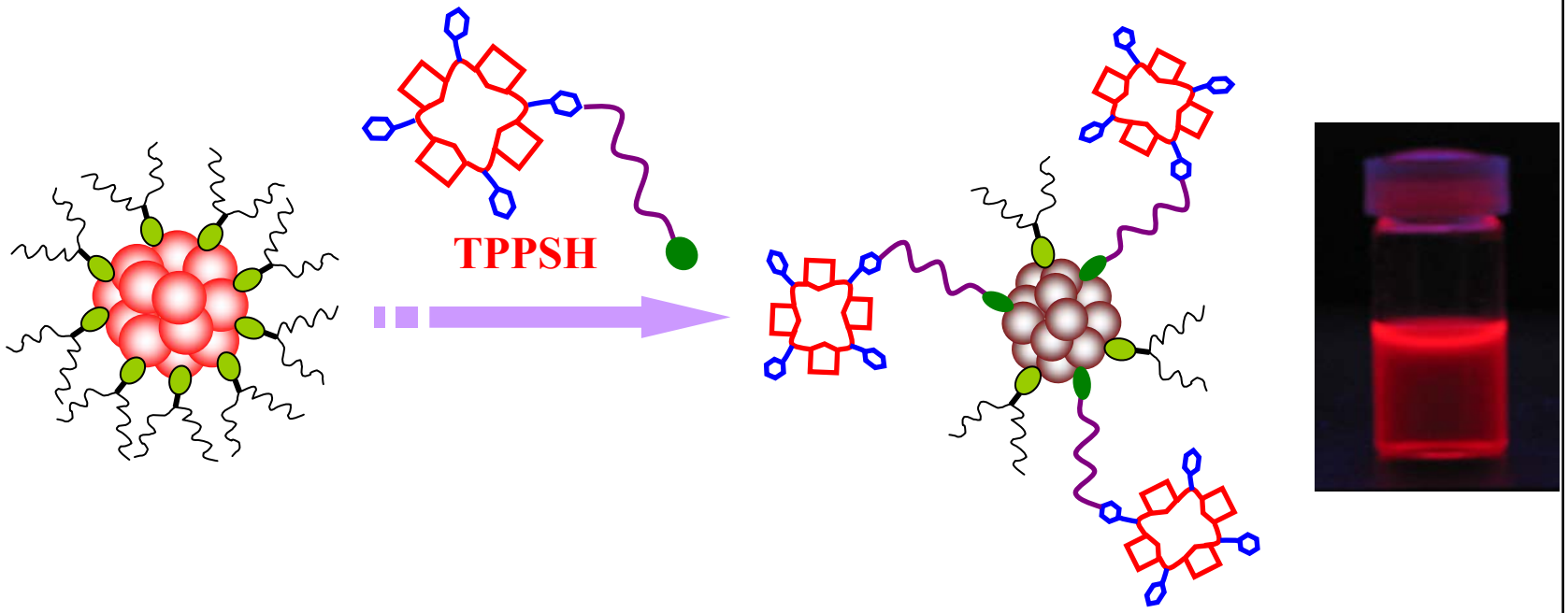
M. A. Habeeb and T. Pradeep, Nano Res. 2008

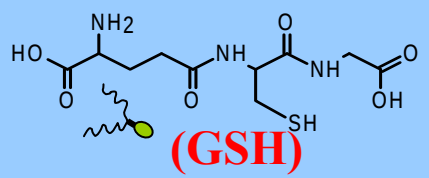
Au_{22} CLUSTERS

$(TPPSH)_{Toluene}$

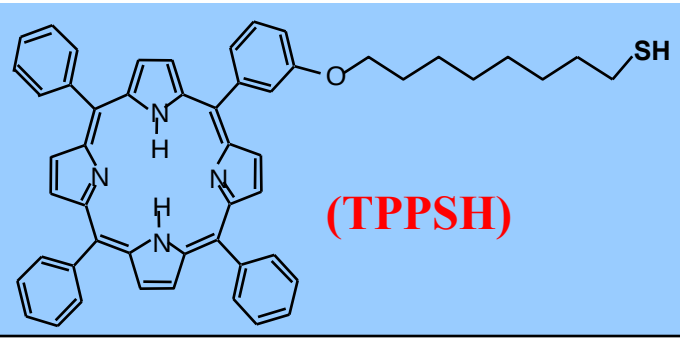
Core reduction followed by ligand exchange

$[Au_{25}SG_{18}]_{aq}$ → $[Au_{22}(SG)_{15}(TPPS)_2]_{aq}$





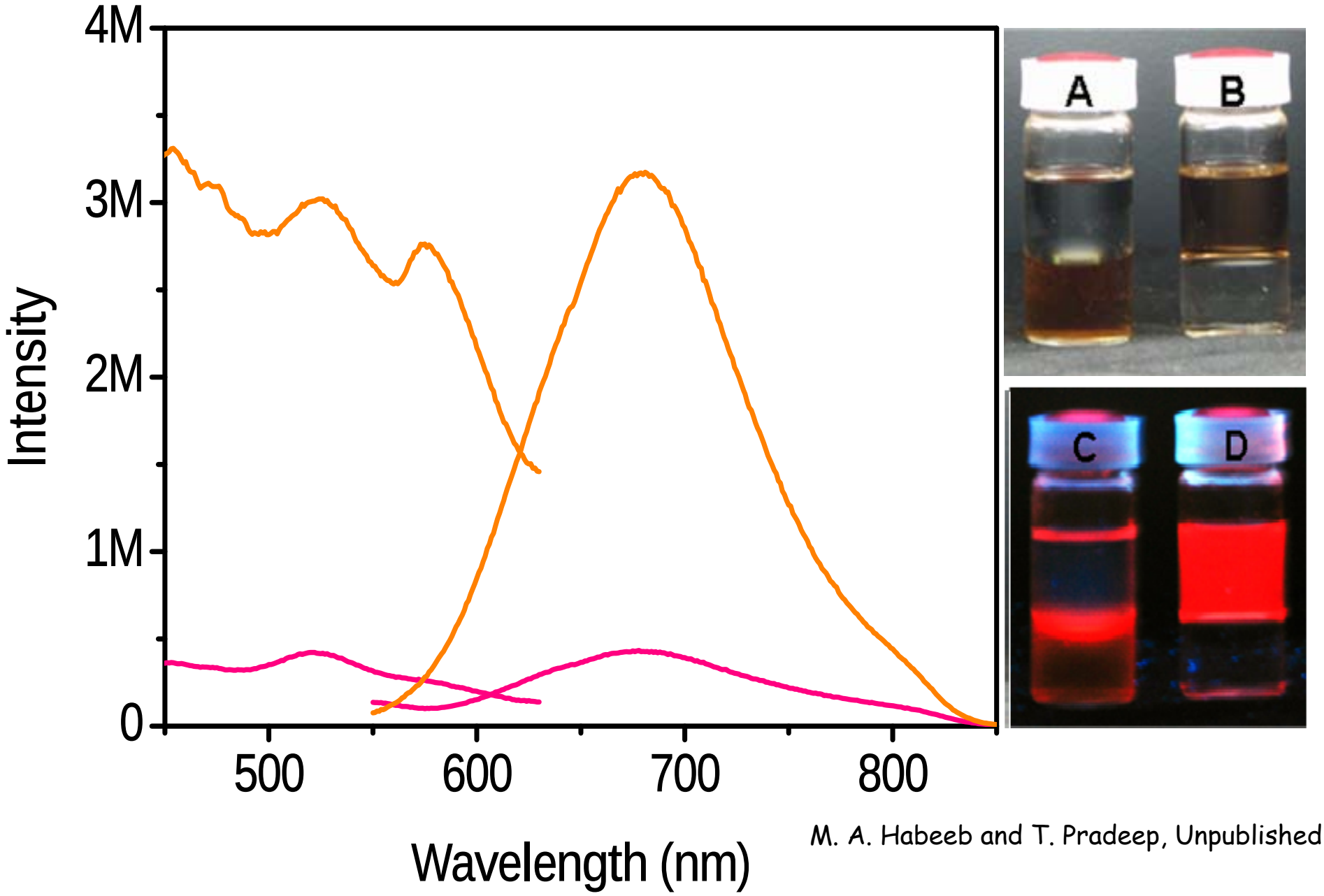
(GSH)



(TPPSH)

E. S. Shibu and T. Pradeep Unpublished

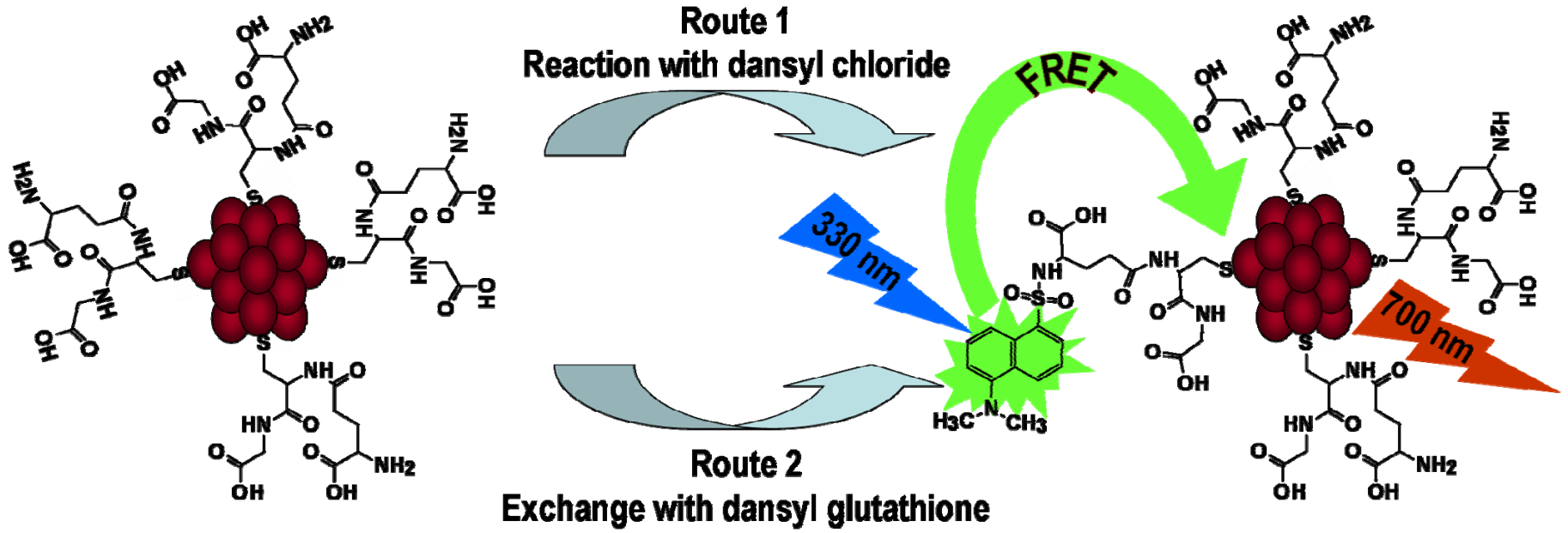
Red emitting clusters



M. A. Habeeb and T. Pradeep, Unpublished

FRET of clusters

Au_{25} clusters



Approaches Used for the Functionalization of Dansyl Chromophore on the Au_{25} Cluster.

Habeeb Muhammmed et al. J. Phys. Chem. C 2008

Outline

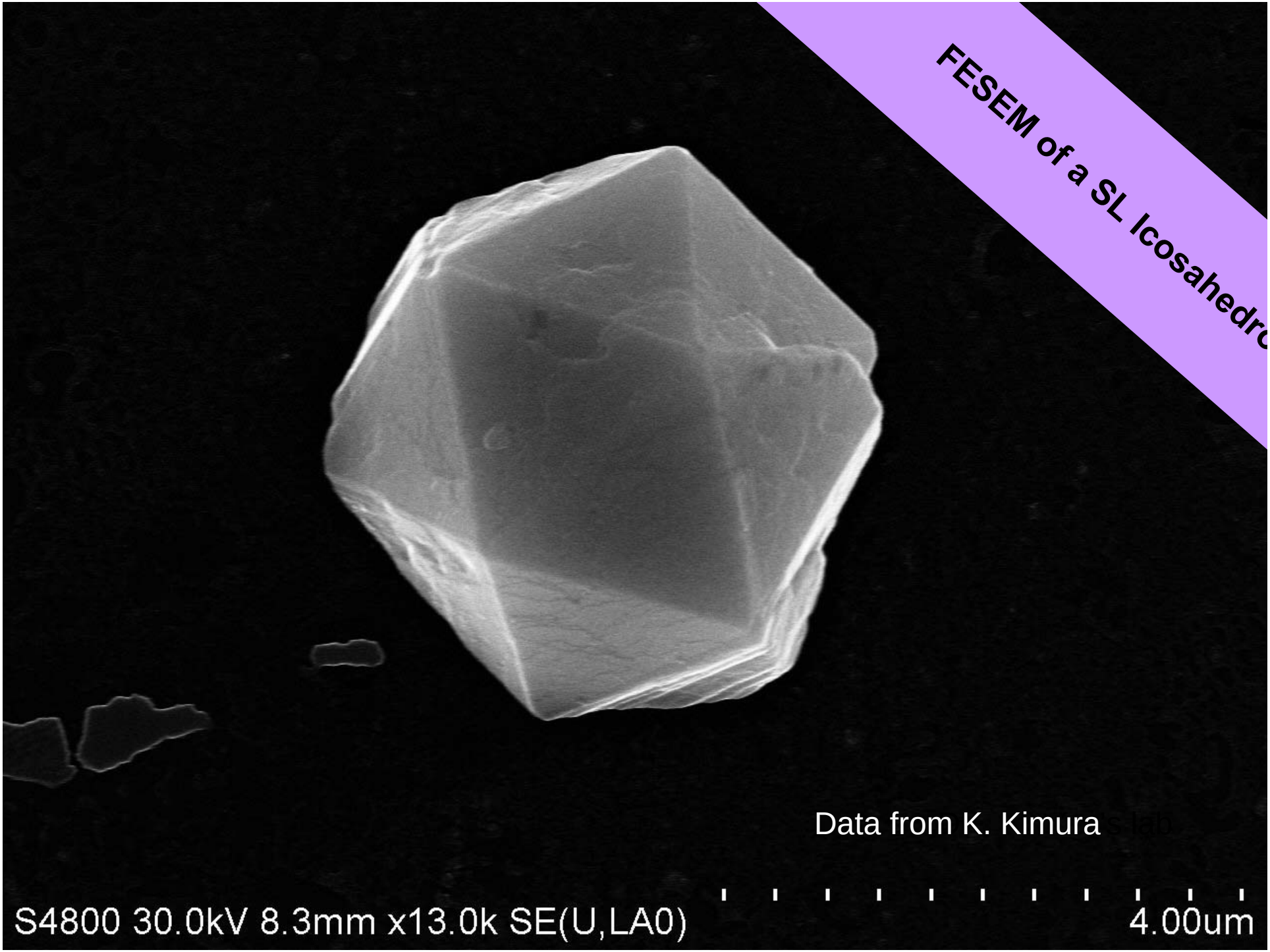
Metal nanoparticle superlattices

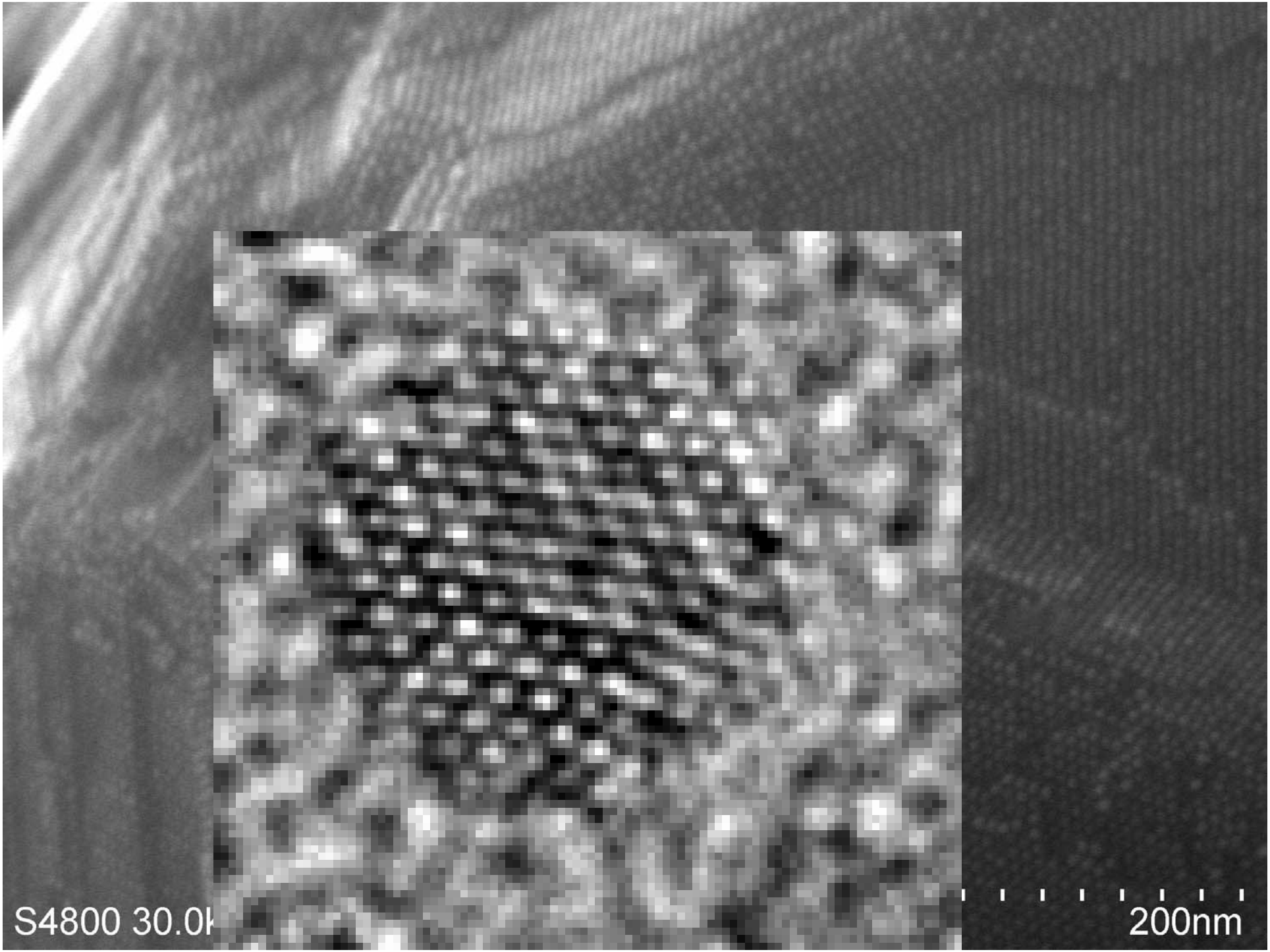
Particle crystals
Multiple periodicity
Particles may not have orientational or
Unit cells of a few nm
New applications
Summary

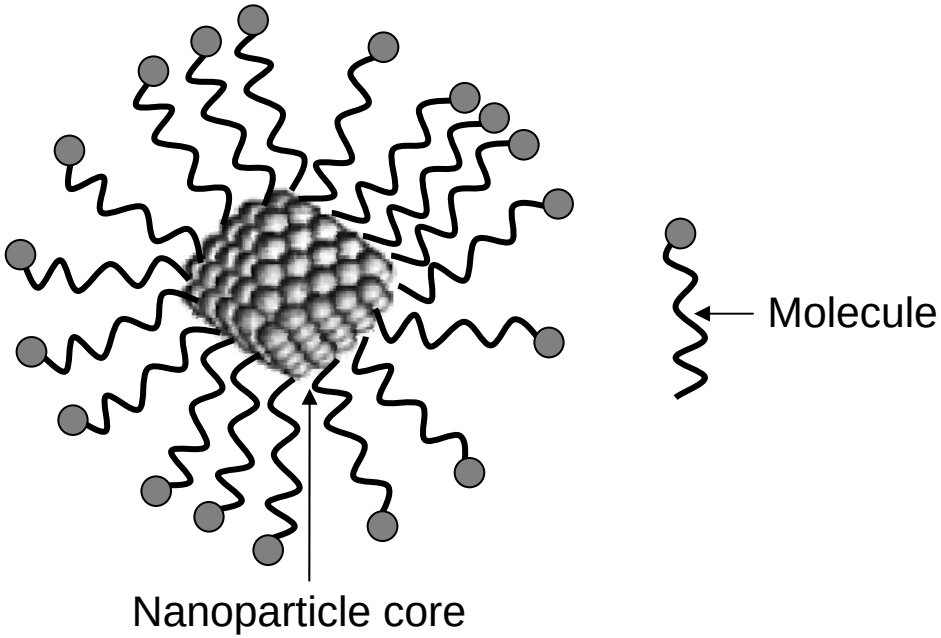
Fluorescent Superlattices of dansyl glutathione capped gold nanoparticles as new materials

Detection of BSA using the dansyl ring of the SLs in mM-nM concentration

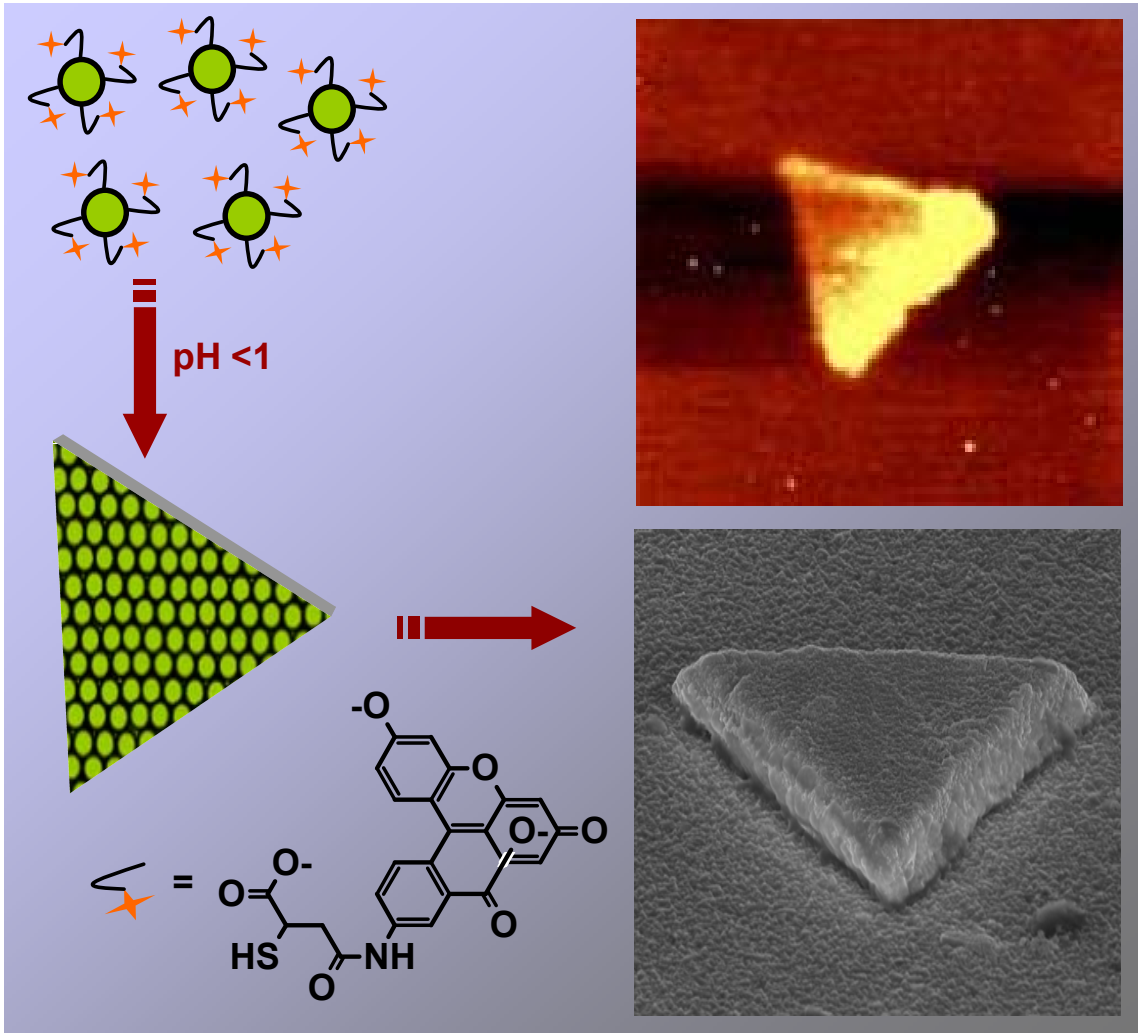
New gas sensors


FESEM of a SL Icosahedro
Data from K. Kimura
S4800 30.0kV 8.3mm x13.0k SE(U,LA0)
4.00um


S4800 30.0k
200nm


Molecule
Nanoparticle core

SAMSA-Functionalized SLs

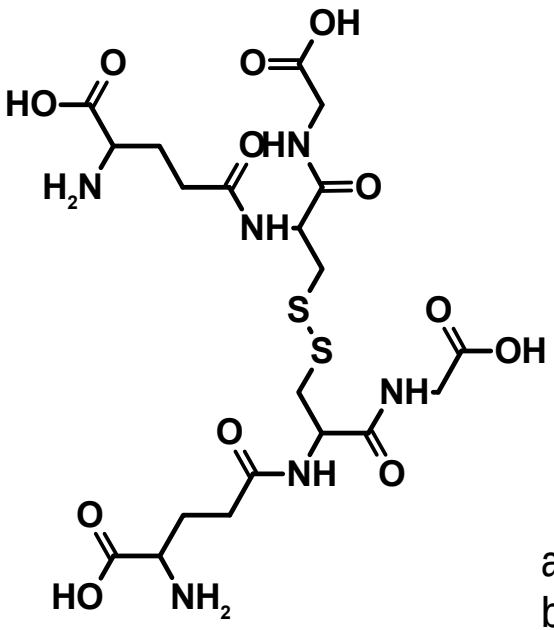


Shibu et al. Adv. Mat. 2008

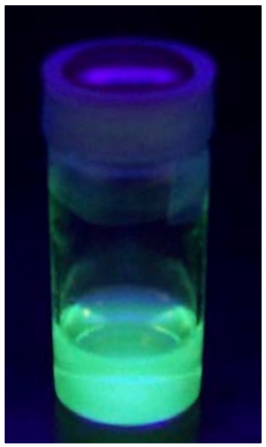
Why Dansylglutathione capped gold nanoparticle SLs?

- Easy to synthesize DGSH
- Stable even in high acidic pH
- High quantum yield
- Solubility in water
- SL can be synthesized in gram sale
- Large number of DGS- can be loaded on nanoparticles
- Utility of dansyl moiety for the selective detection of BSA

SYNTHETIC PROTOCOL

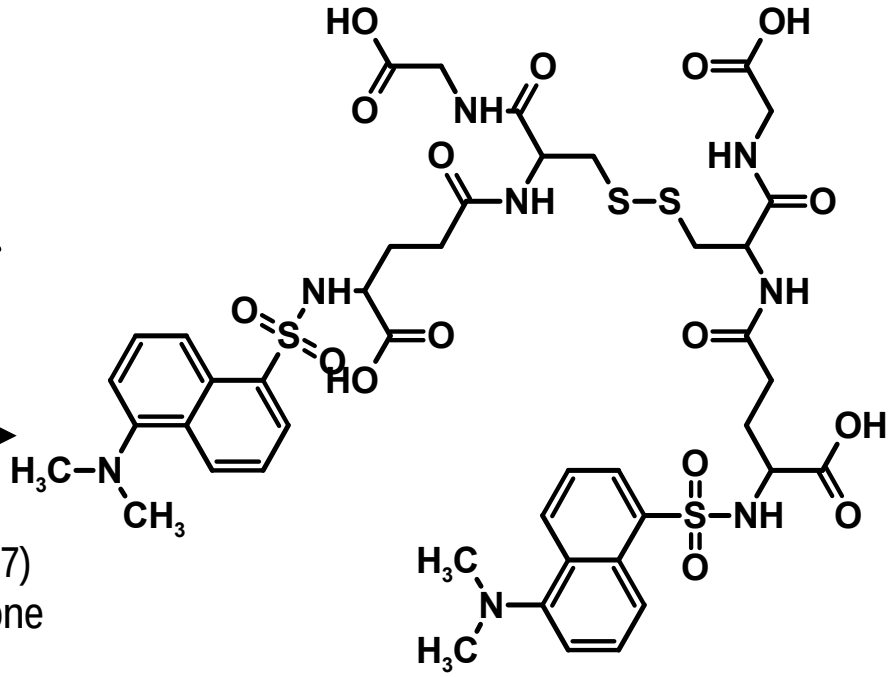


oxidized glutathione

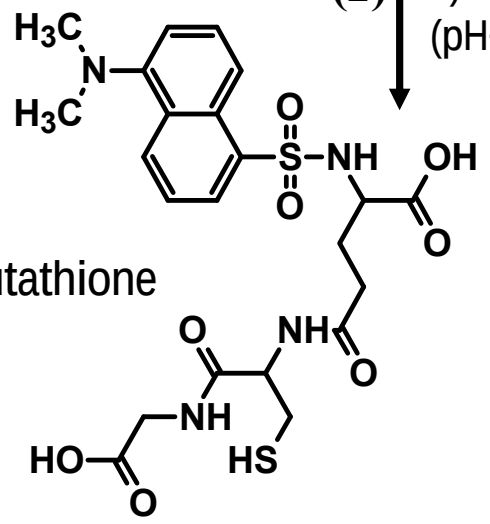


(1)

a) NaOH (pH<7)
b) DnCl/Acetone

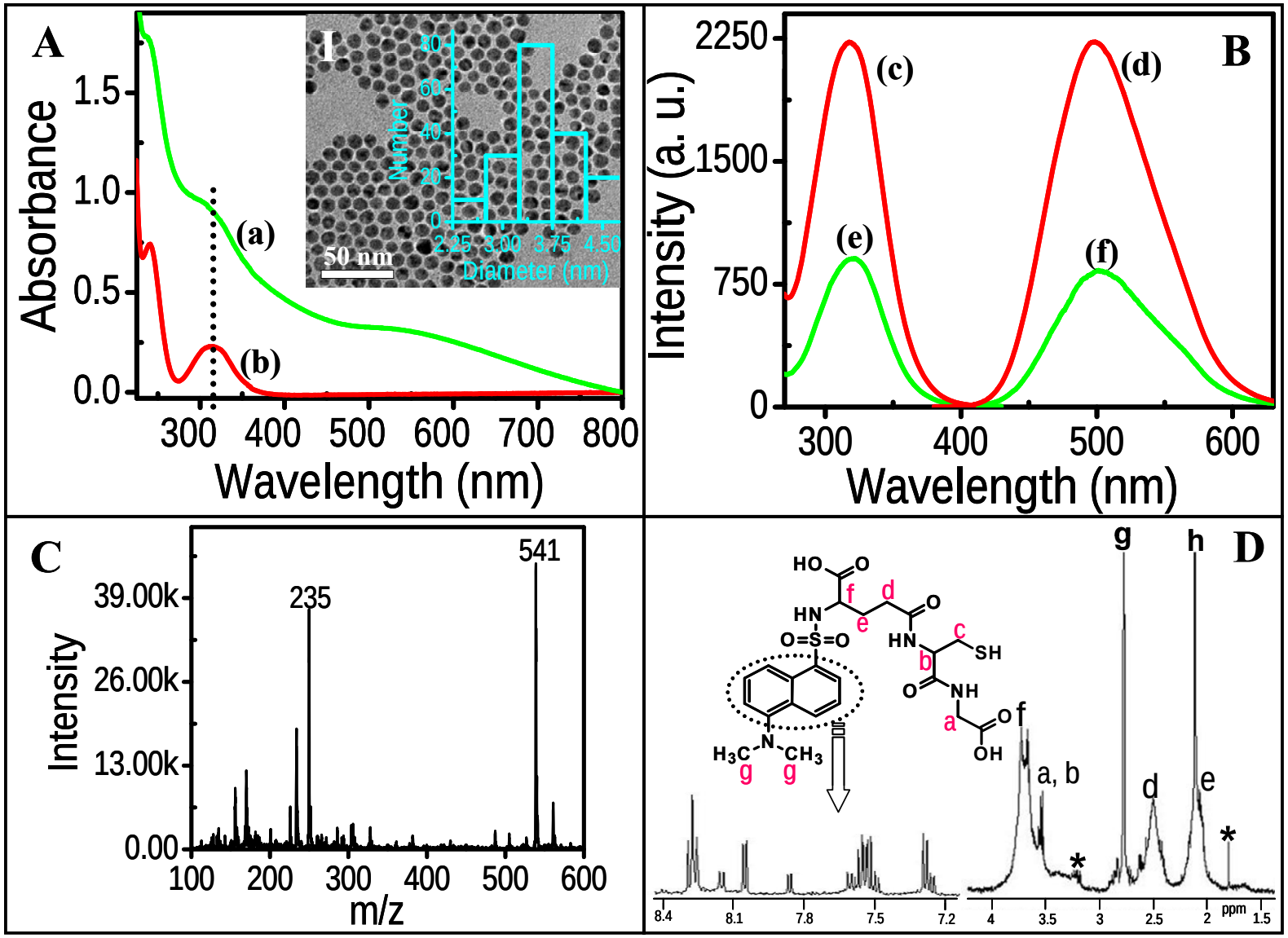


(2) a) DTT/Buffer (pH~8)

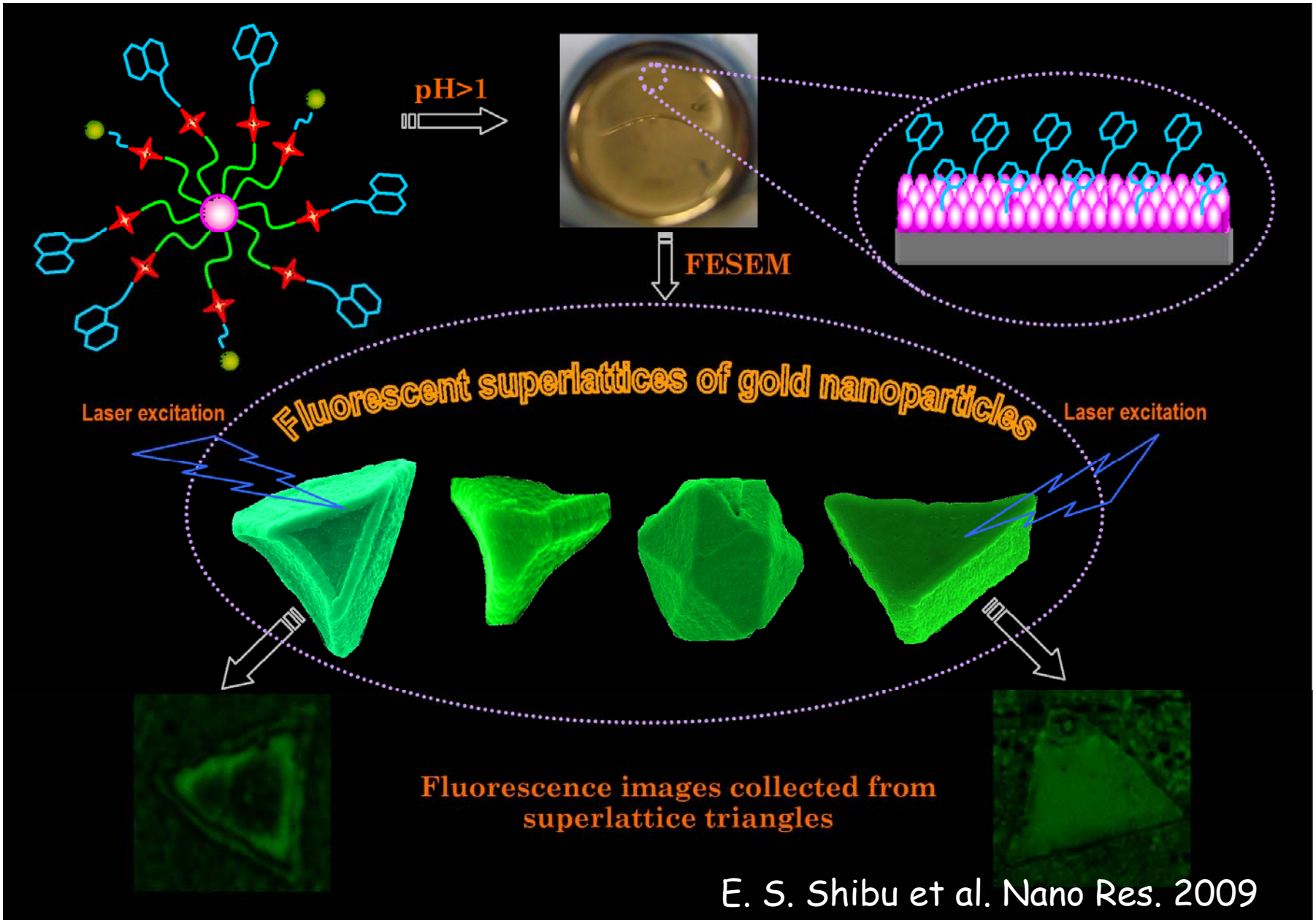


dansyl glutathione

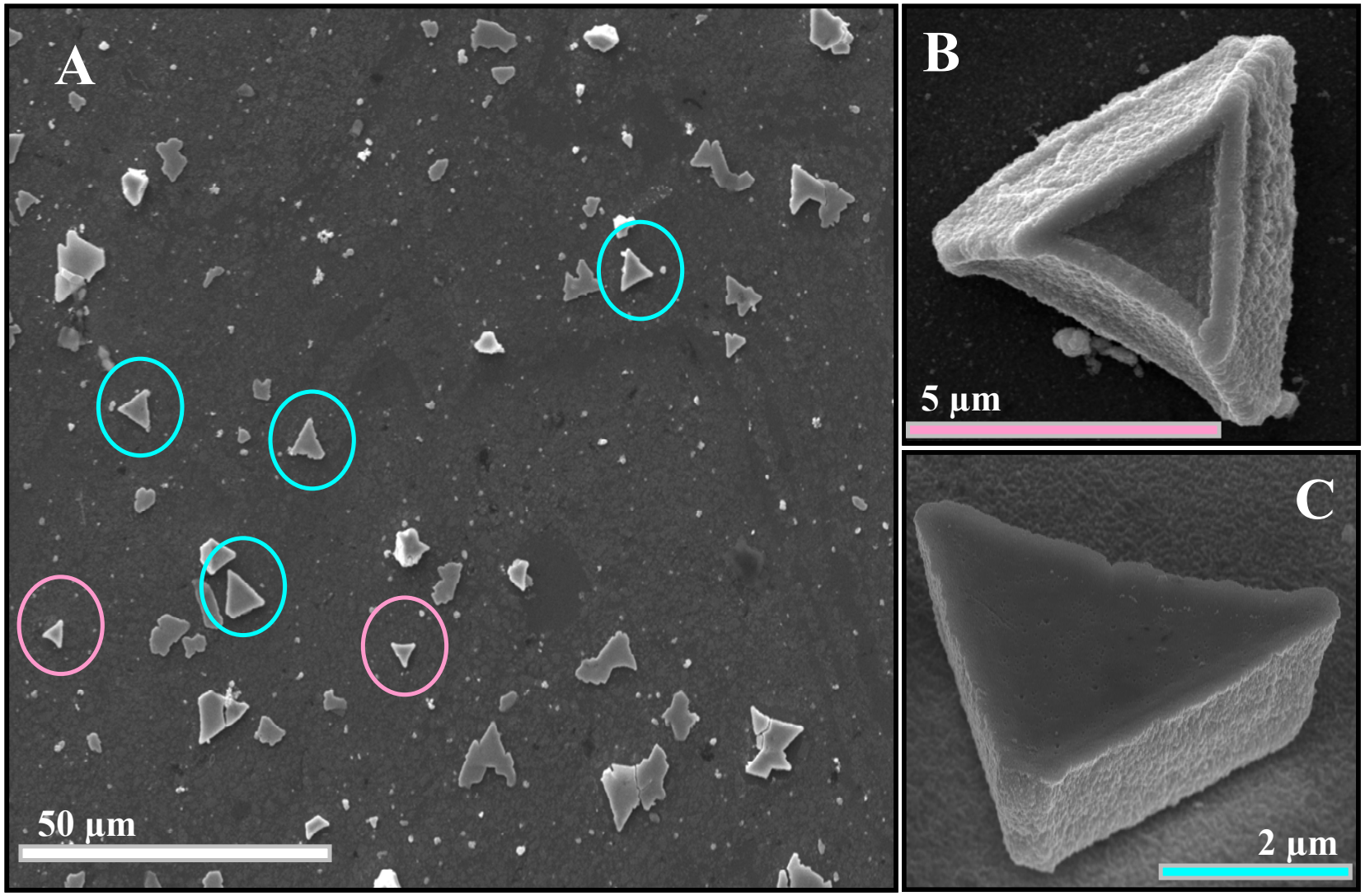
LIGAND CHARACTRIZATION



Overview

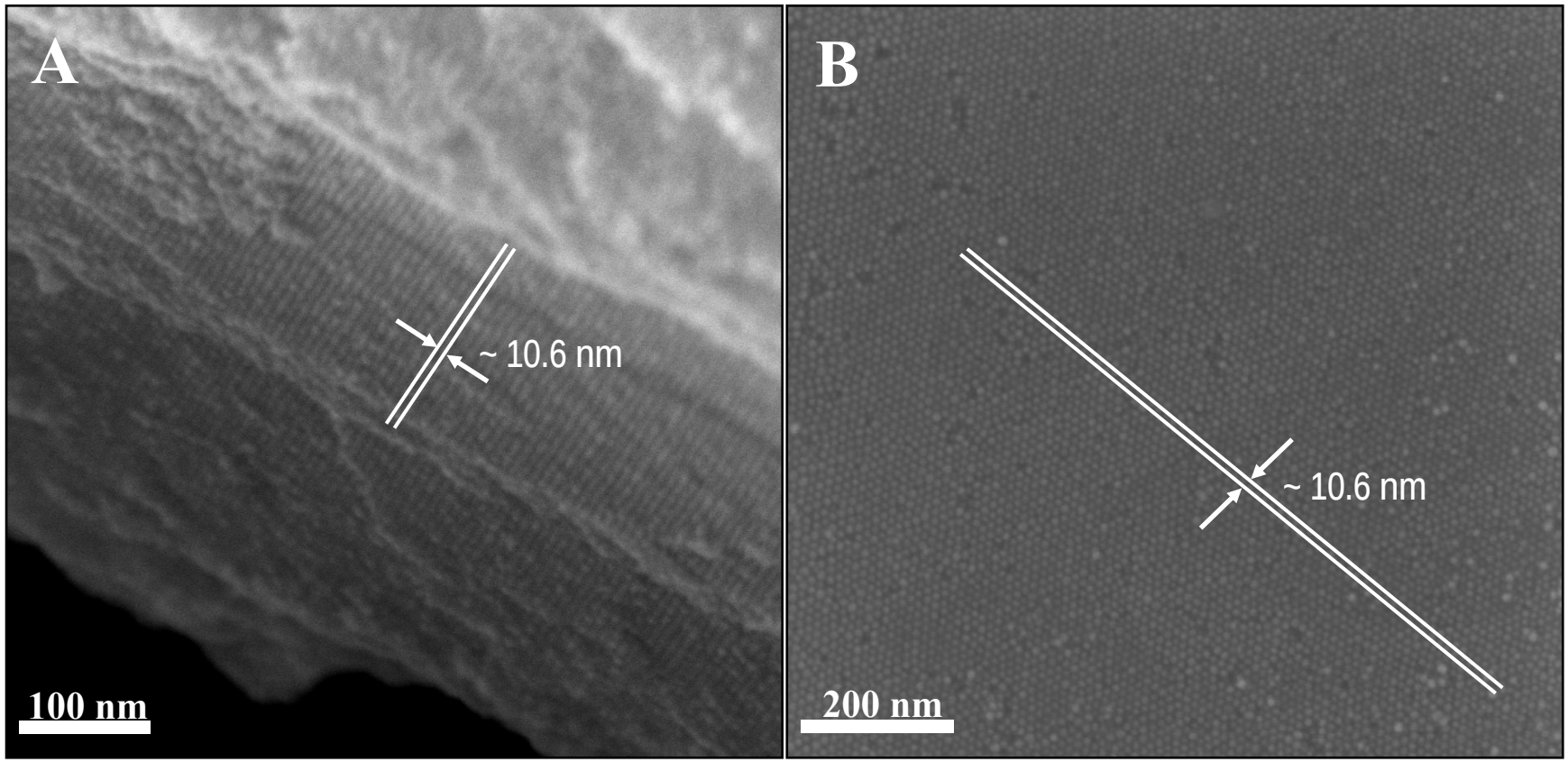

pH>1
FESEM
Fluorescent superlattices of gold nanoparticles
Laser excitation
Laser excitation
Fluorescence images collected from
superlattice triangles
E. S. Shibu et al. Nano Res. 2009

TWO DIFFERENT TRIANGLES

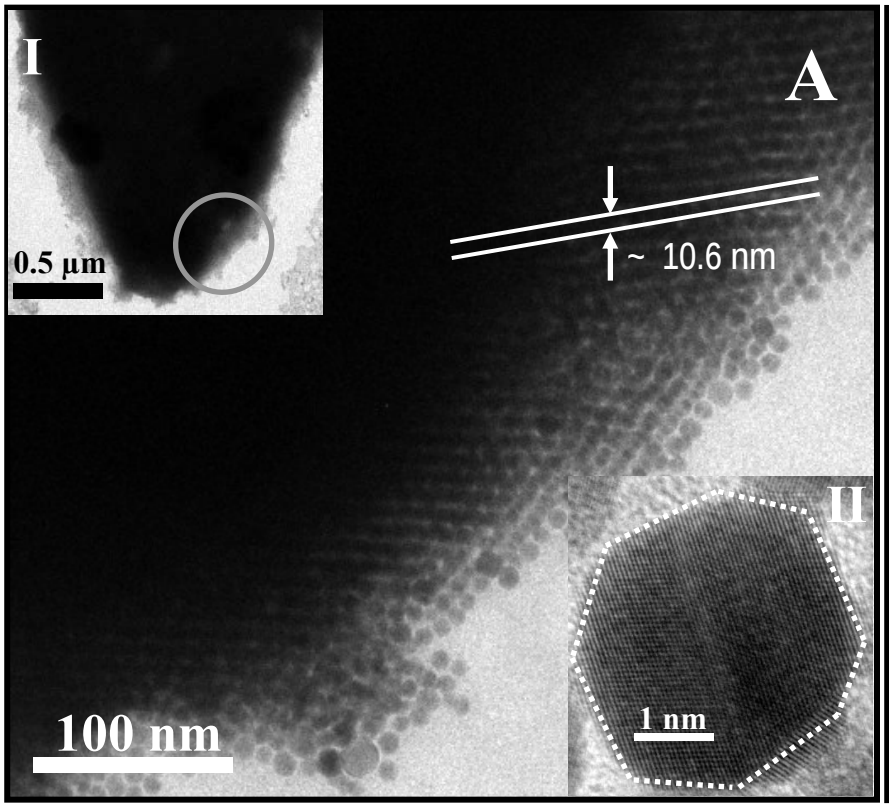


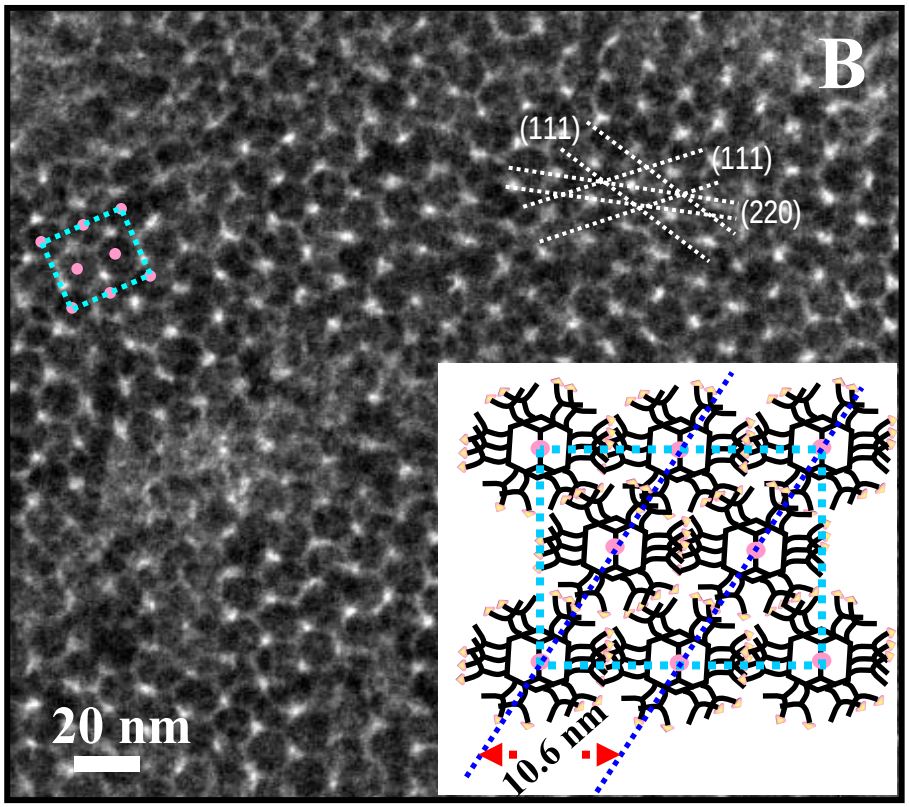
FESEM images – G.U. Kulkarni

LARGE AREA FESEM



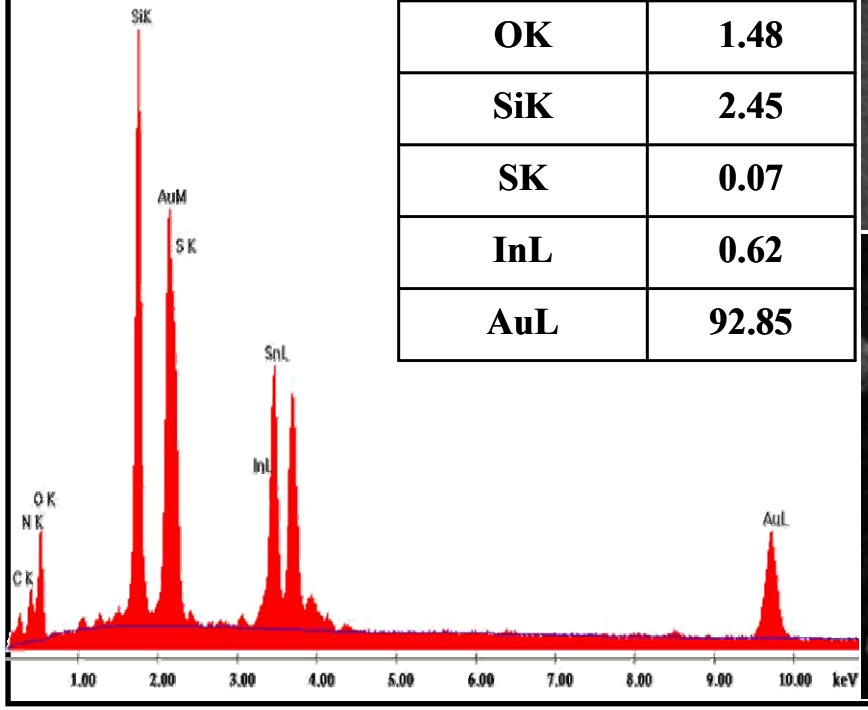
HR TEM-Images

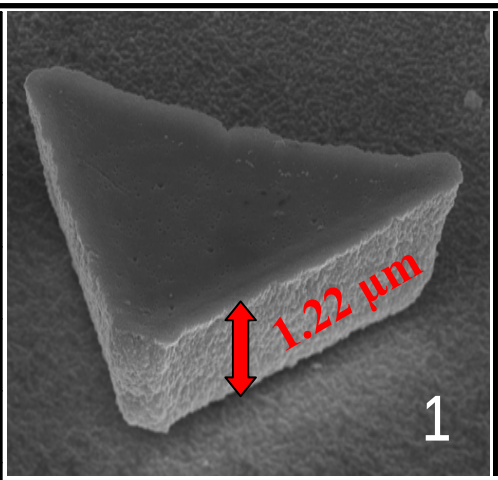


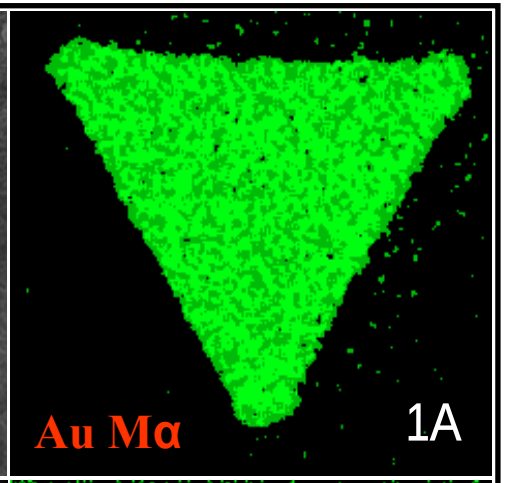


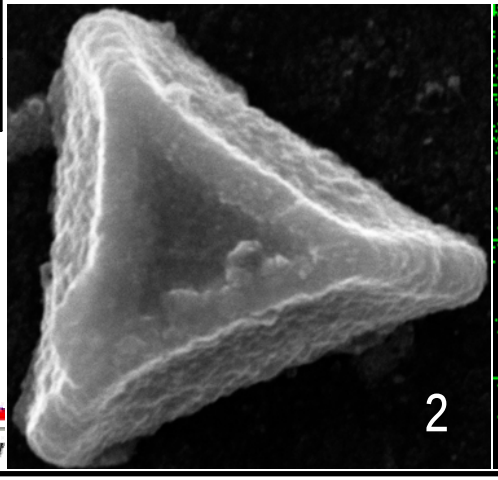
SEM-EDAX

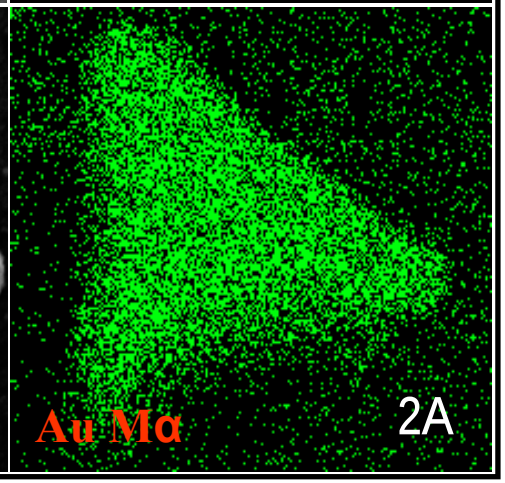
Elements	Wt%
CK	0.94
NK	1.58
OK	1.48
SiK	2.45
SK	0.07
InL	0.62
AuL	92.85



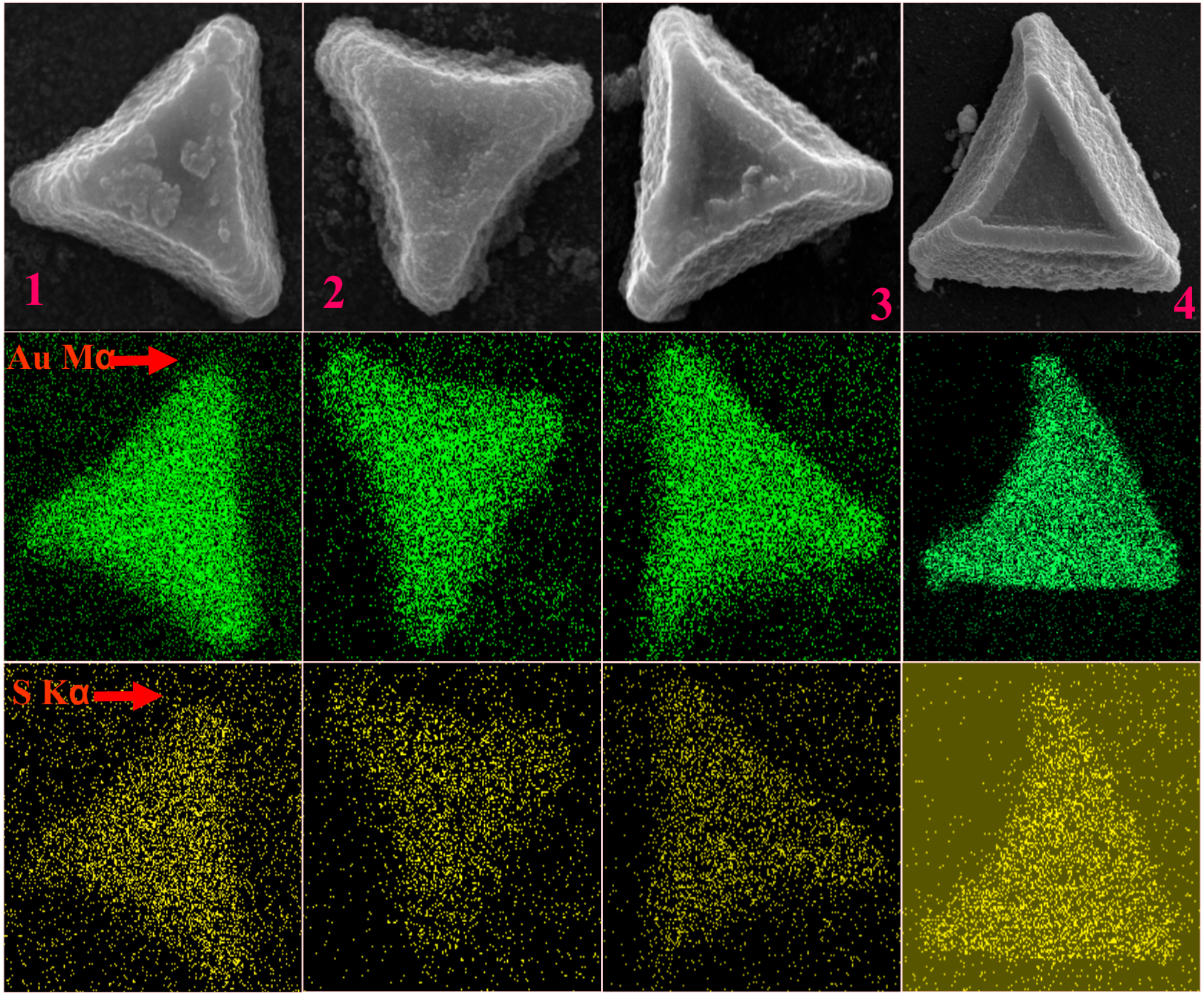




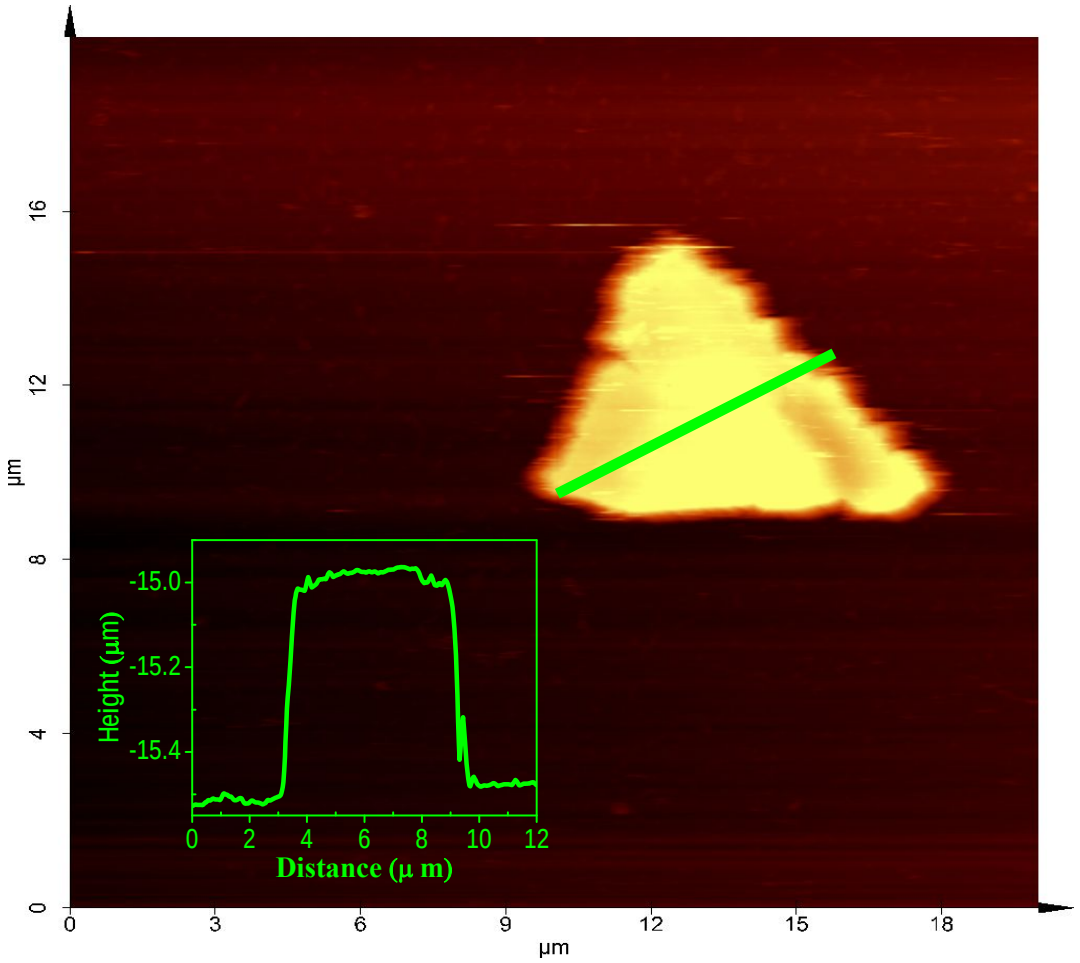




CRYSTAL GROWTH MECHANISM

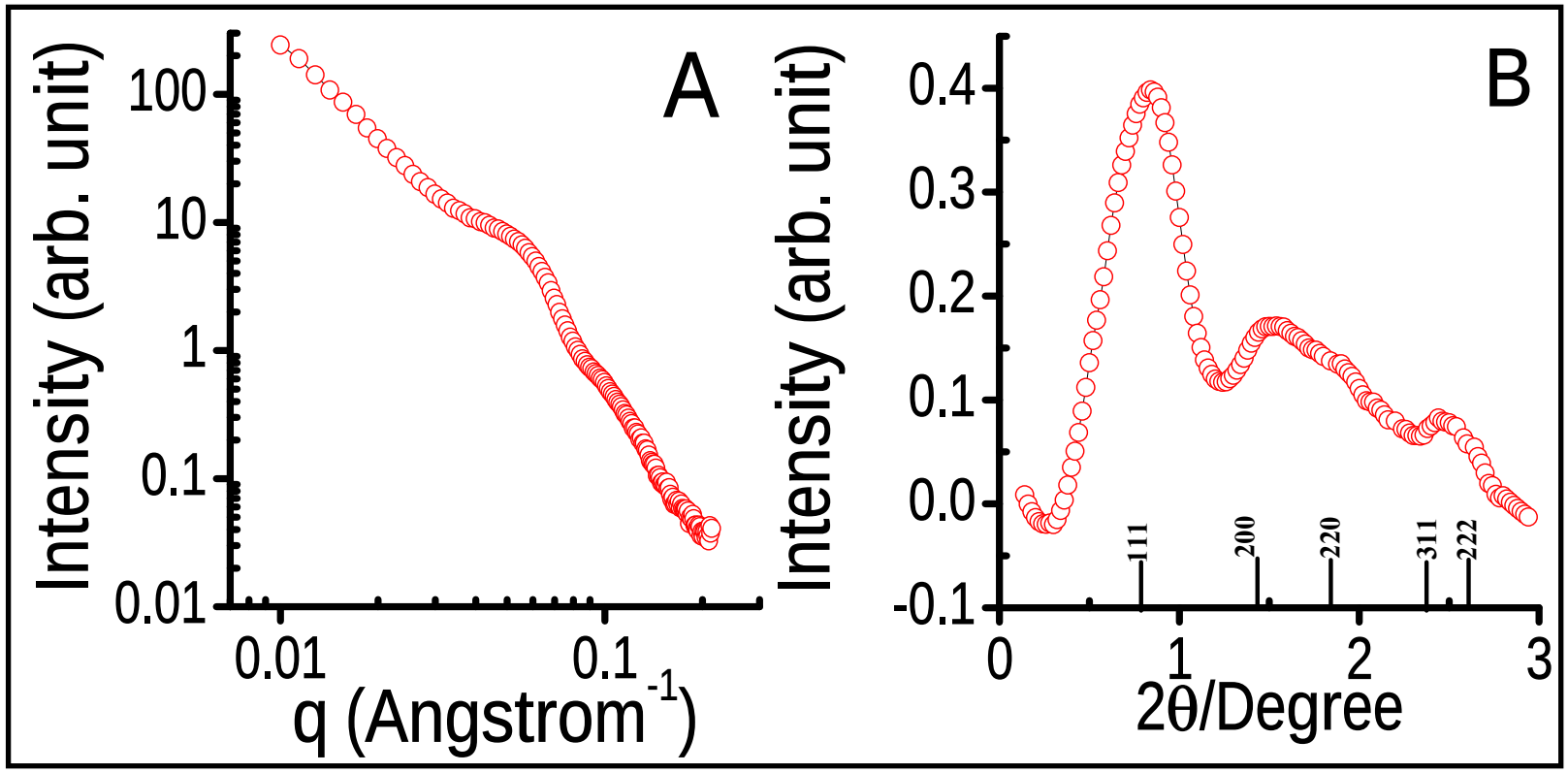


OPTICAL IMAGE


0
4
8
12
16
µm
0
3
6
9
12
15
18
µm
-15.0
-15.2
-15.4
Height (µm)
0
2
4
6
8
10
12
Distance (µ m)

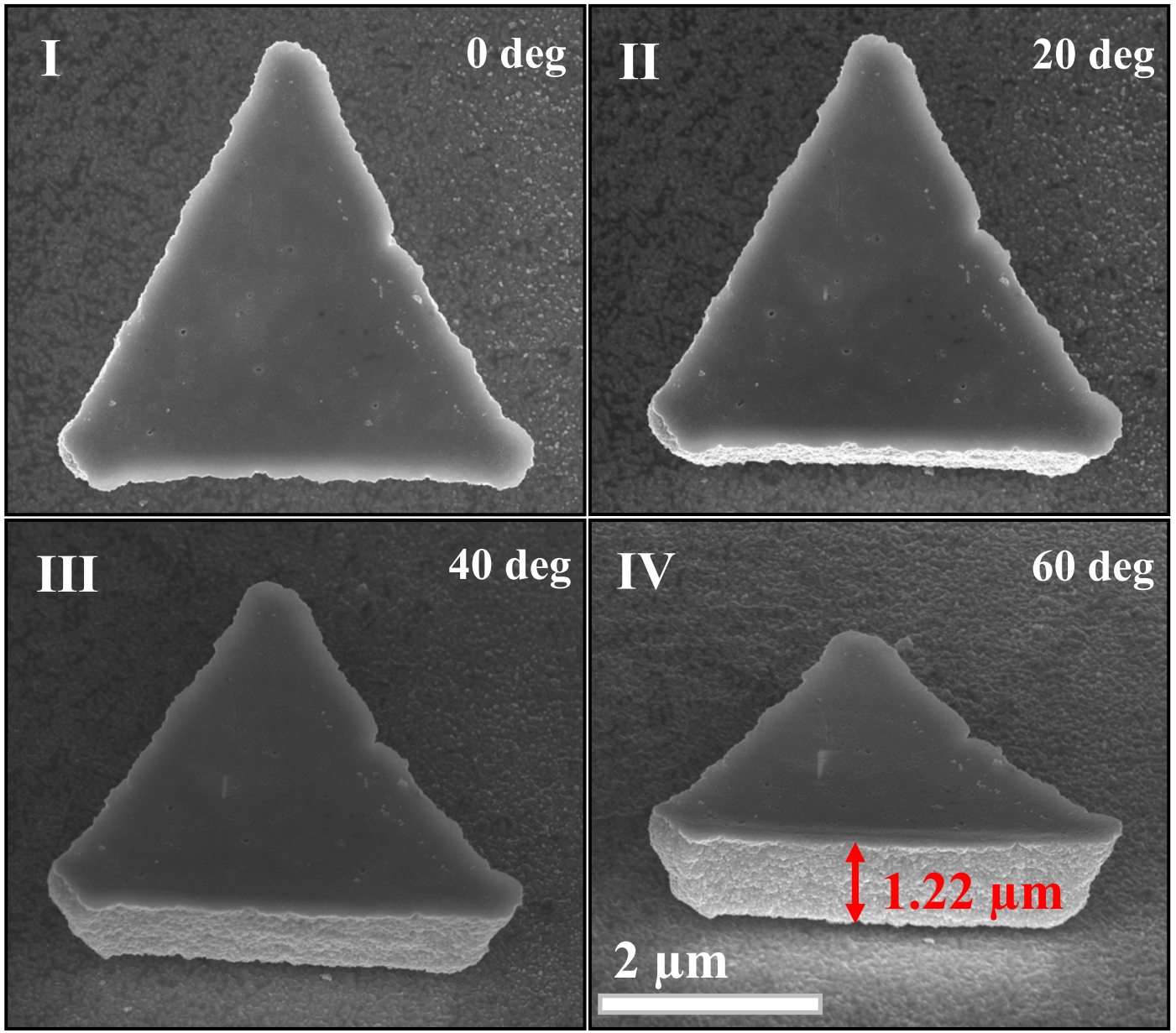
AFM IMAGE

SAXS

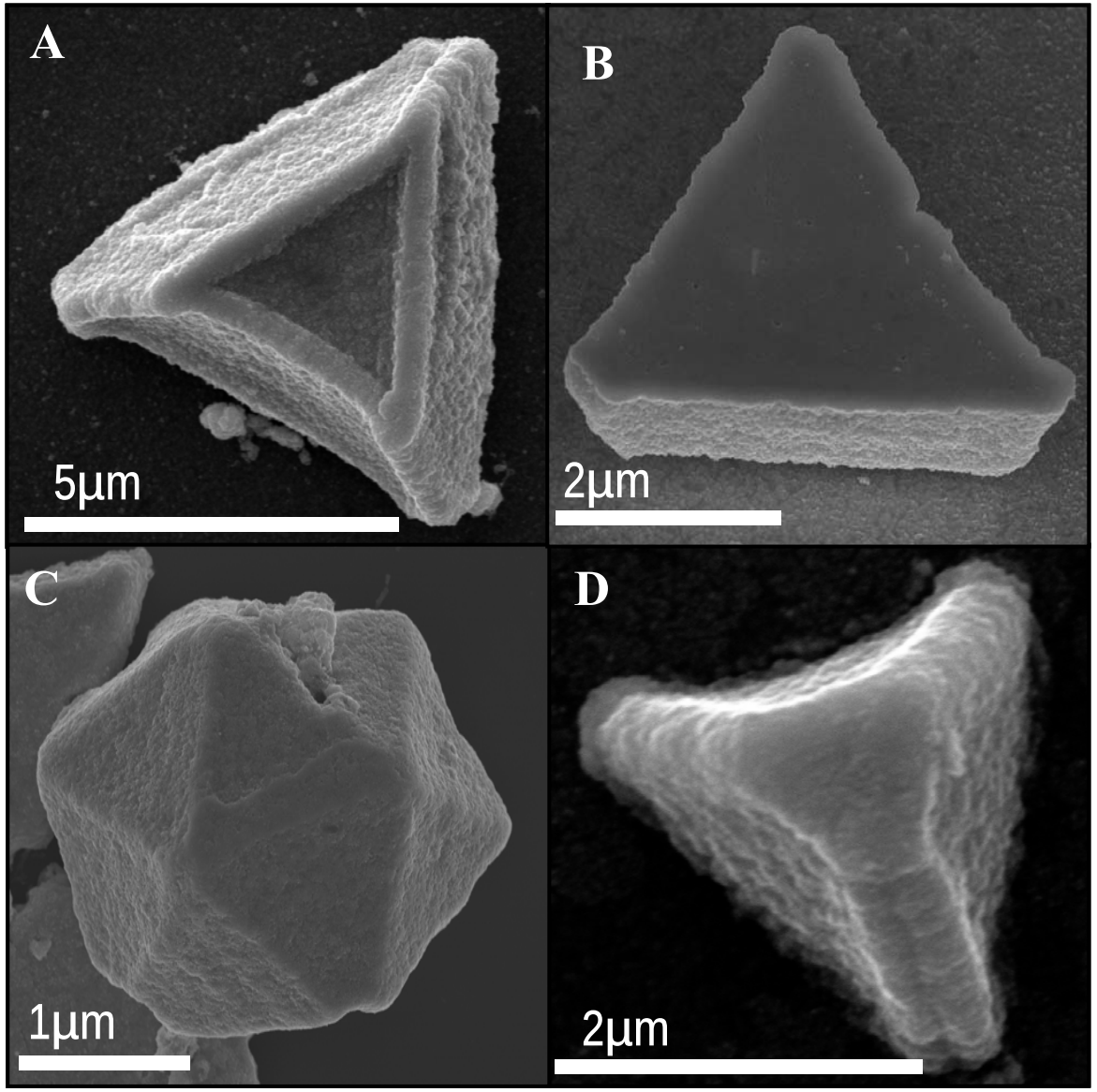


Measured in Prof. C. N. R. Rao's Lab

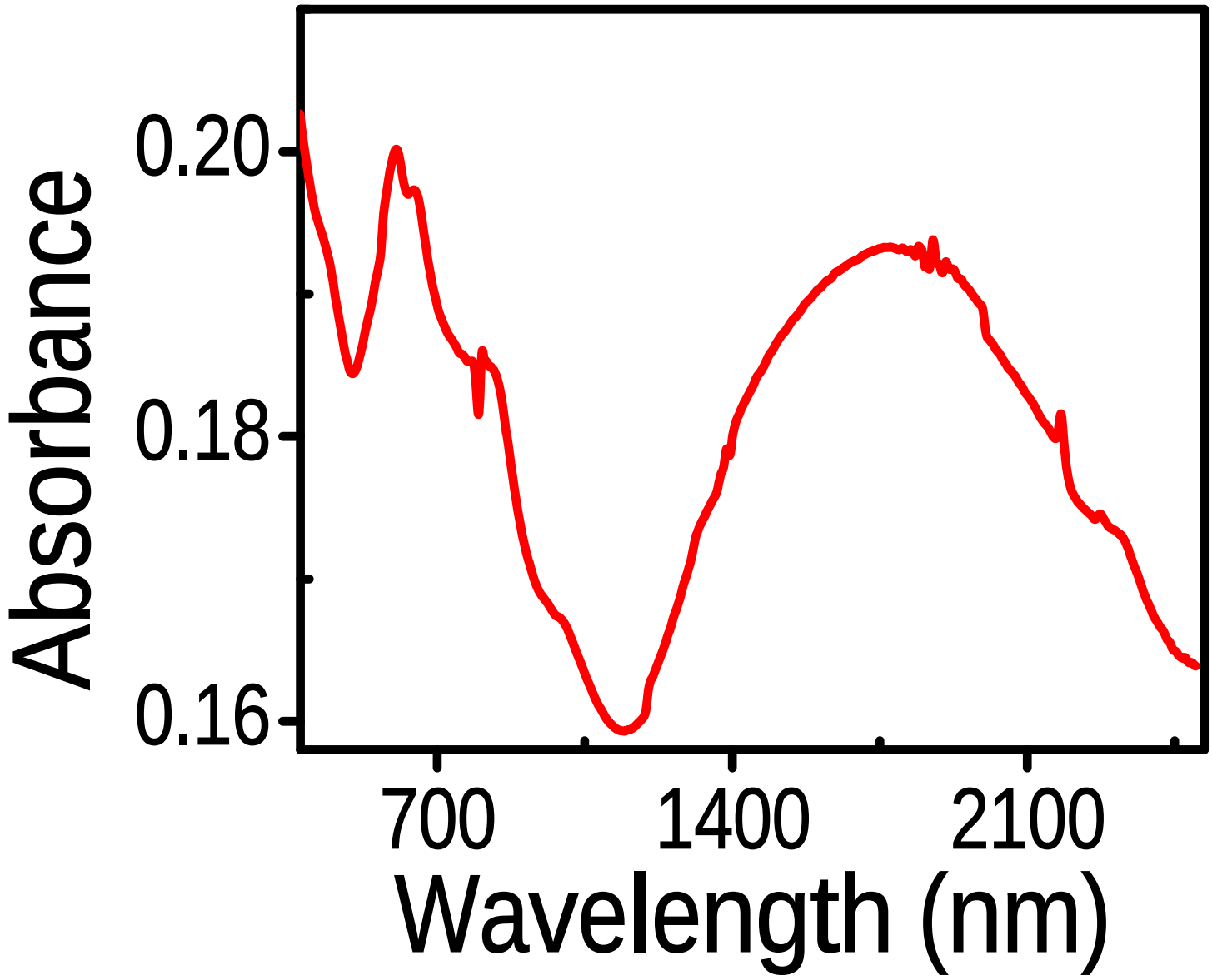
CRYSTAL THICKNESS



OTHER MORPHOLOGIES

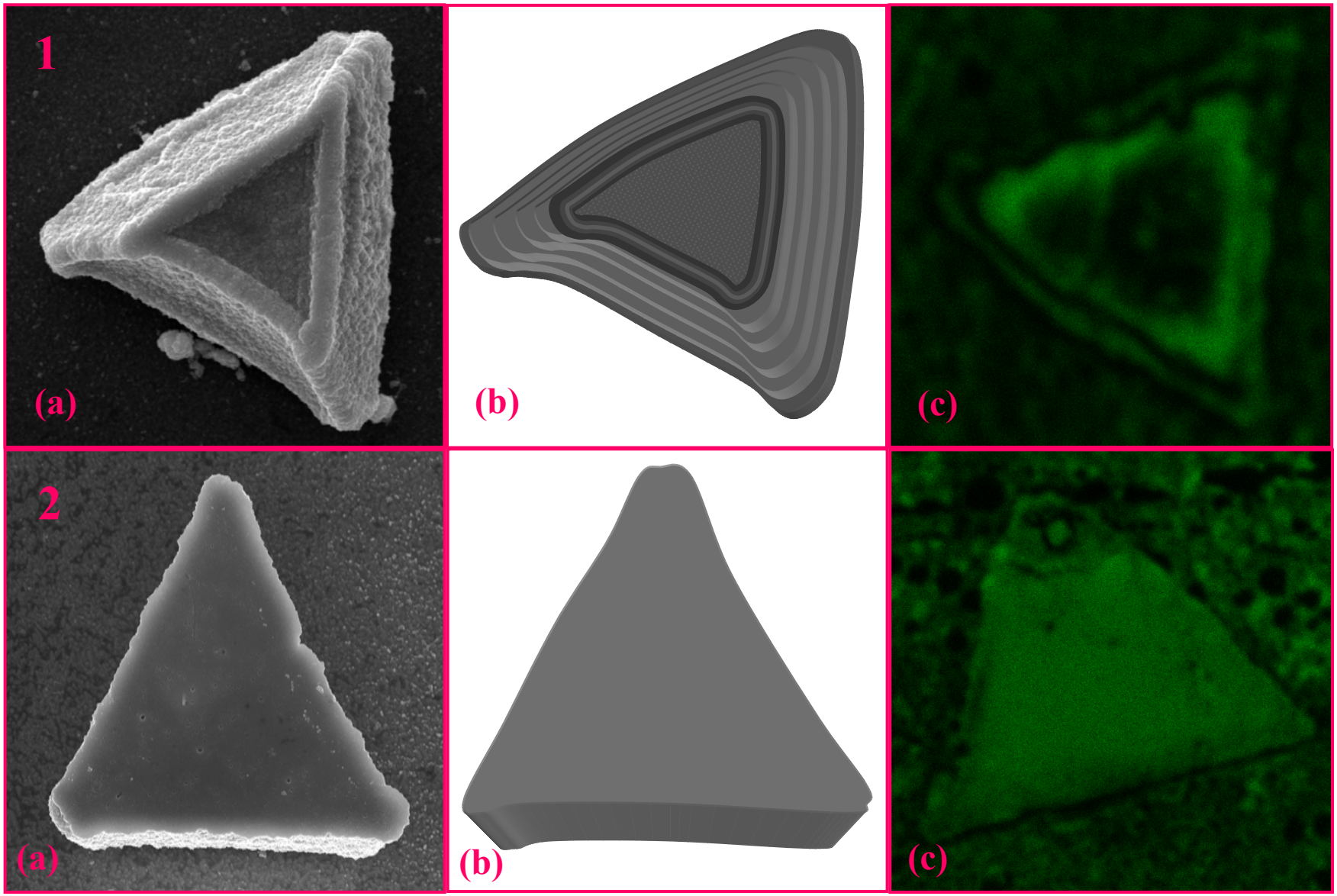


Inter-Plasmon coupling

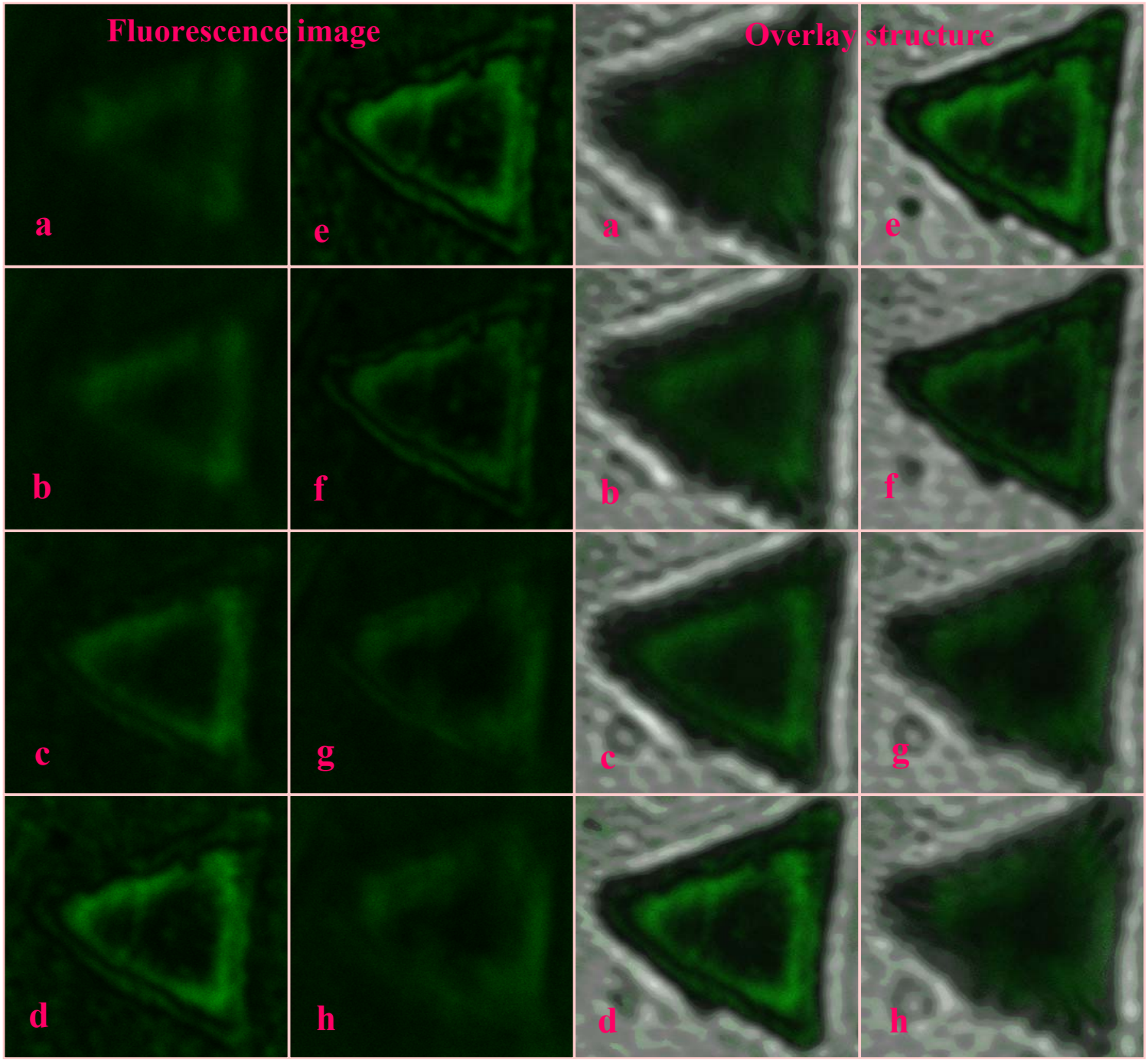


NIR ABSORPTION

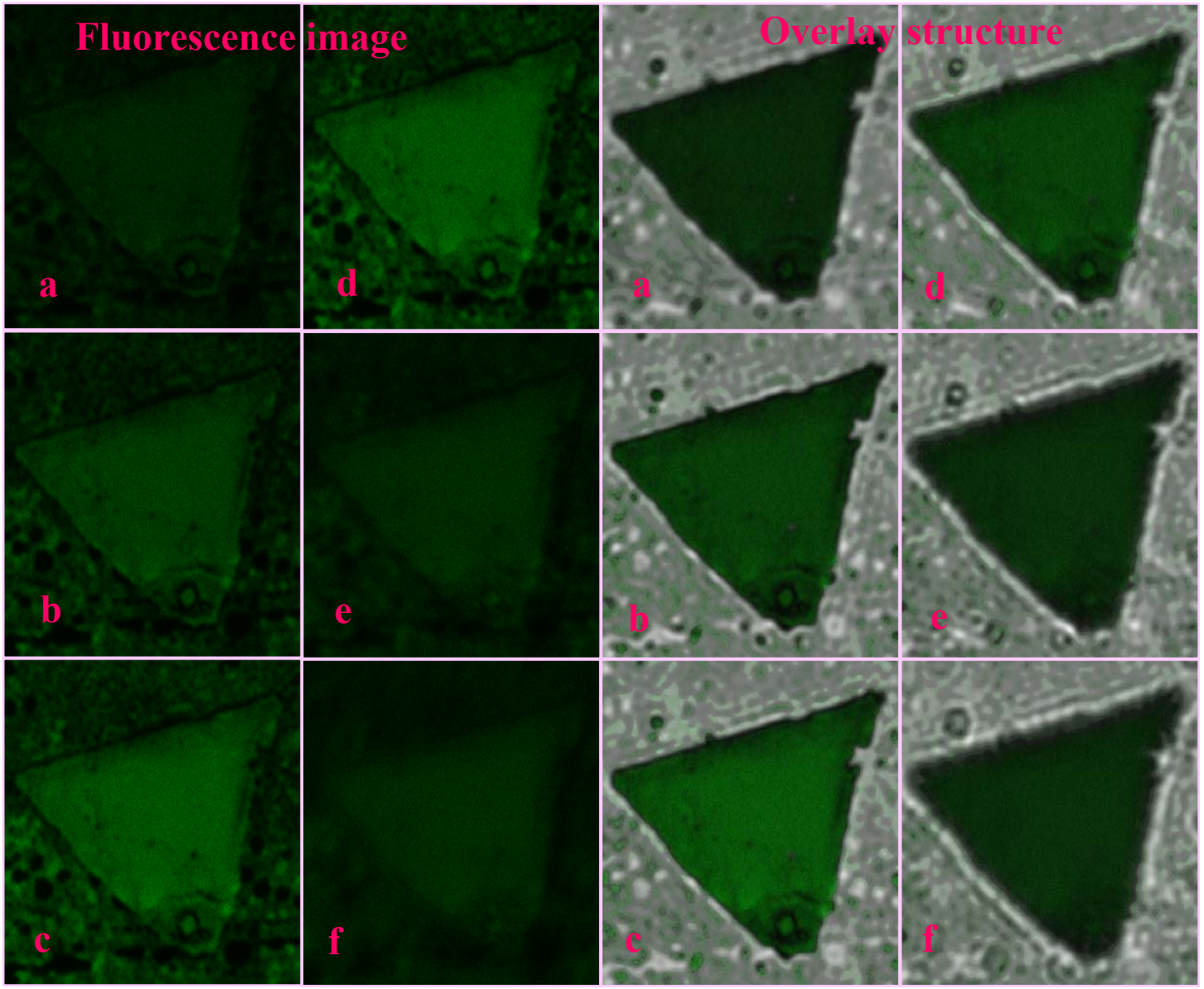
Investigation of crystal fluorescence

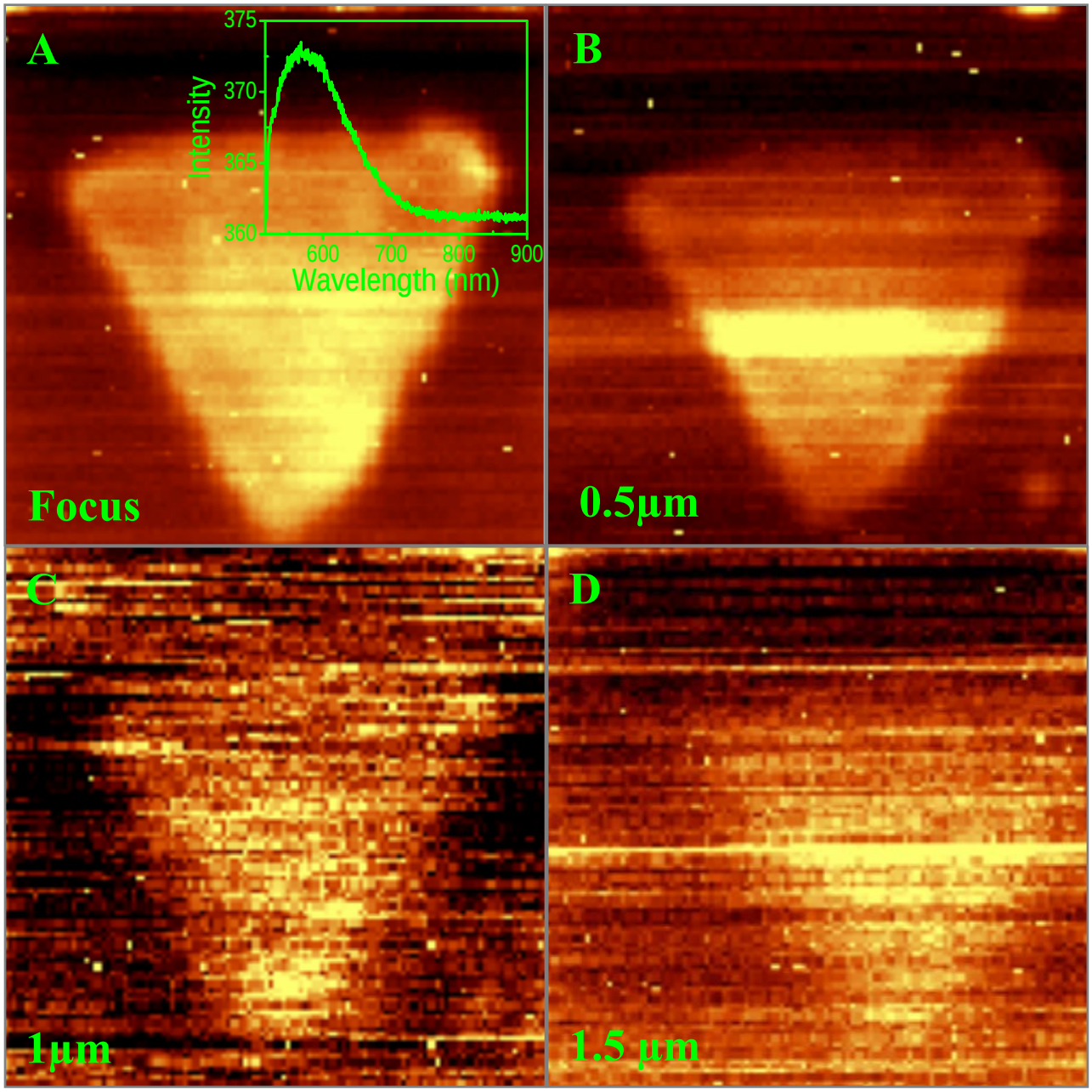


CRYSTAL 1



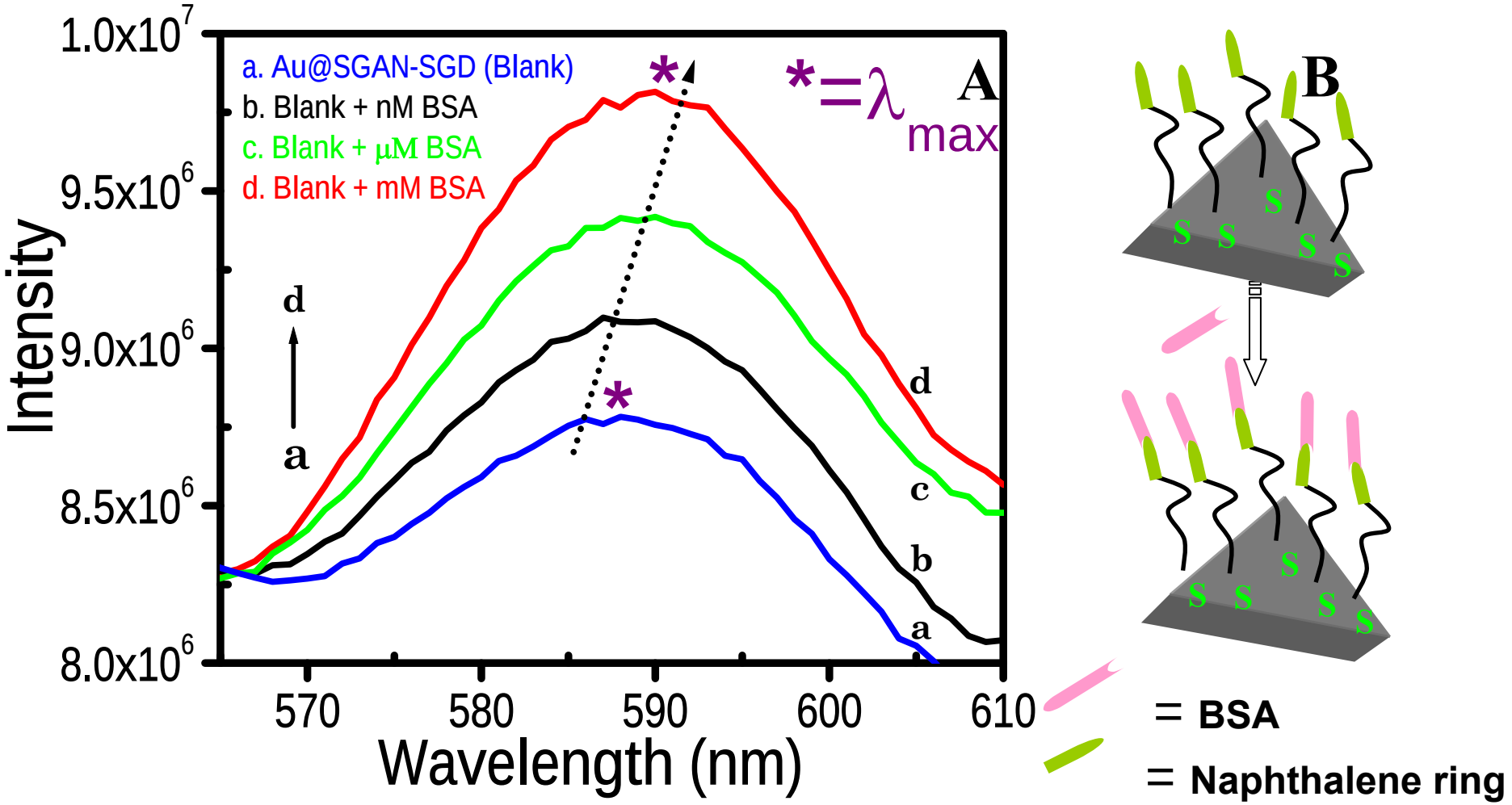
CRYSTAL 2



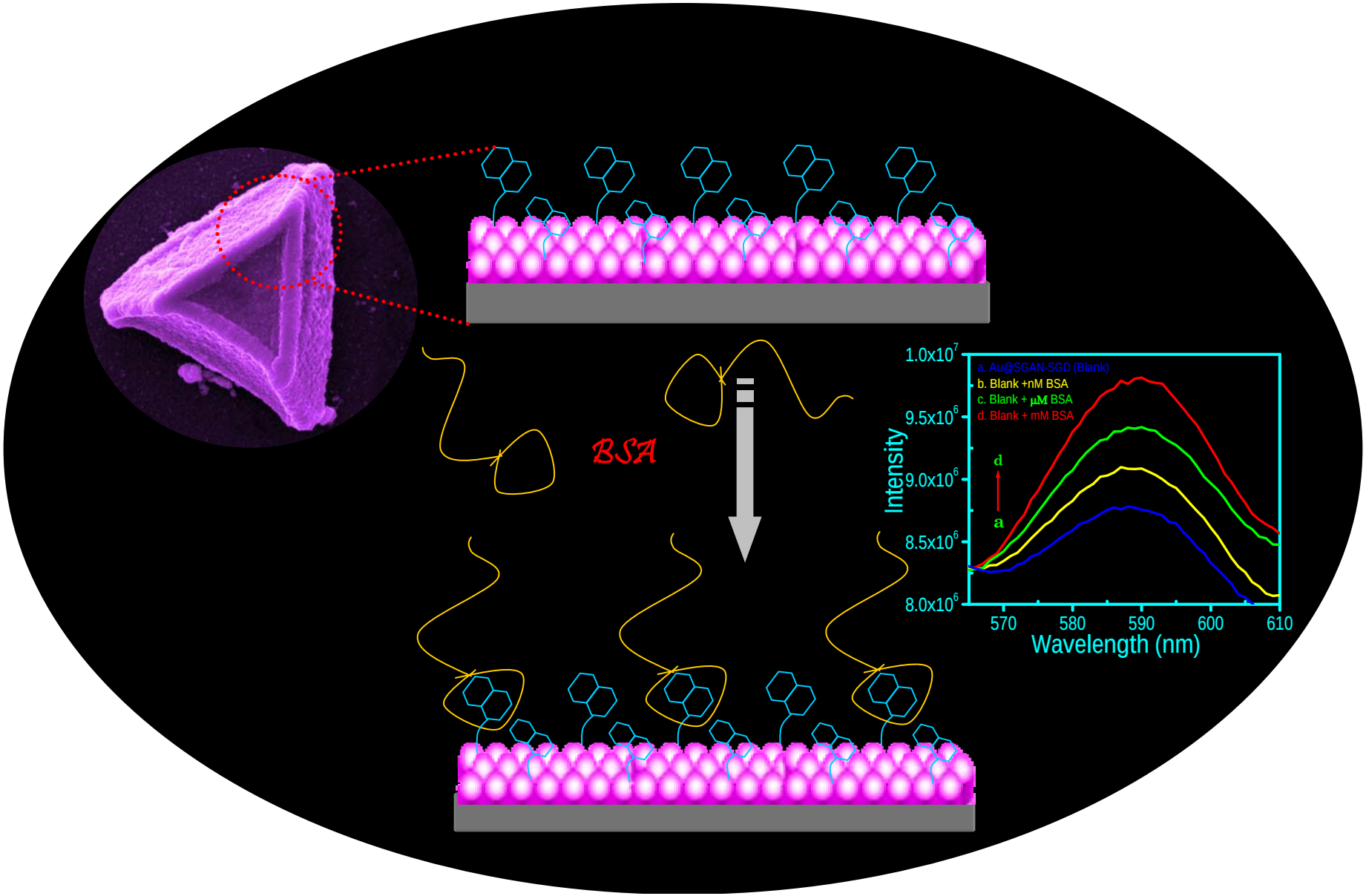


CONFOCAL FLUO- IMAGES

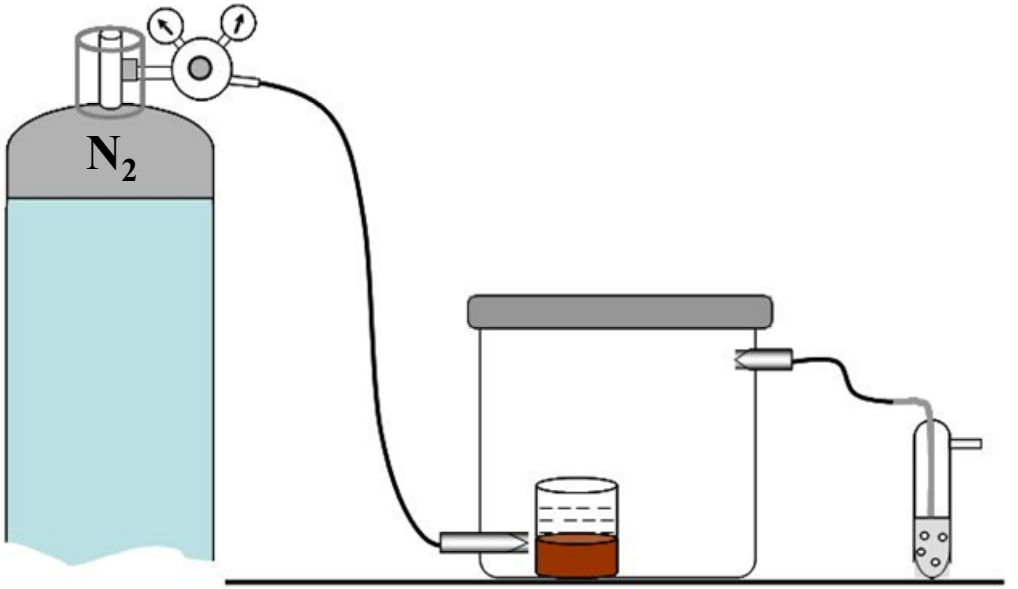
Selective detection of BSA using dansylglutathione SLs

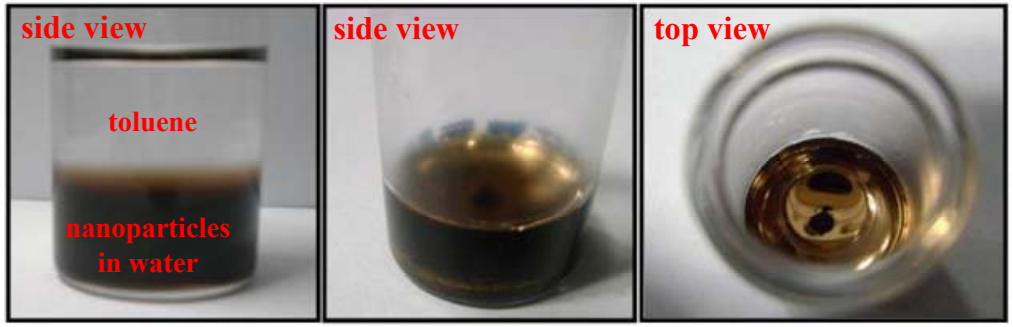


Mechanism of selective detection



Interfacial synthesis – superlattices in one day





Stage 1 Stage 2 Stage 3

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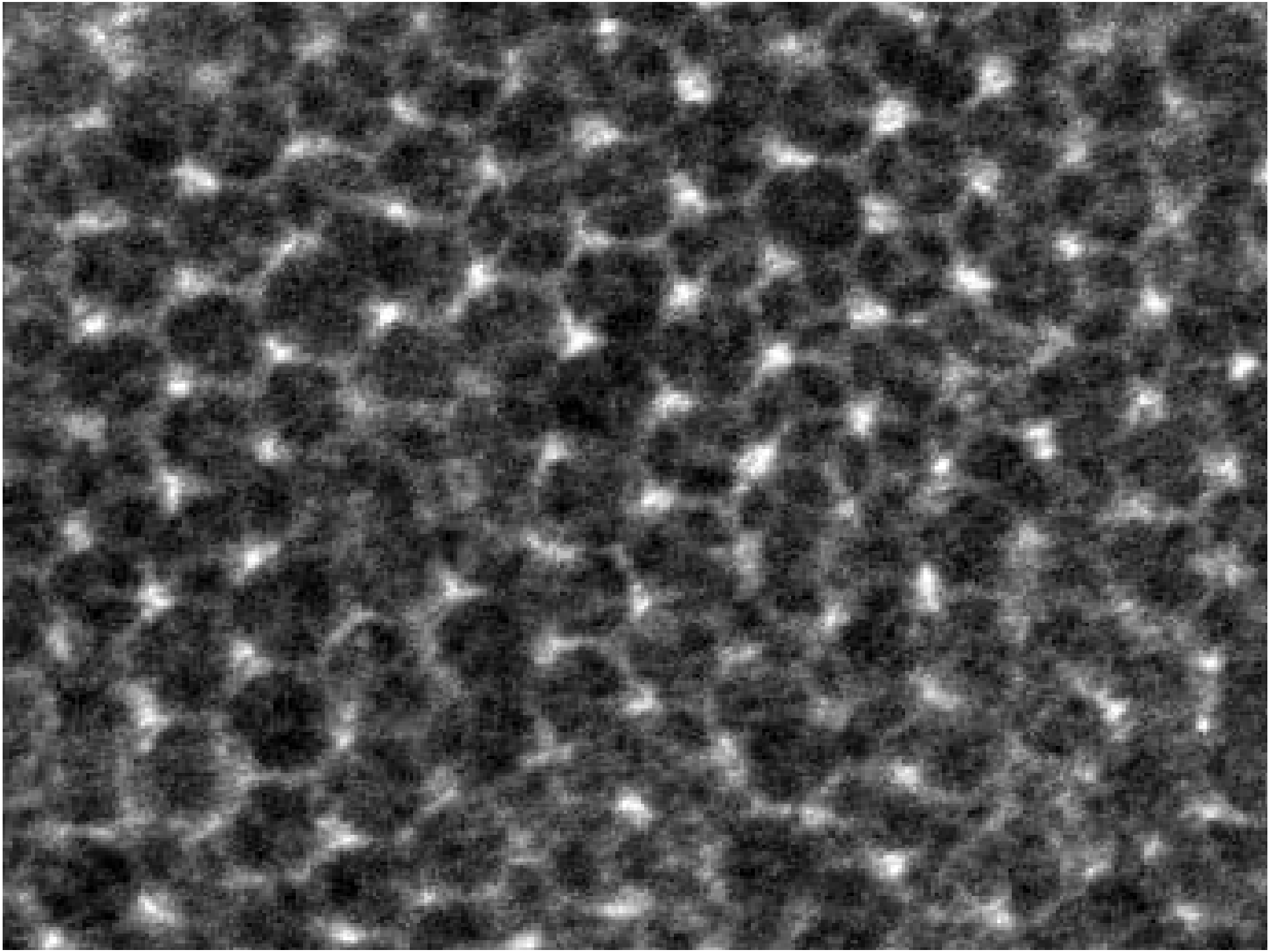
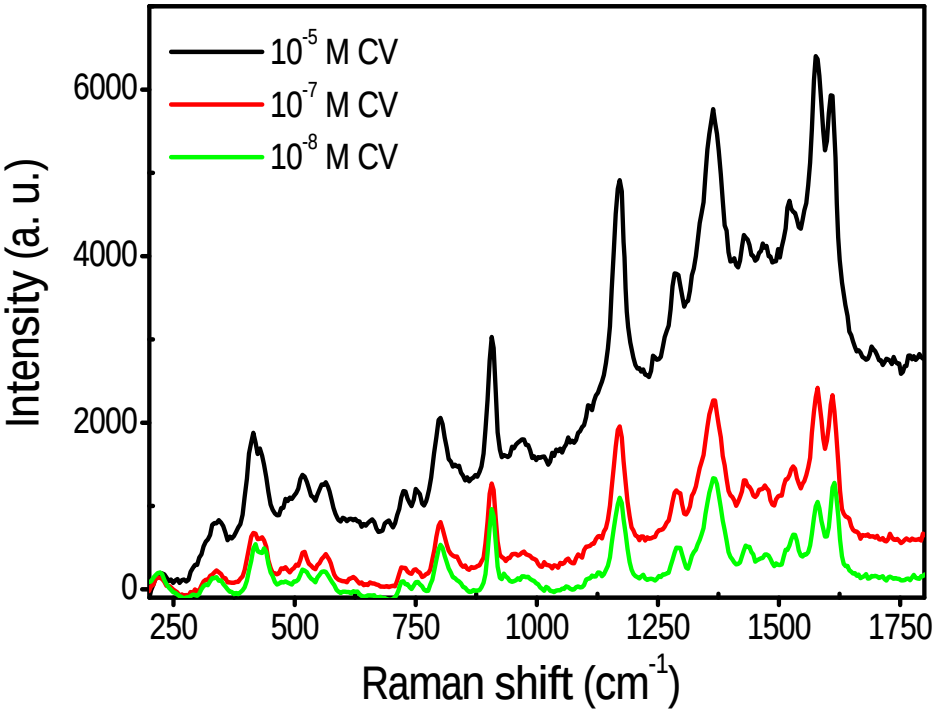
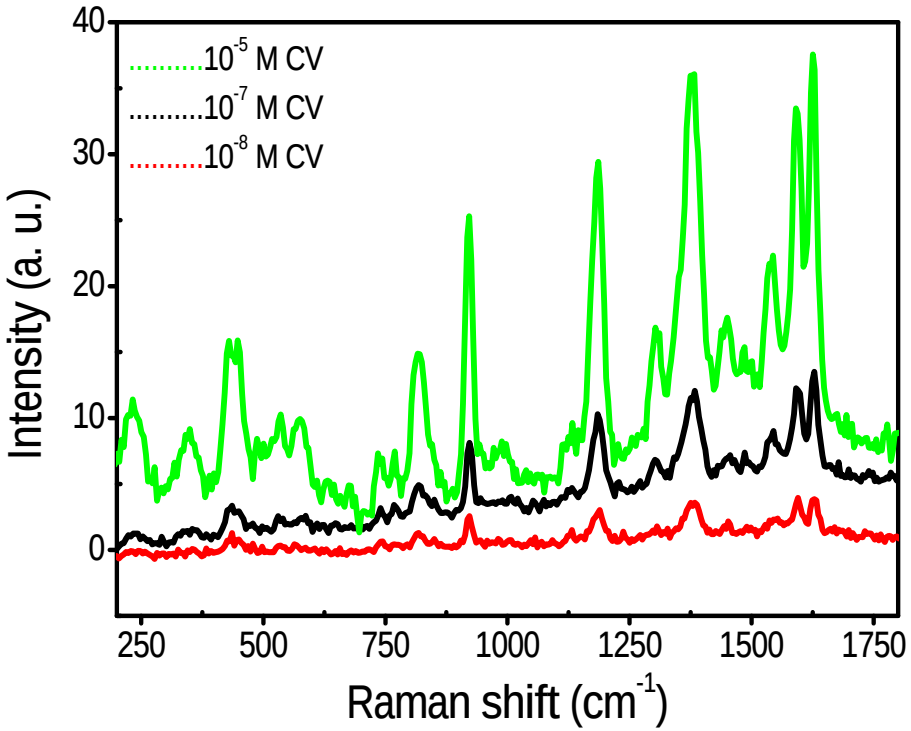
PHOTOGRAPH OF THE SET-UP



SERS- Crystal violet as an analyte

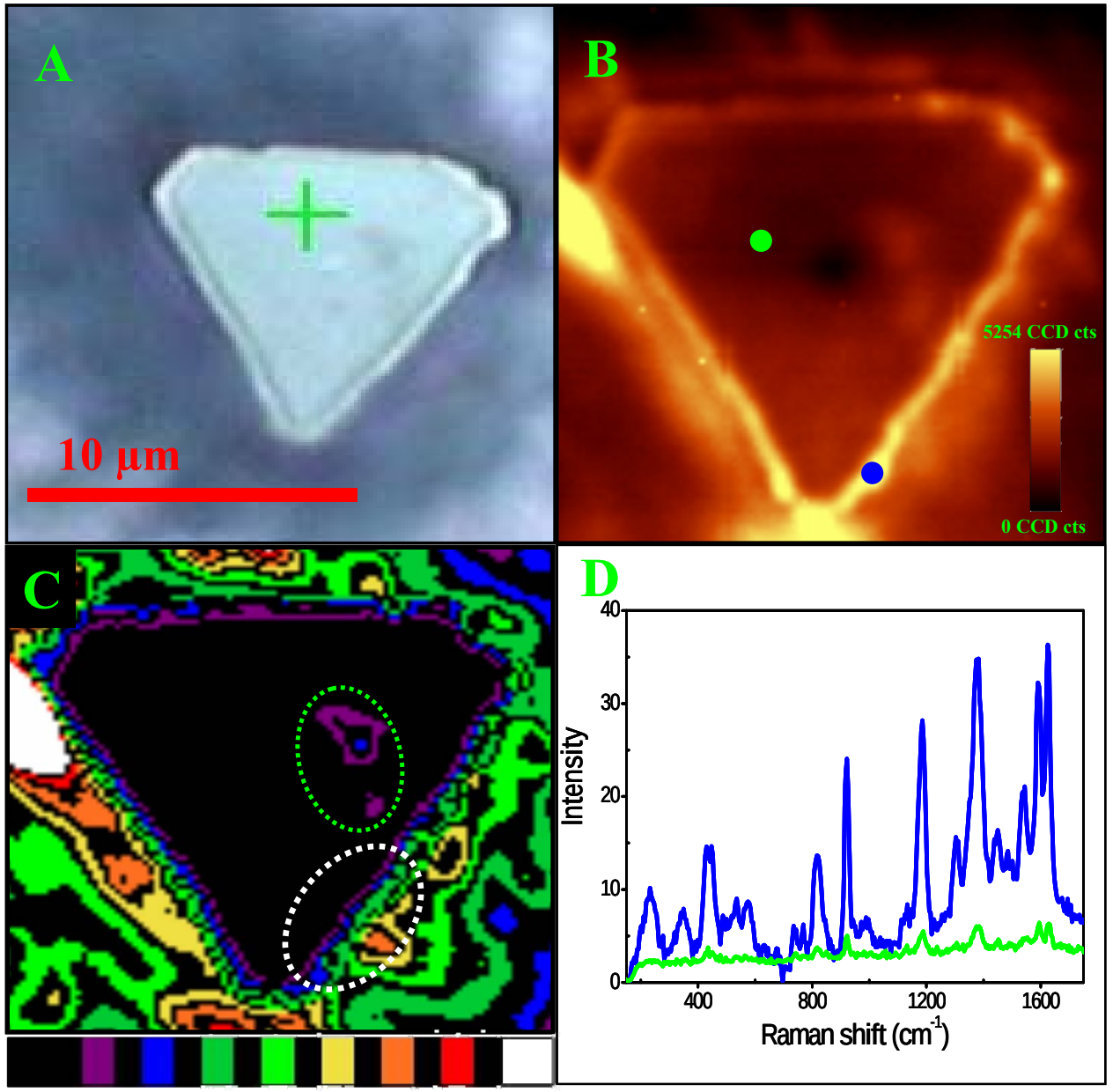


Au@MSA



Au@SGAN

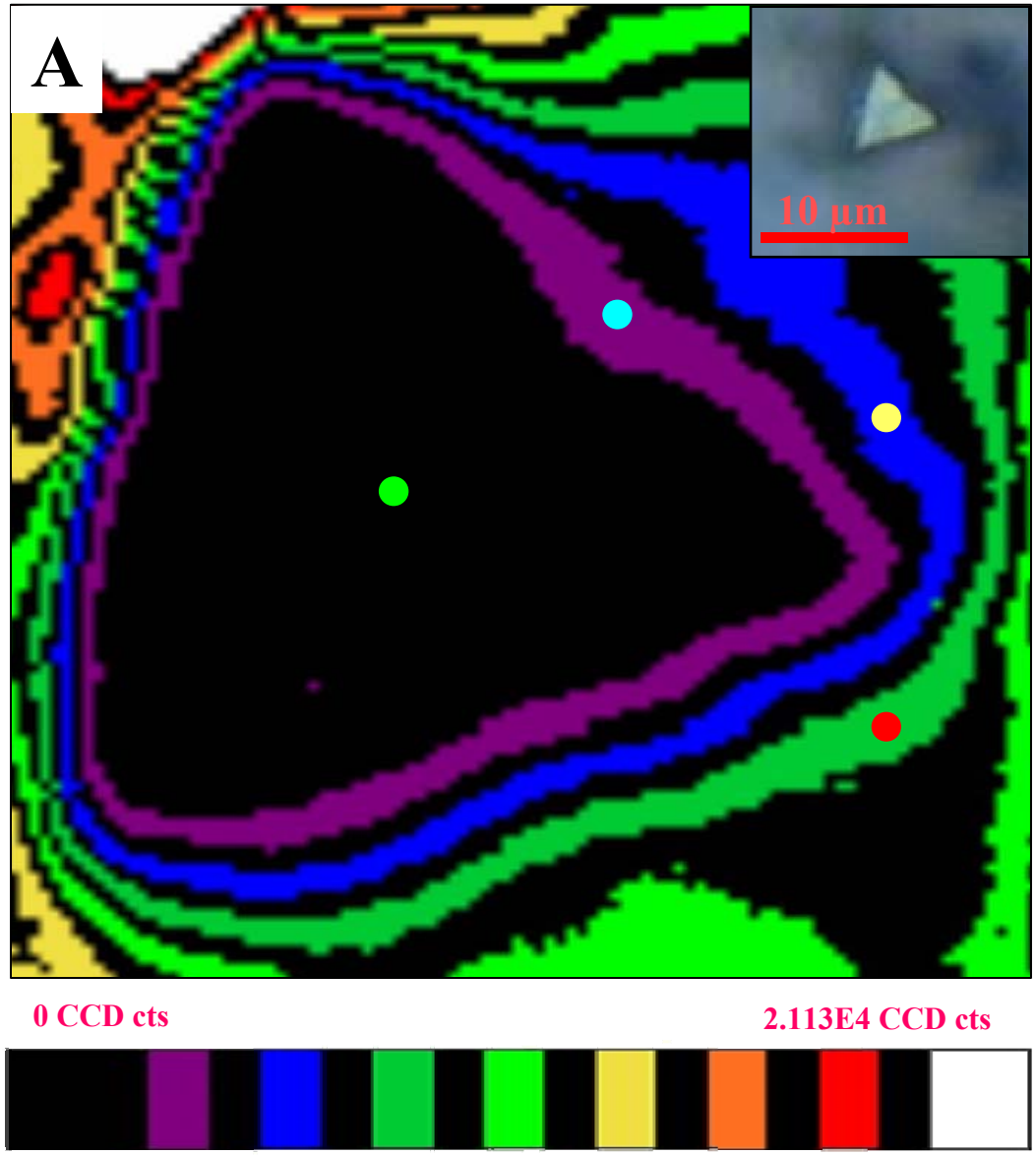
RAMAN MAPPING



Au@MSA SL Triangles

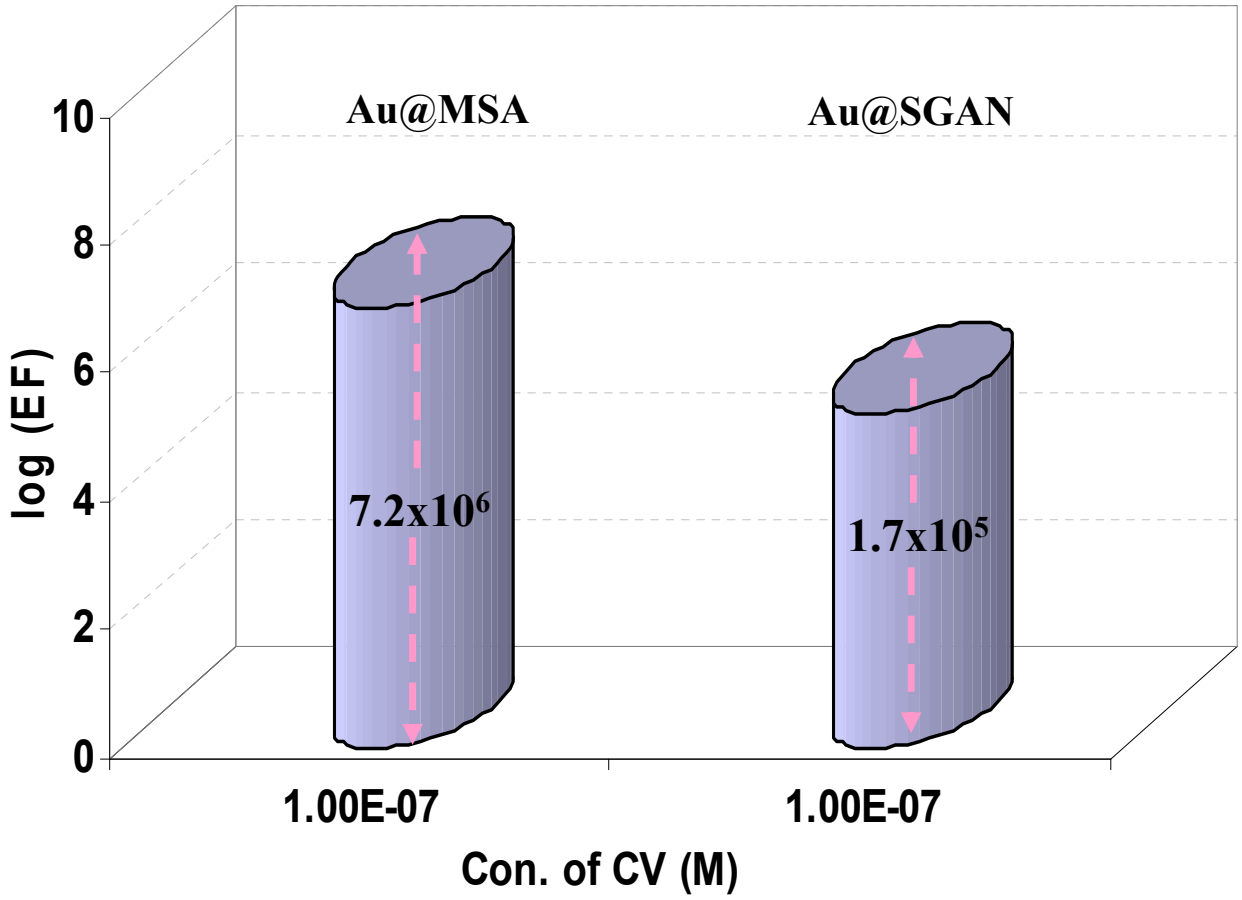
E. S. Shibu and T. Pradeep, Submitted

COLOR CODED RAMAN IMAGE

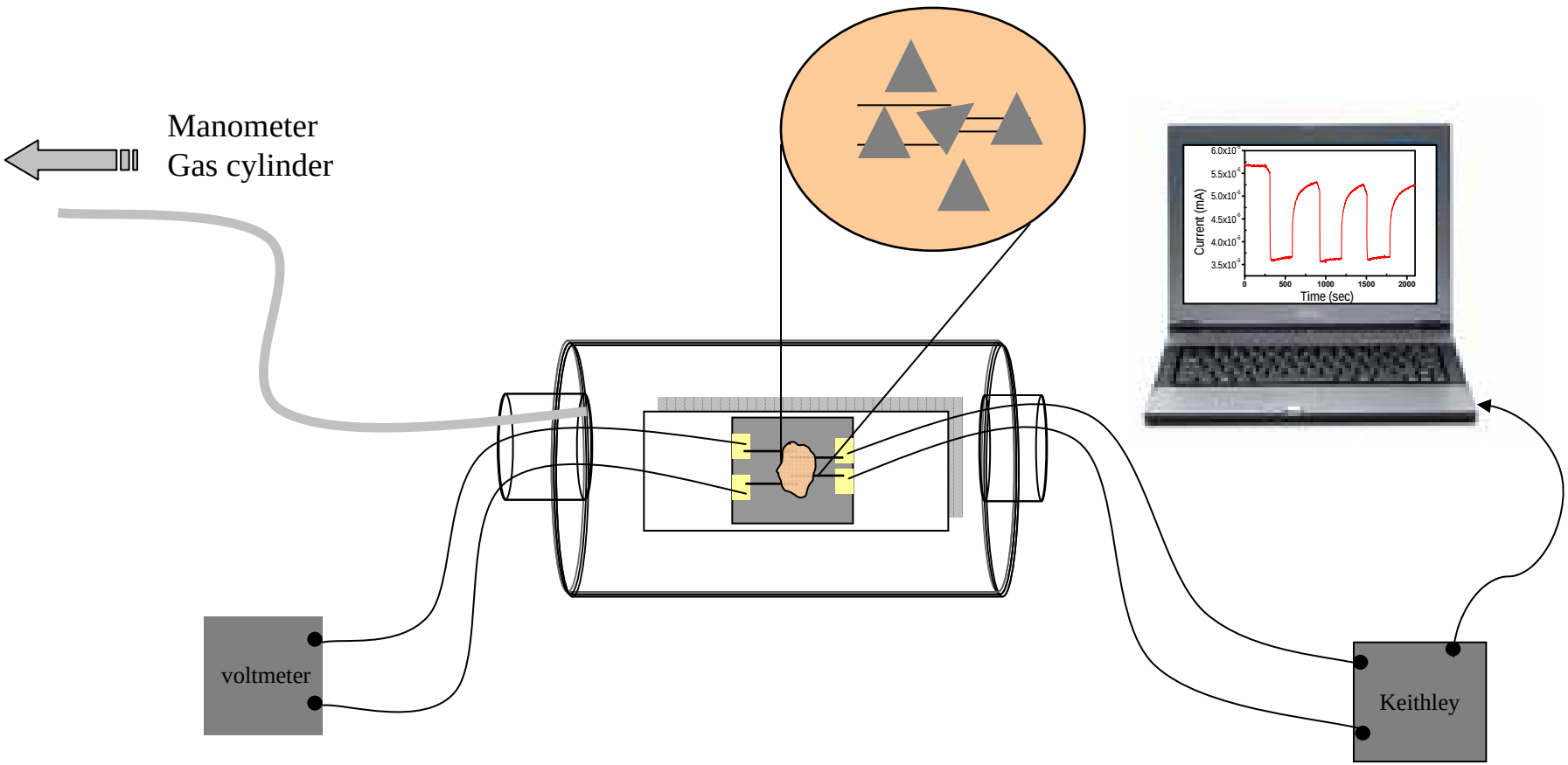


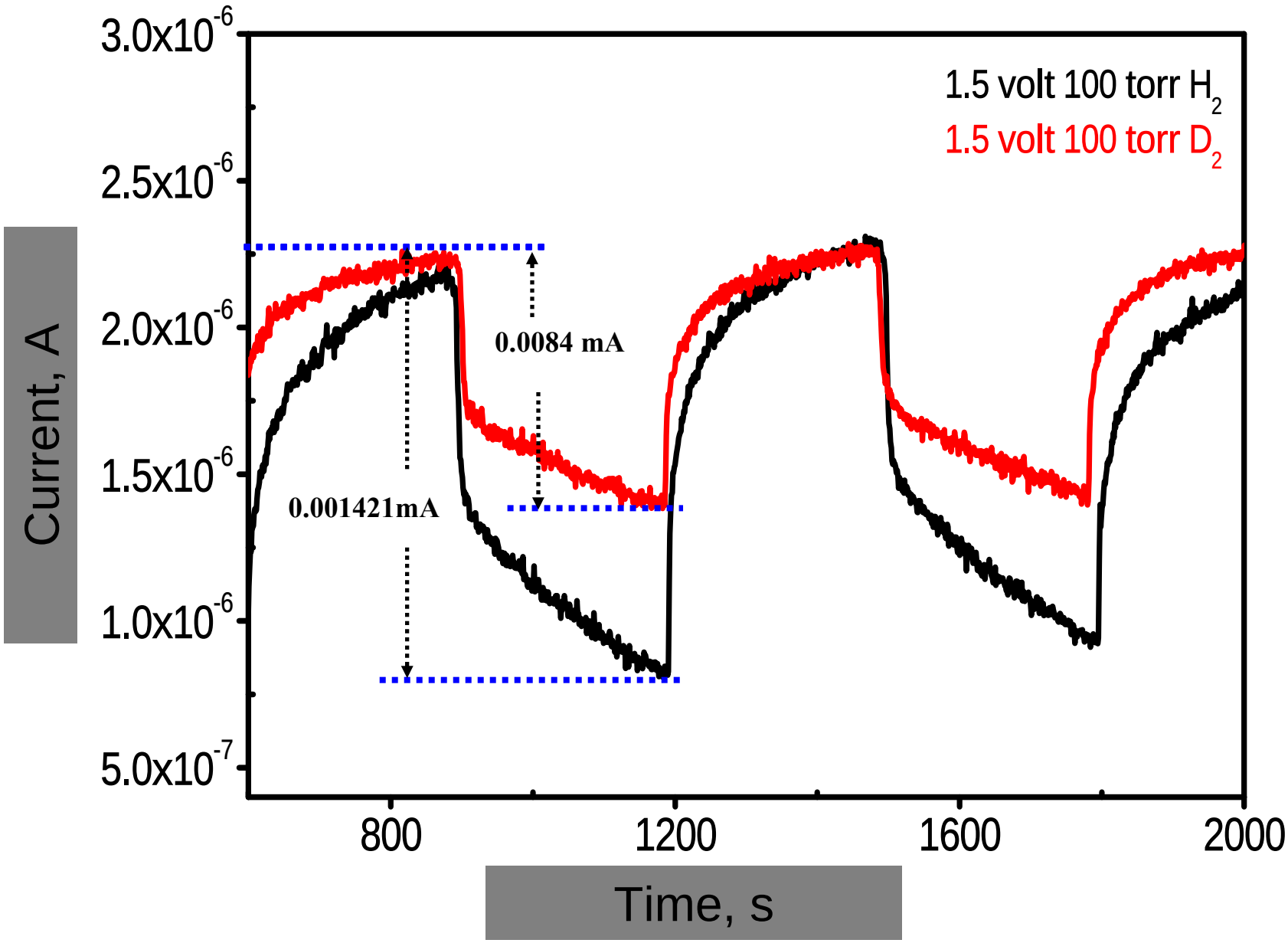
Au@SGAN SL triangle

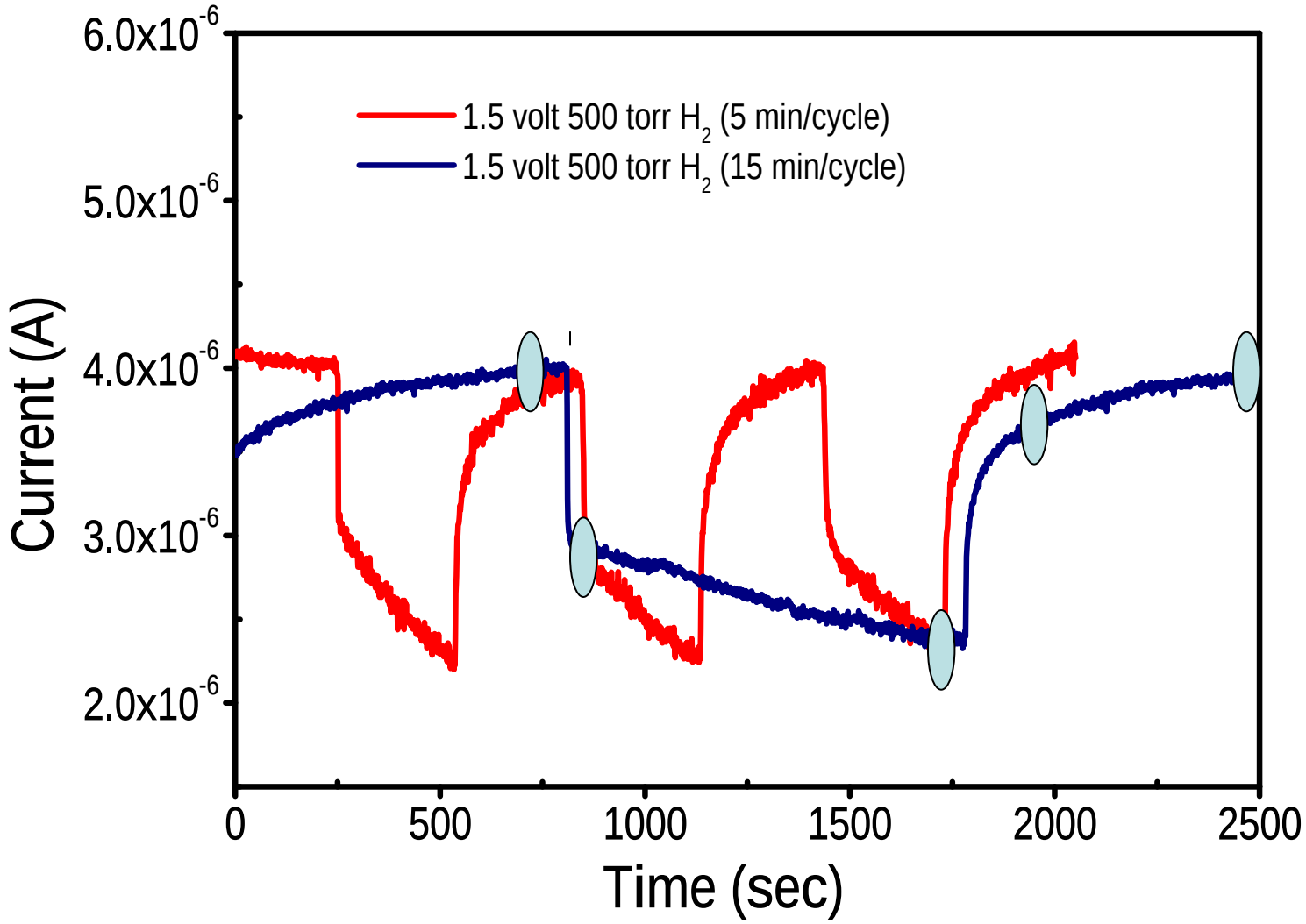
ENHANCEMENT FACTOR



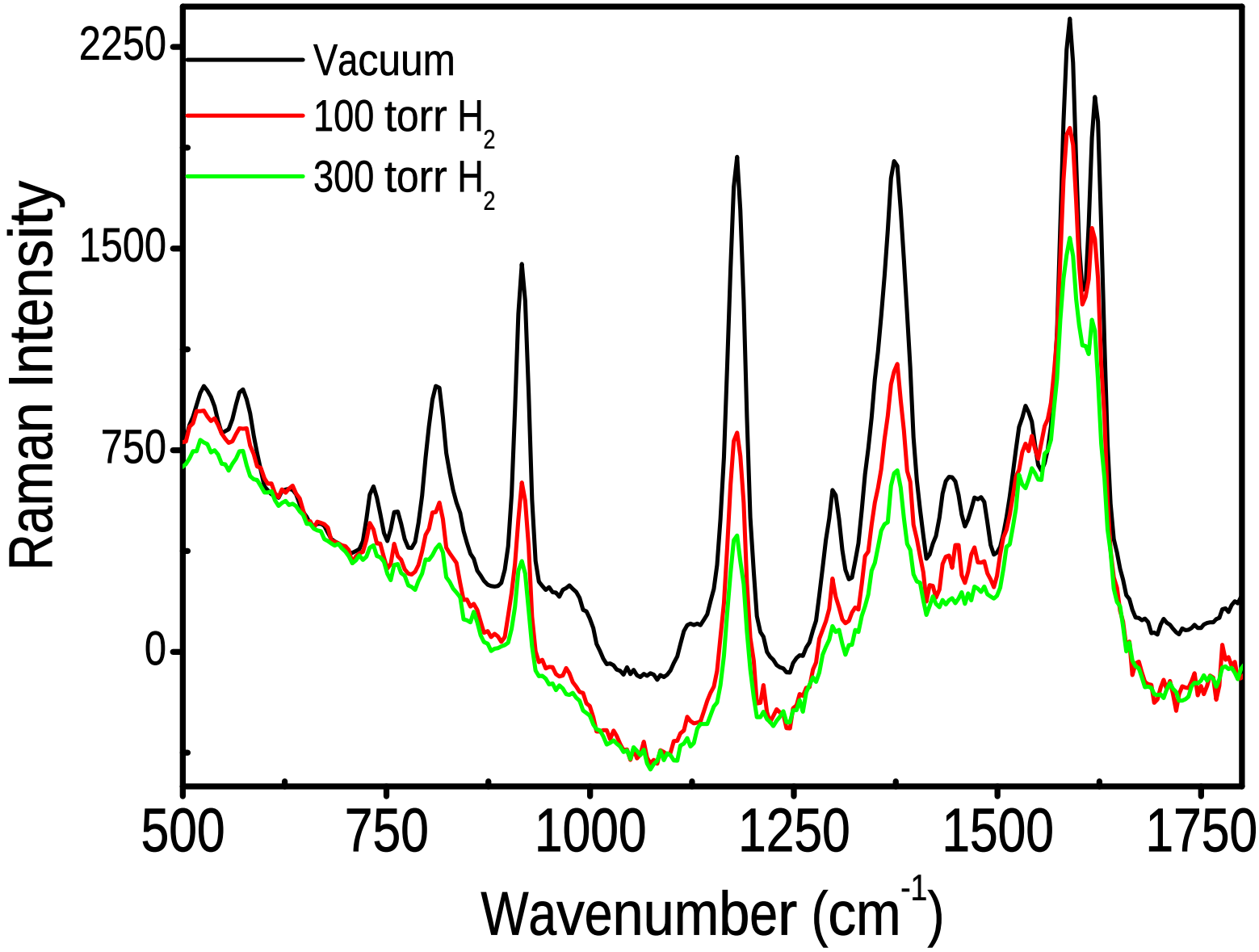
Superlattices as gas sensors

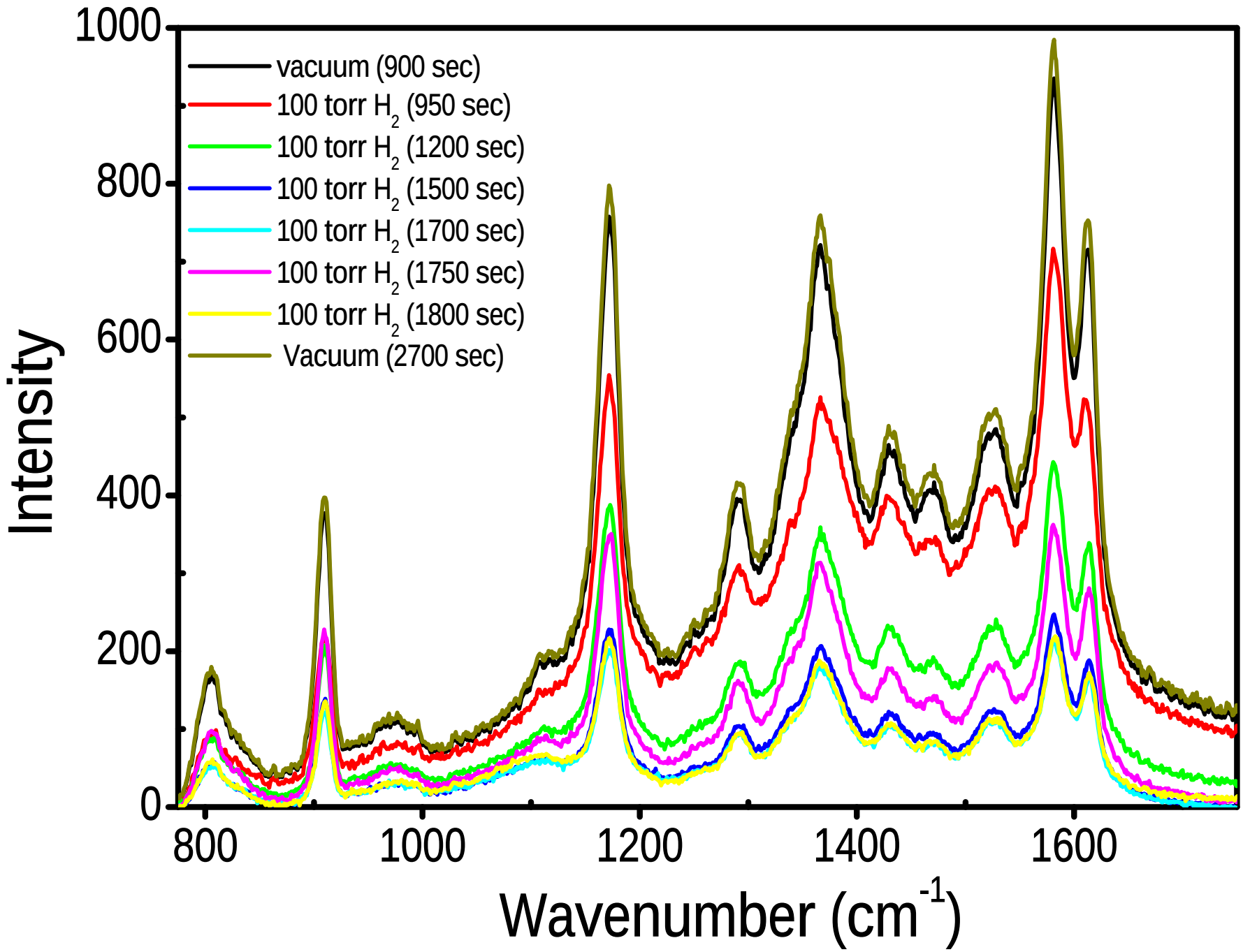

Manometer
Gas cylinder
voltmeter
Keithley
Current (mA)
Time (sec)

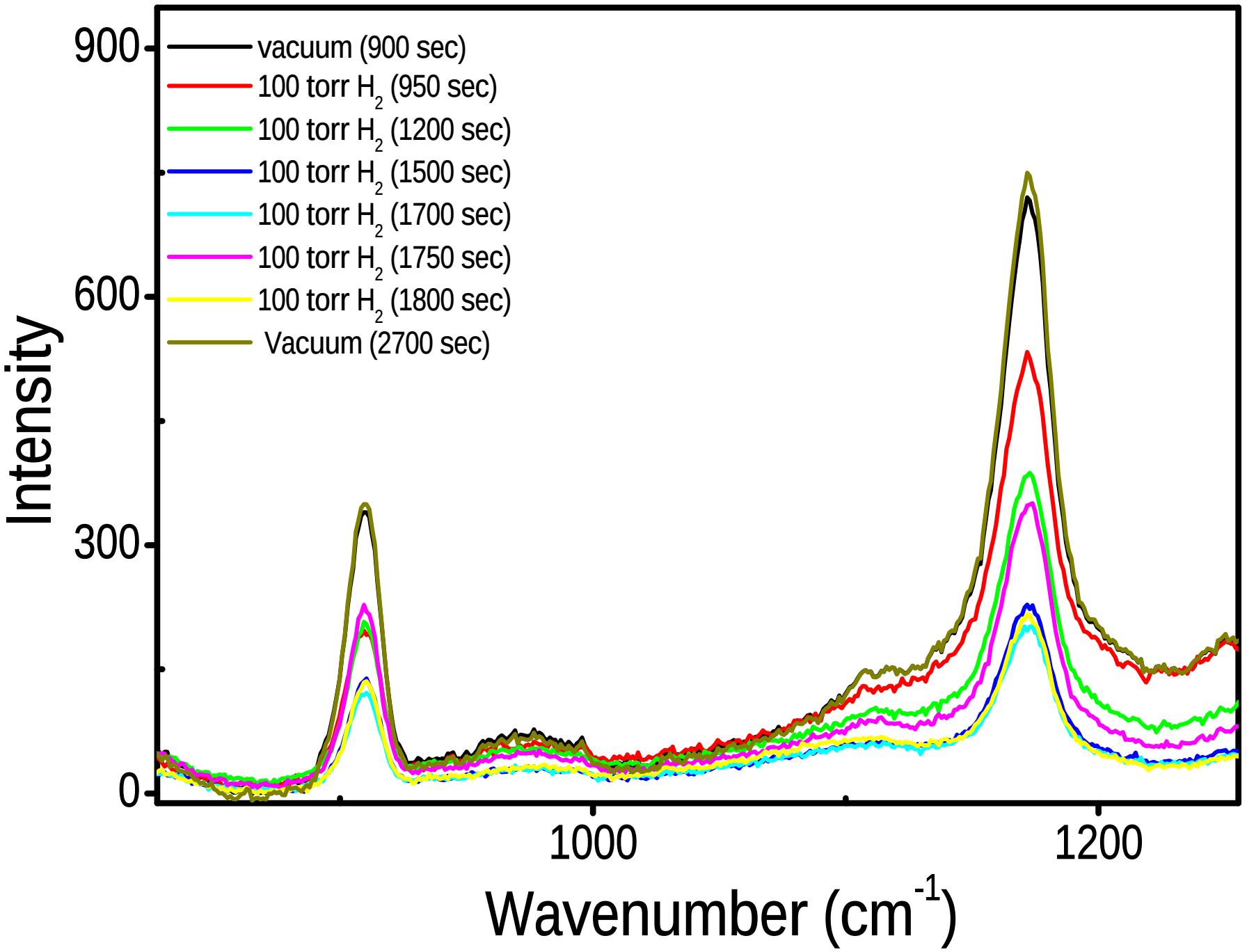

3.0x10-6
2.5x10-6
2.0x10-6
1.5x10-6
1.0x10-6
5.0x10-7
Current, A
800
1200
1600
2000
Time, s
1.5 volt 100 torr H2
1.5 volt 100 torr D2
0.0084 mA
0.001421mA

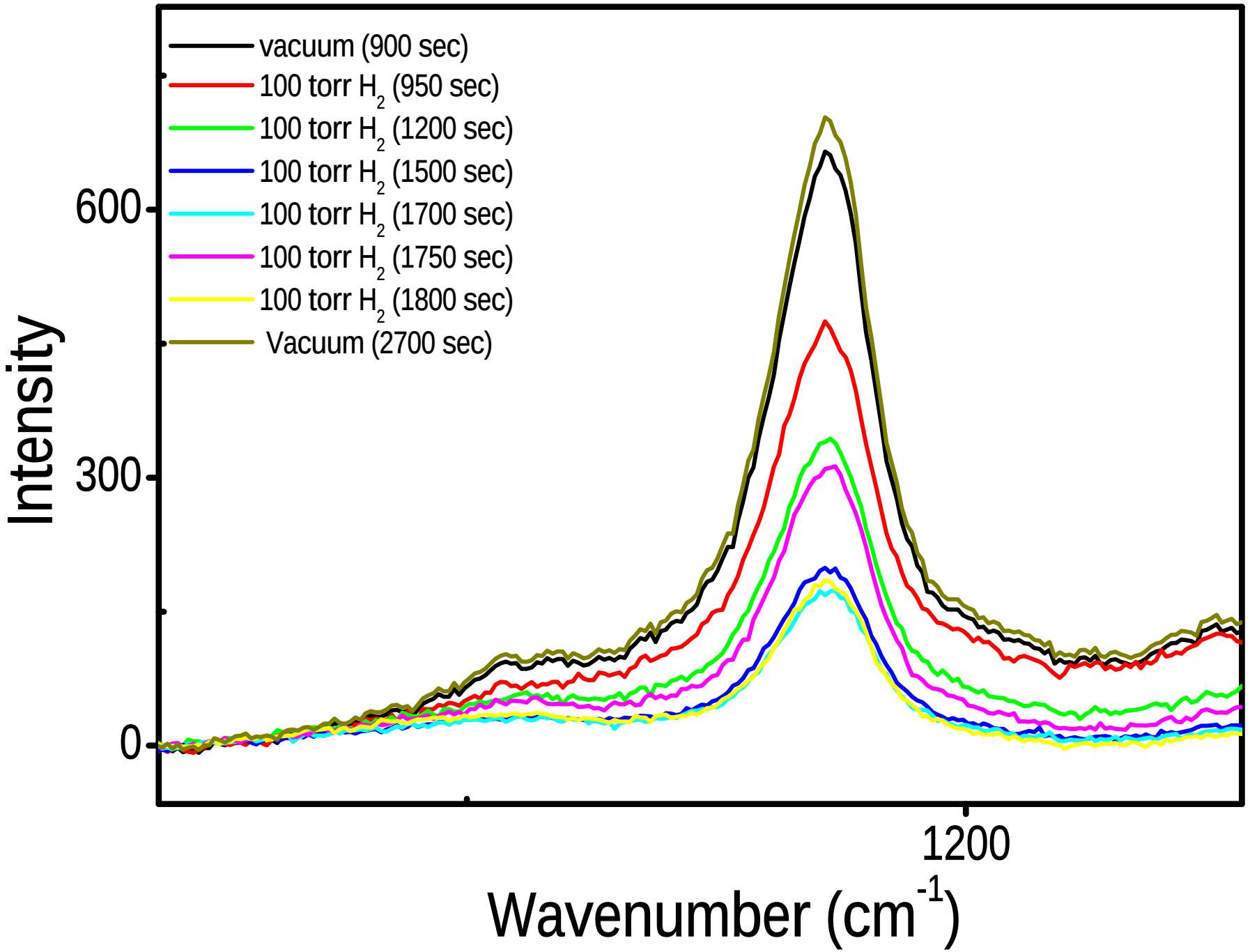

6.0x10-6
5.0x10-6
4.0x10-6
3.0x10-6
2.0x10-6
Current (A)
1.5 volt 500 torr H2 (5 min/cycle)
1.5 volt 500 torr H2 (15 min/cycle)
0
500
1000
1500
2000
2500
Time (sec)

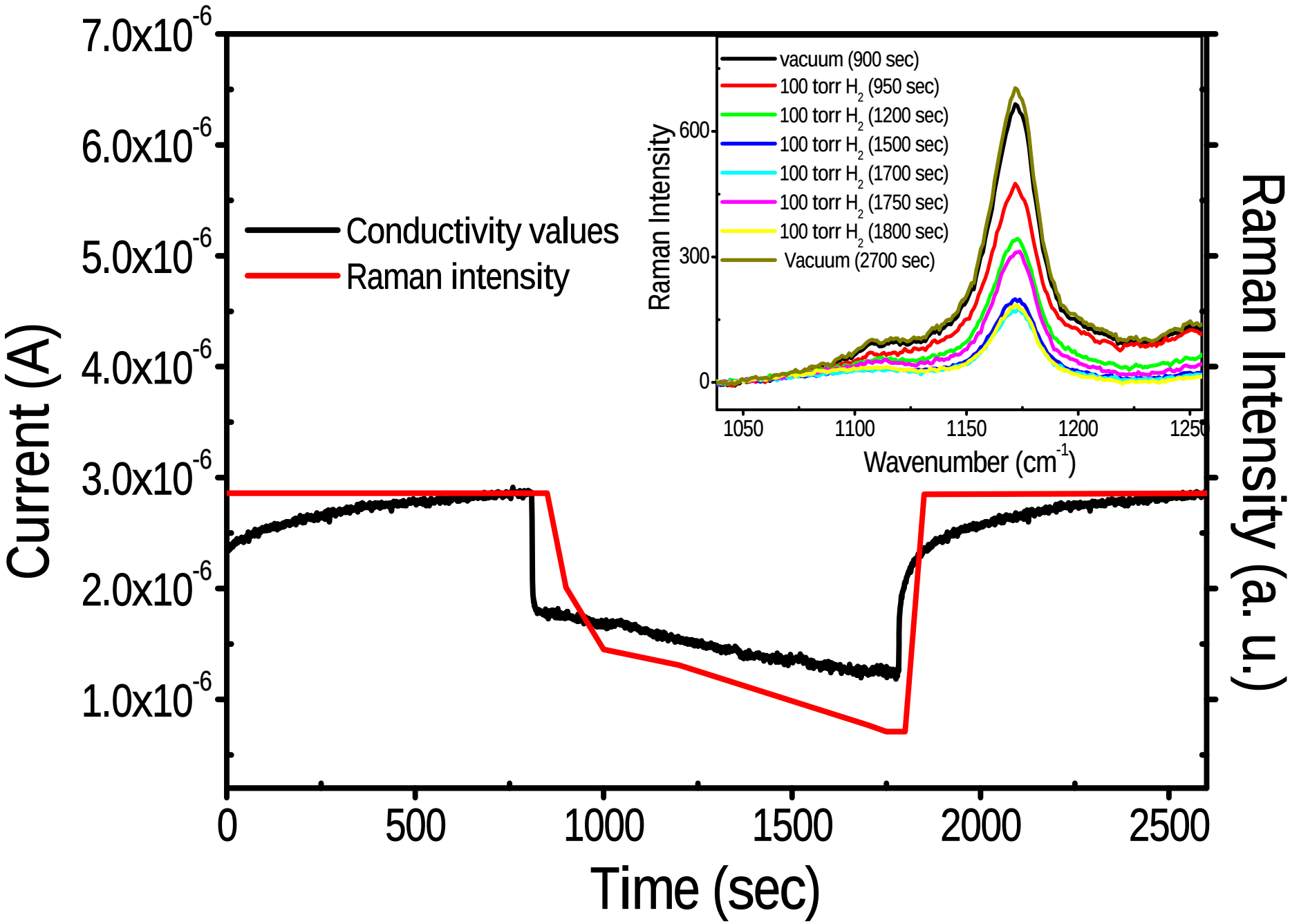
SERS OF CRYSTALS UNDER H2 GAS



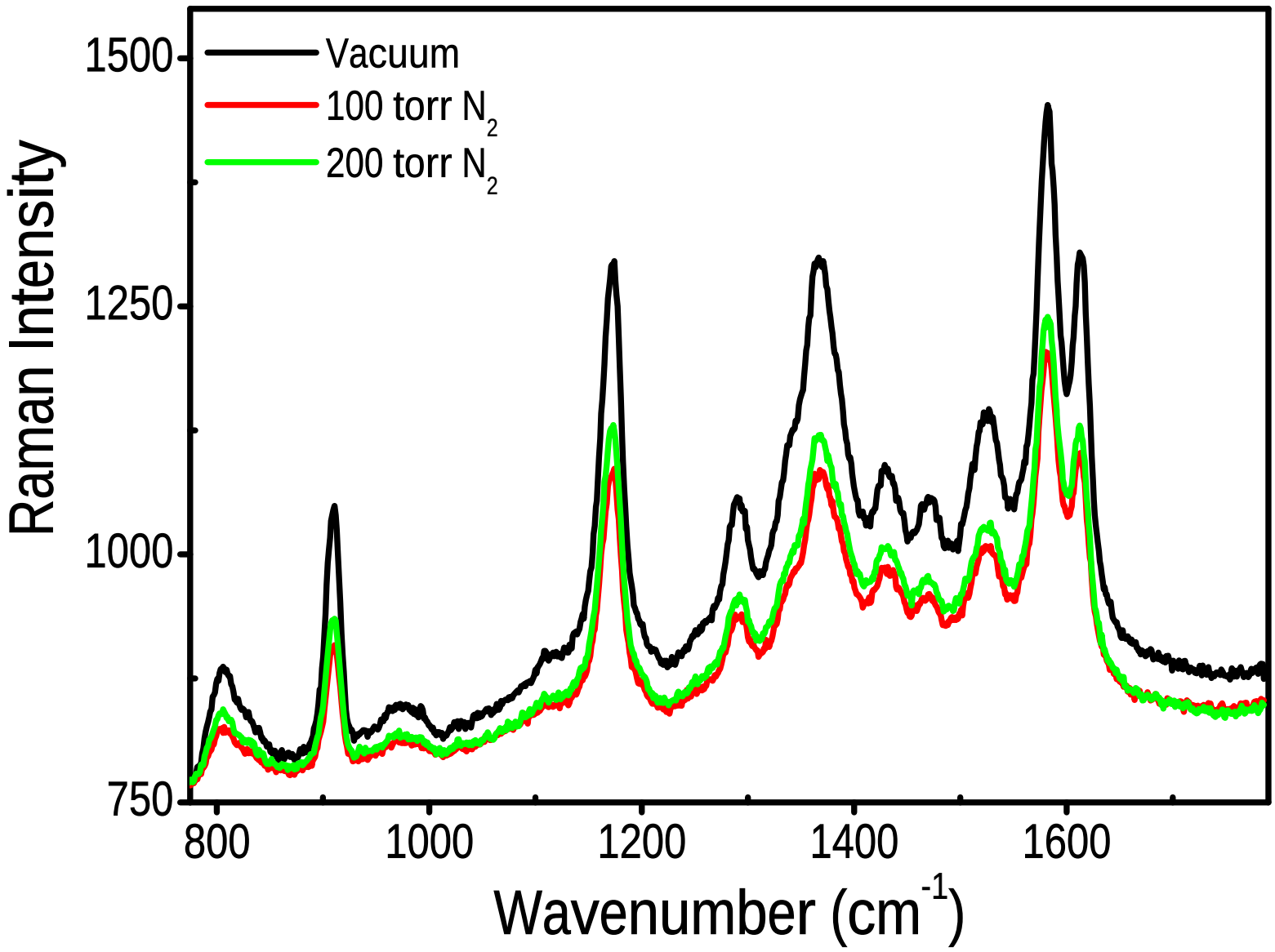

vacuum (900 sec)
100 torr H2 (950 sec)
100 torr H2 (1200 sec)
100 torr H2 (1500 sec)
100 torr H2 (1700 sec)
100 torr H2 (1750 sec)
100 torr H2 (1800 sec)
Vacuum (2700 sec)
Intensity
0
200
400
600
800
1000
800
1000
1200
1400
1600
Wavenumber (cm-1)


vacuum (900 sec)
100 torr H2 (950 sec)
100 torr H2 (1200 sec)
100 torr H2 (1500 sec)
100 torr H2 (1700 sec)
100 torr H2 (1750 sec)
100 torr H2 (1800 sec)
Vacuum (2700 sec)
Intensity
900
600
300
0
1000
1200
Wavenumber (cm-1)

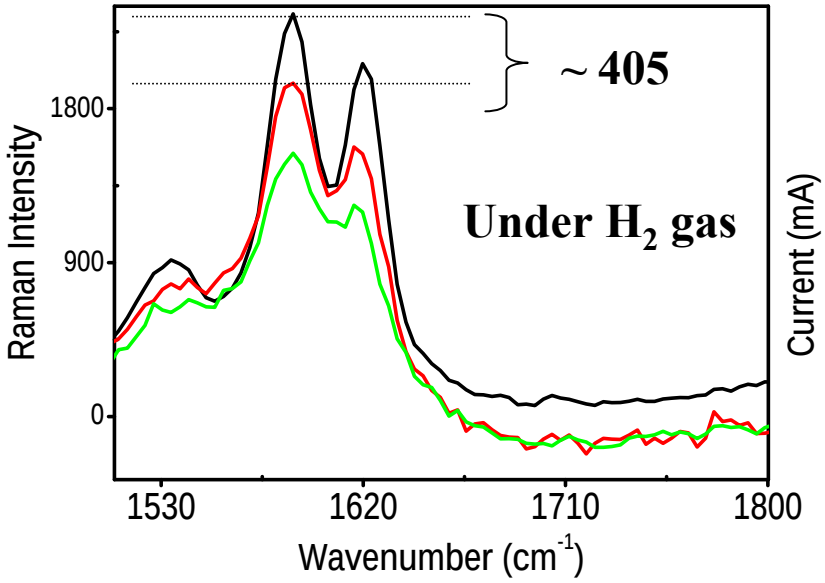

vacuum (900 sec)
100 torr H2 (950 sec)
100 torr H2 (1200 sec)
100 torr H2 (1500 sec)
100 torr H2 (1700 sec)
100 torr H2 (1750 sec)
100 torr H2 (1800 sec)
Vacuum (2700 sec)
Intensity
600
300
0
1200
Wavenumber (cm-1)

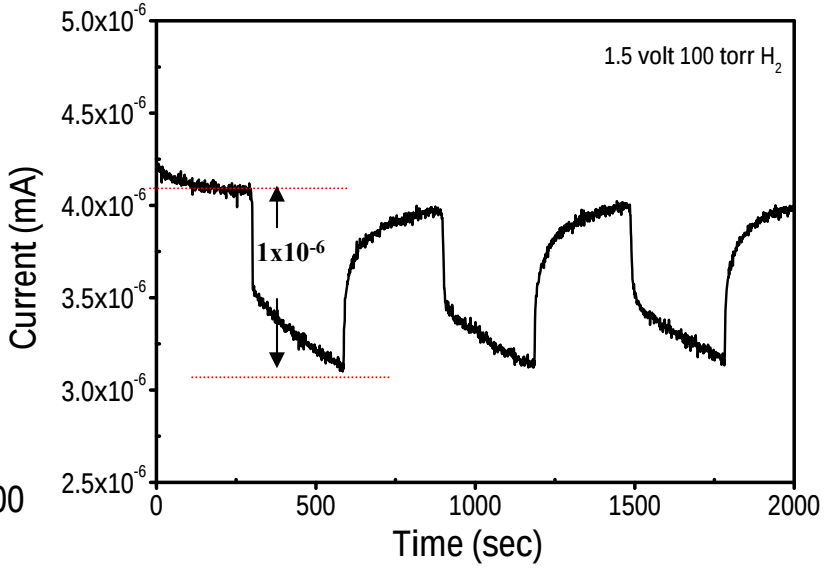

Current (A)
7.0x10-6
6.0x10-6
5.0x10-6
4.0x10-6
3.0x10-6
2.0x10-6
1.0x10-6
Conductivity values
Raman intensity
0
500
1000
1500
2000
2500
Time (sec)
Raman Intensity (a. u.)
Raman Intensity
600
300
0
vacuum (900 sec)
100 torr H2 (950 sec)
100 torr H2 (1200 sec)
100 torr H2 (1500 sec)
100 torr H2 (1700 sec)
100 torr H2 (1750 sec)
100 torr H2 (1800 sec)
Vacuum (2700 sec)
1050
1100
1150
1200
Wavenumber (cm-1)

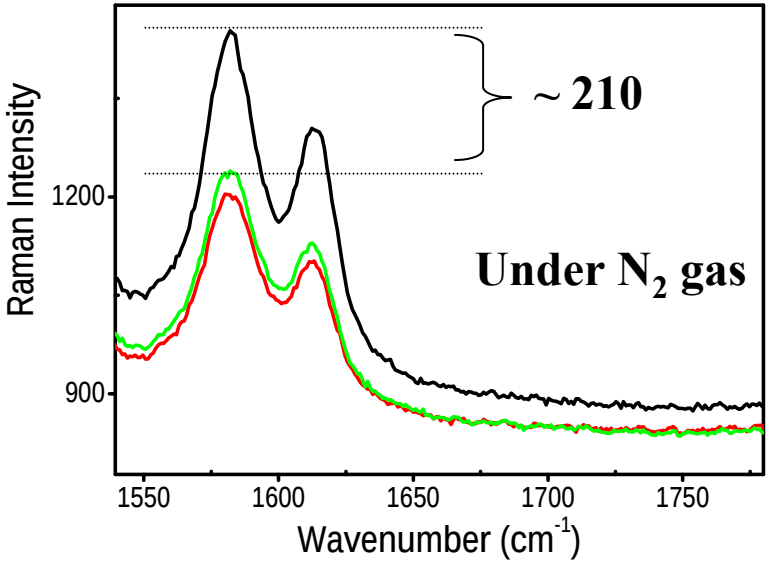
SERS OF CRYSTALS UNDER N2 GAS

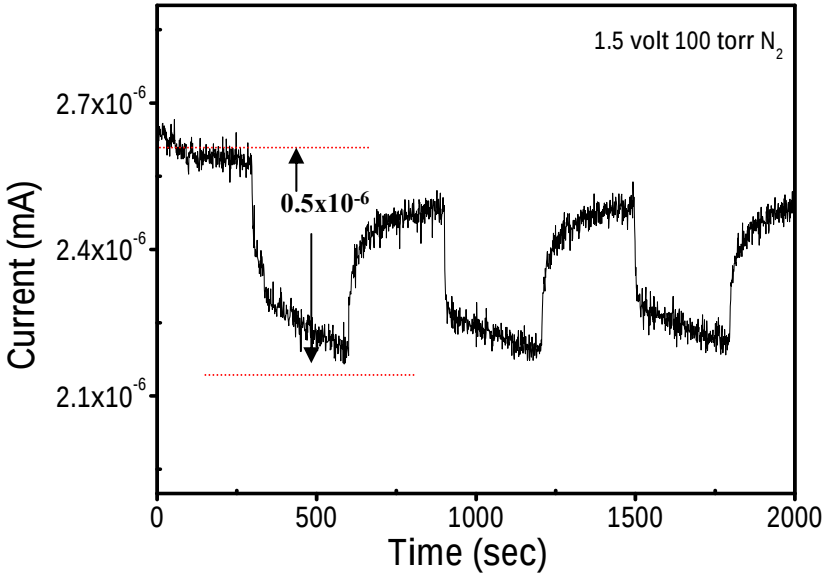


ΔI *Vs* ΔIn









$\Delta I\ N_2 / \Delta I\ H_2 = 0.5$

$\Delta In\ N_2 / \Delta In\ H_2 = 0.5$

SUMMARY

Functional nanoparticle-based crystals have been made
They show fluorescence and associated properties
Fluorescence can used for the selective detection of BSA in nM-mM range
They are new surface enhanced Raman active substrates
They show gas sensing

Nano Mission, DST