Light emitting clusters and nanoparticle superlattices

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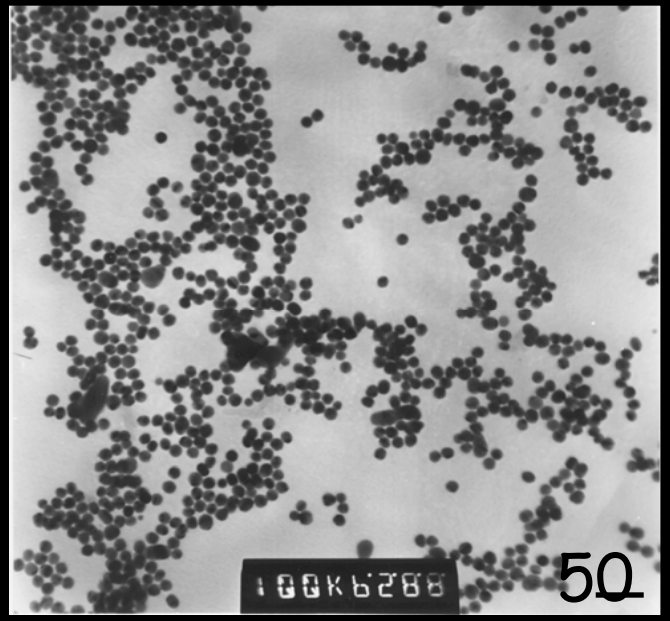
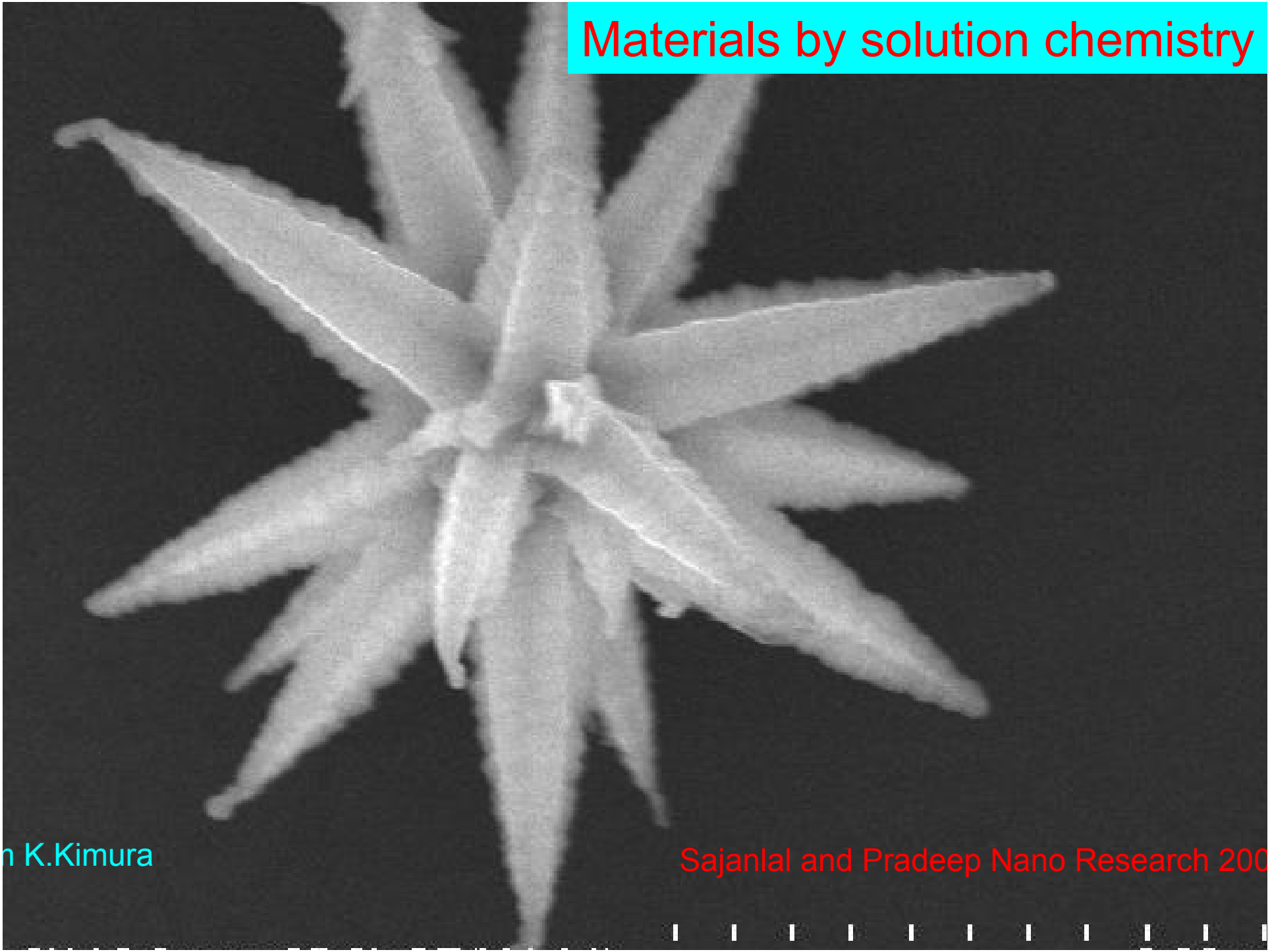
Frontiers in Scalable Nanostructured Interface Materials: A US-India Joint Workshop
Purdue University March 10-12, 2009

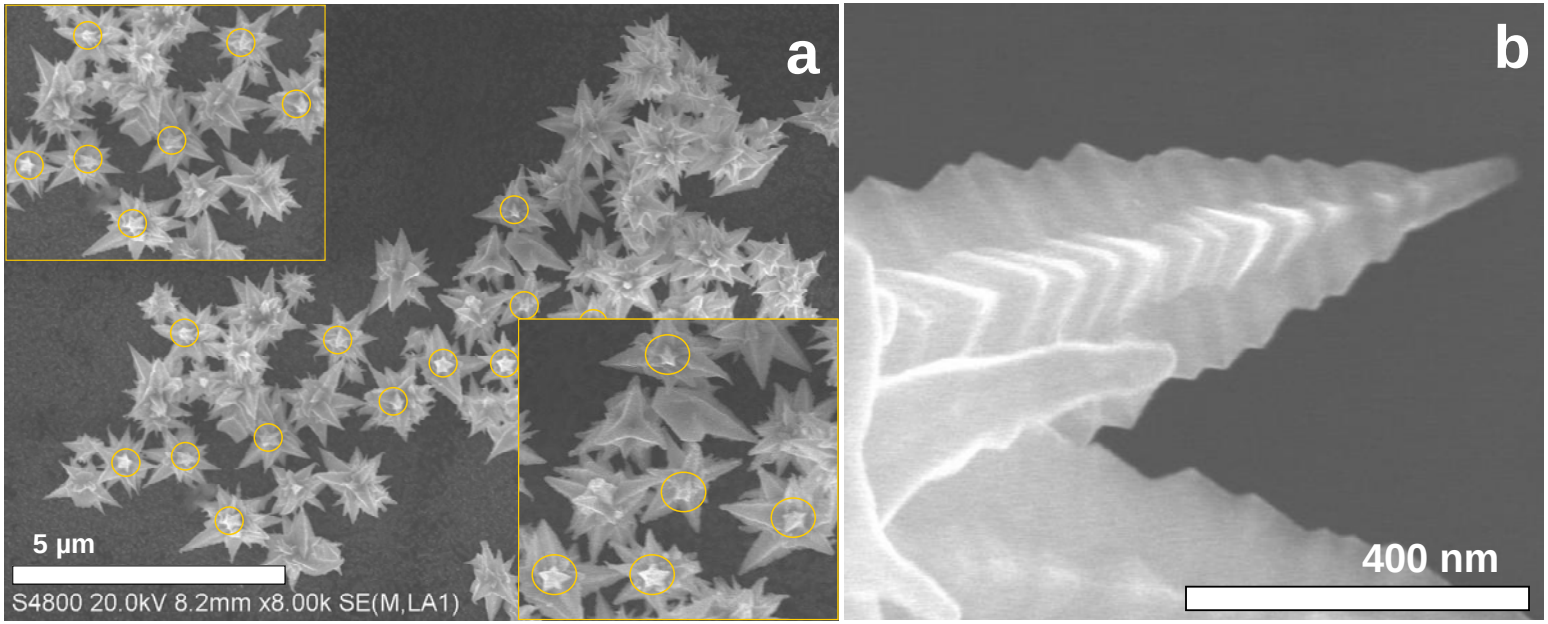
Group-2008

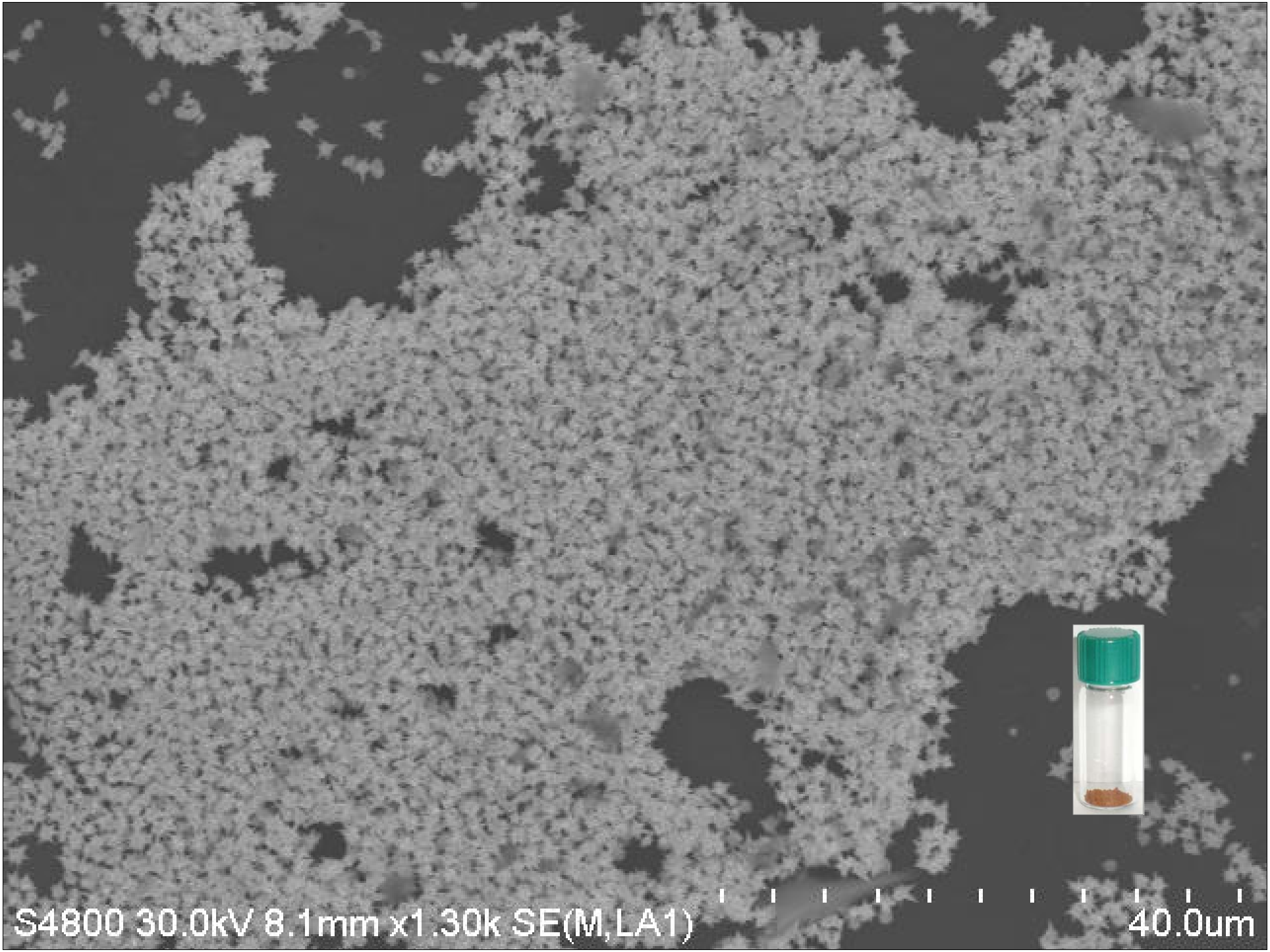


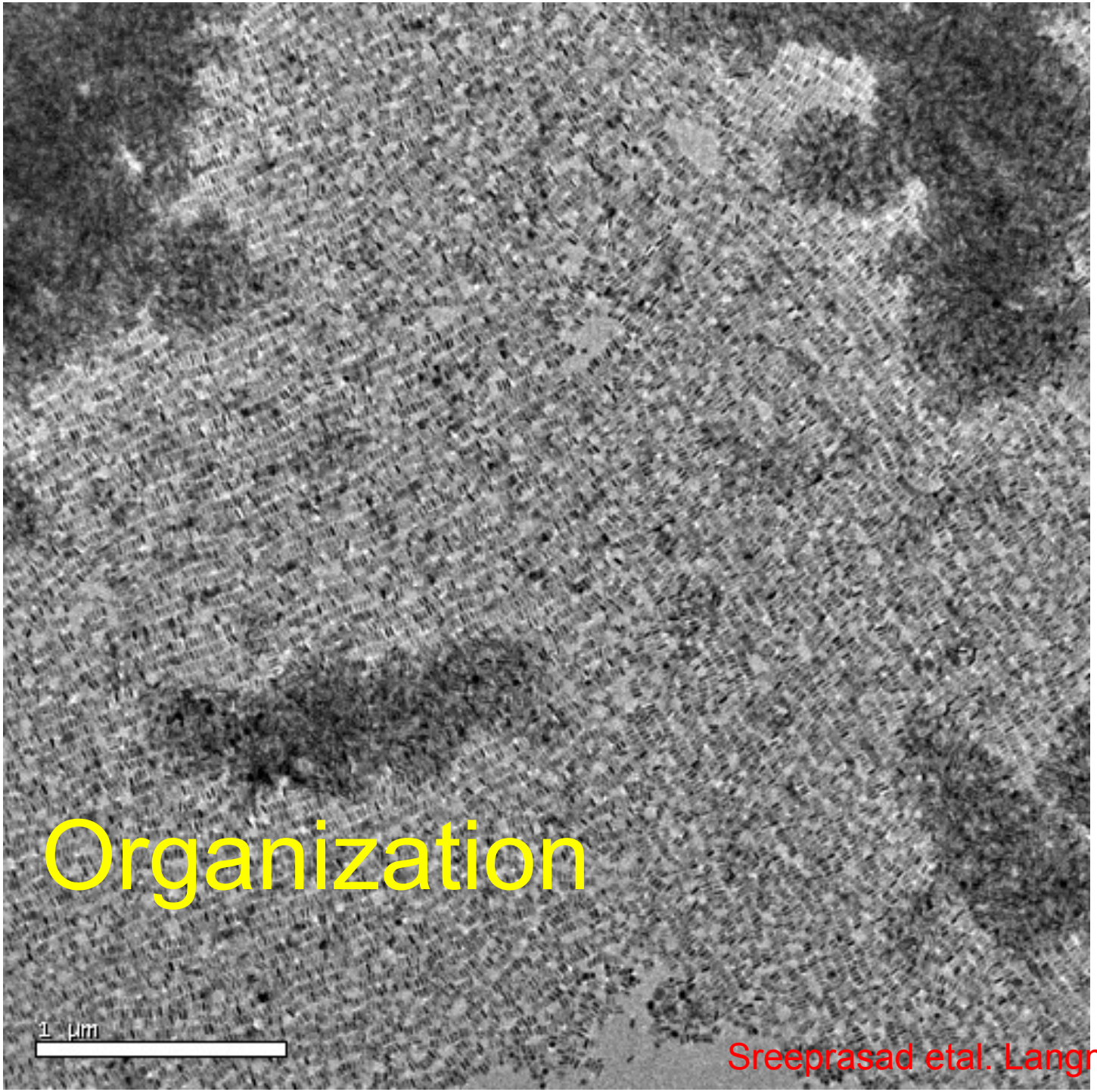
Faraday's gold preserved in Royal Institution. From the site, http://www.rigb.org/rimain/heritage/faradaypage.jsp

Noble metal nanoparticles for drinking water purification – Nanotechnology for clean water
Invited feature article – Thin solid films

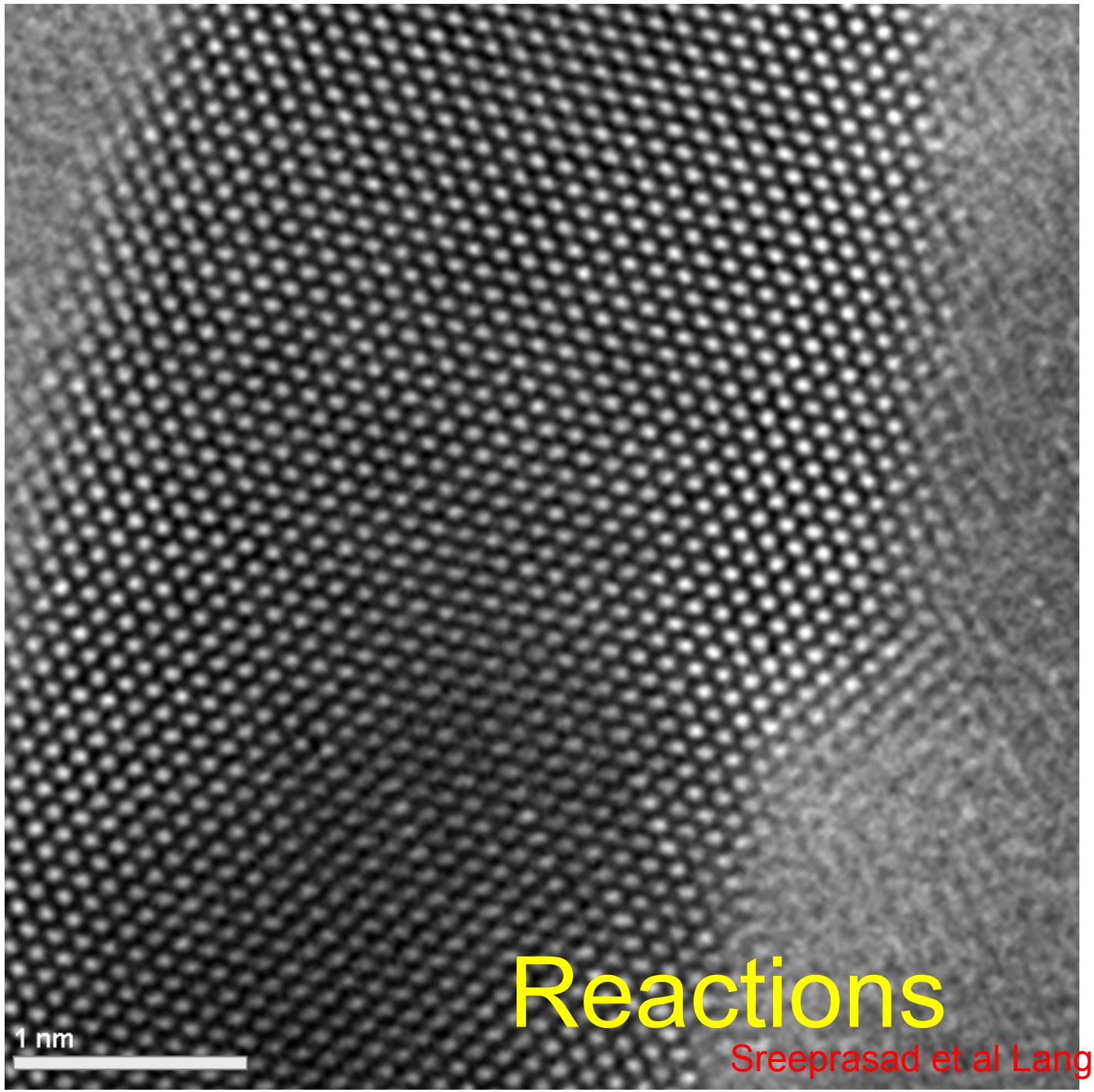

Materials by solution chemistry
n K.Kimura
Sajanlal and Pradeep Nano Research 200


a
5 µm
S4800 20.0kV 8.2mm x8.00k SE(M,LA1)
b
400 nm


S4800 30.0kV 8.1mm x1.30k SE(M,LA1)
40.0um

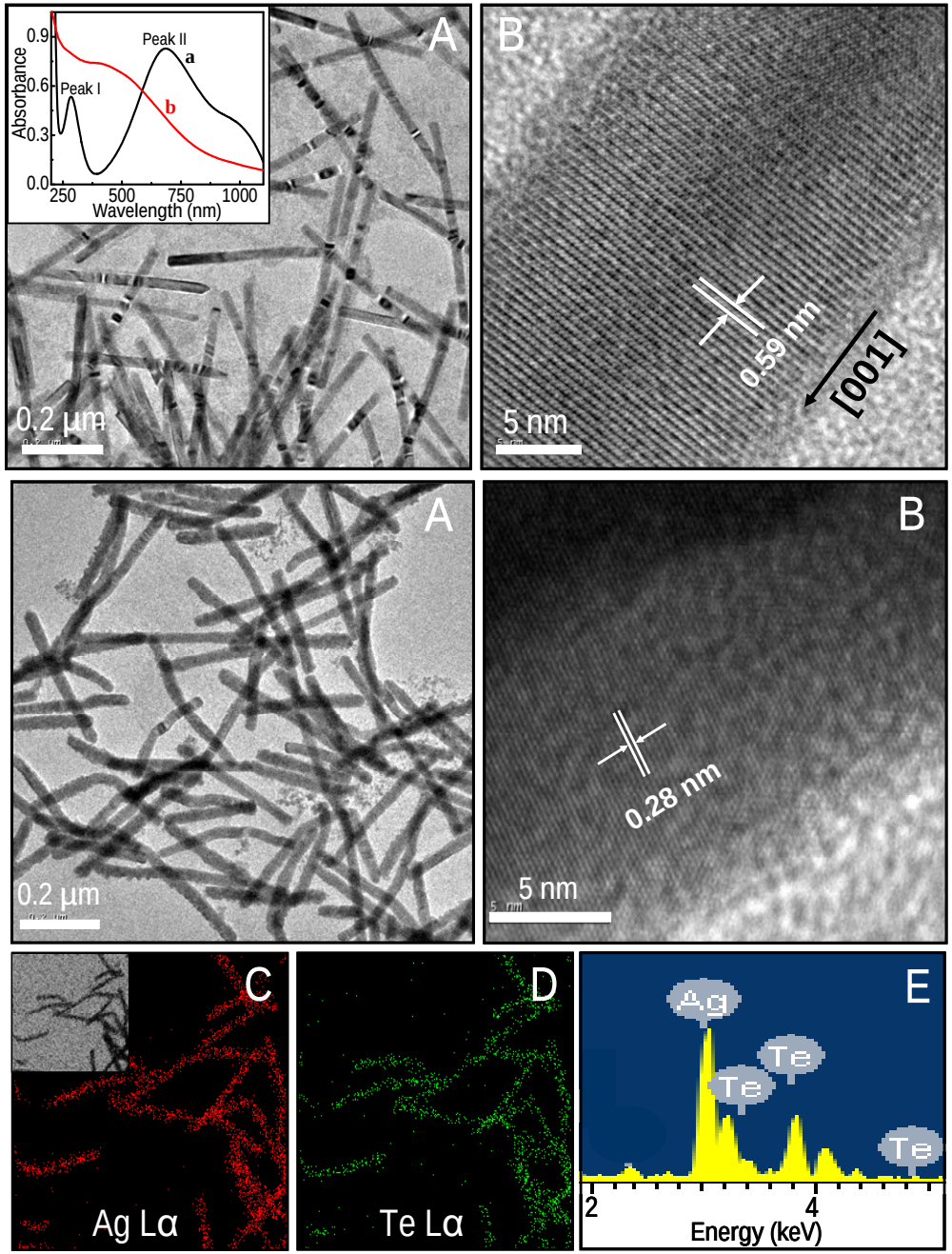


Sreeprasad etal. Langmuir 2008

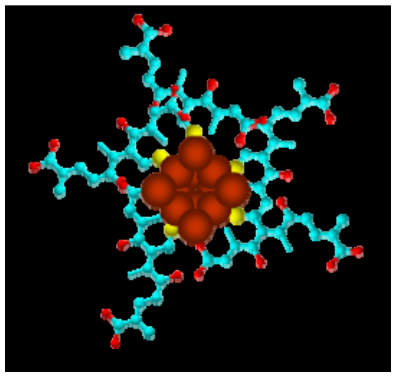


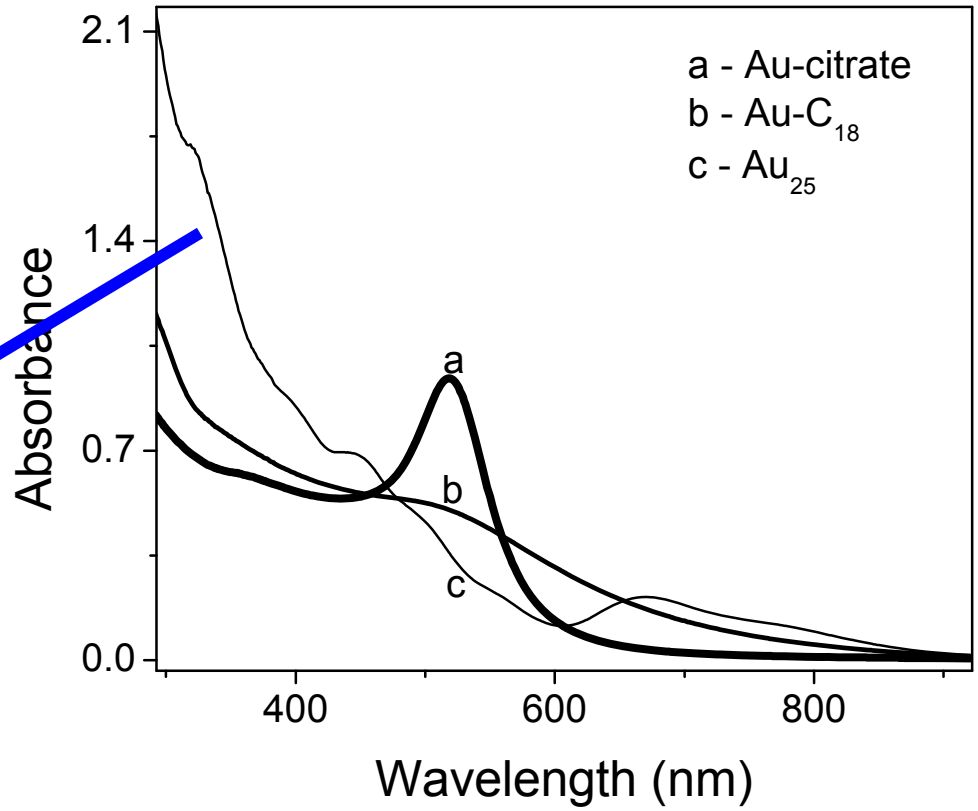
Reactions

Sreeprasad et al Langmuir 2007


A
Absorbance
0.9
0.6
0.3
0.0
Peak II
a
Peak I
b
250
500
750
1000
Wavelength (nm)
0.2 µm
B
0.59 nm
[001]
5 nm
A
0.2 µm
B
0.28 nm
5 nm
C
Ag Lα
D
Te Lα
E
Ag
Te
Te
Te
2
4
Energy (keV)

Materials at interfaces

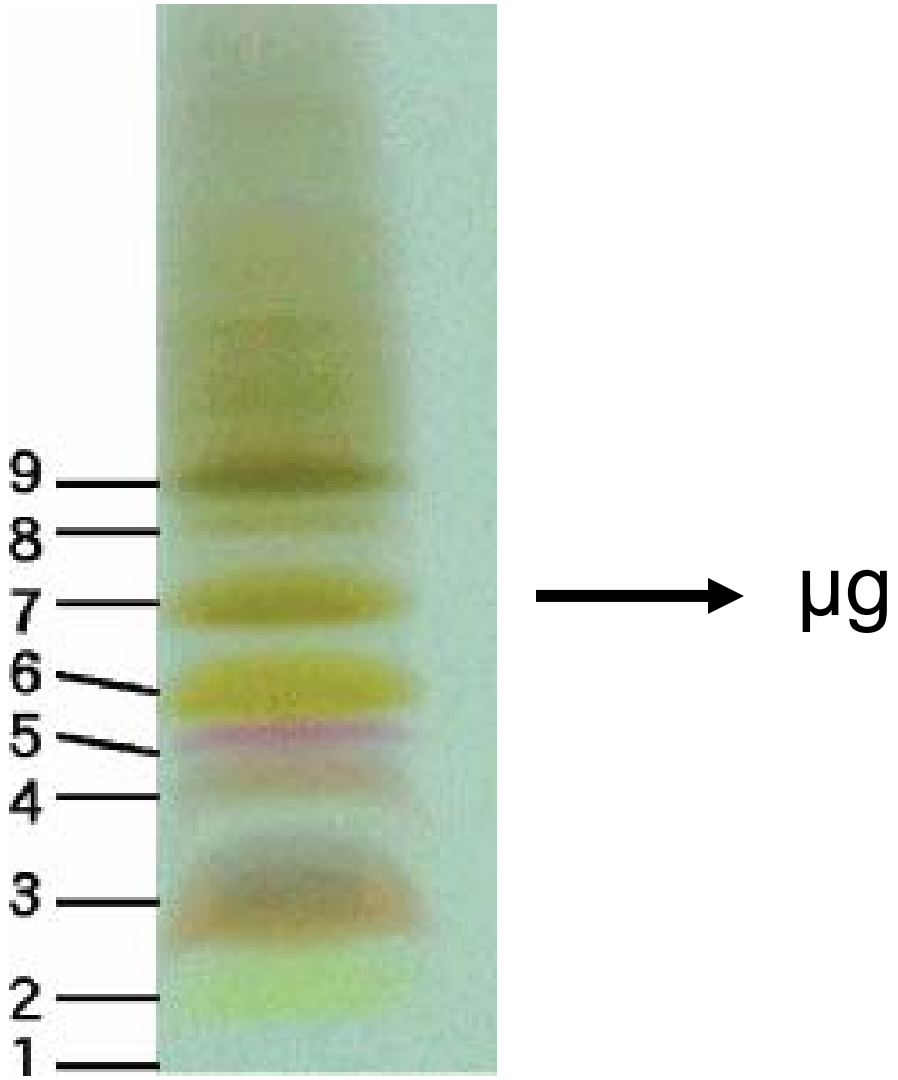




Optical absorption (extinction) spectrum of (a) 15 nm gold particles in aqueous solution (labeled Au@citrate). The spectrum of (b) 3 nm particles in toluene is also shown. See the broadening of the plasmon feature. The spectrum of (c) Au_{25} in water. In this, there is no plasmon excitation and all the features are due to molecular absorptions of the cluster.

Das, Choi, Yu and Pradeep, *Nanofluids*, John Wiley, New York, 2008

Polyacrylamide gel electrophoresis (PAGE)

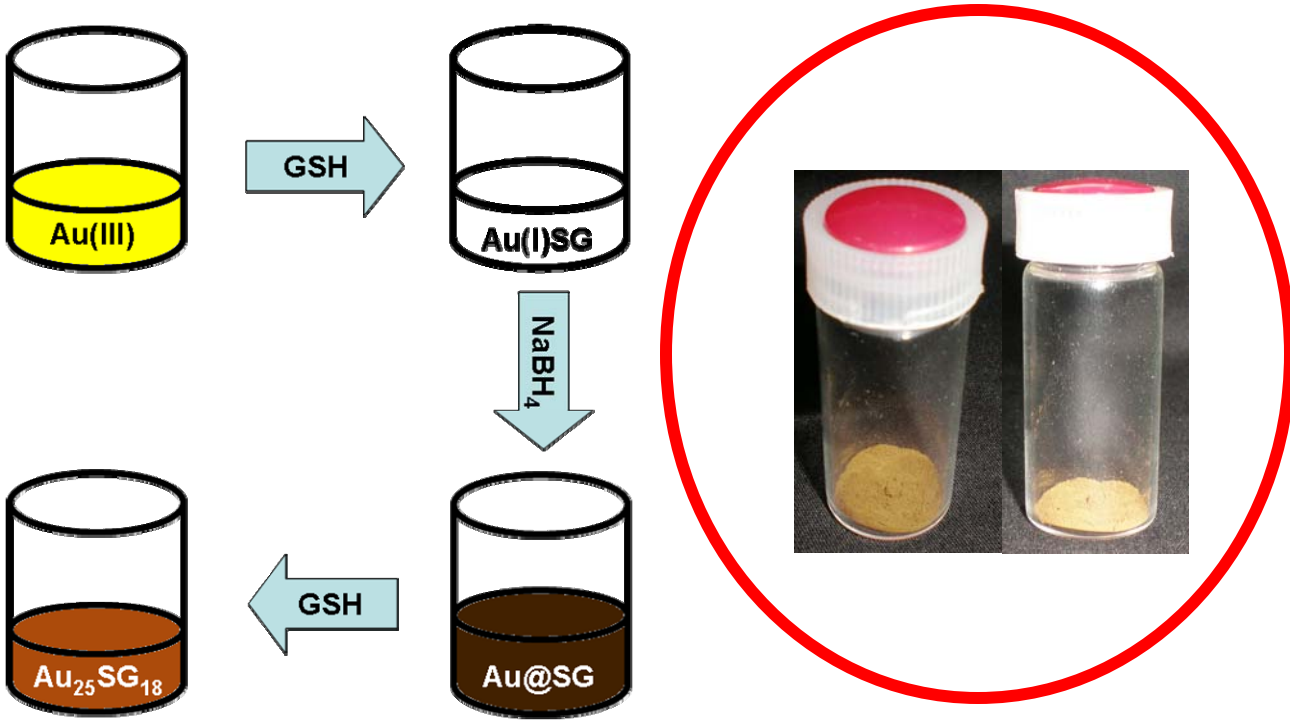


Negishi, Y.; Nobusada, K.; and Tsukuda, T. Glutathione-Protected Gold Clusters Revisited: Bridging the Gap between Gold(I)-Thiolate Complexes and Thiolate-Protected Gold Nanocrystals. *J. Am. Chem. Soc*. 2005, *127*, 5261-70.

Gram scale synthesis

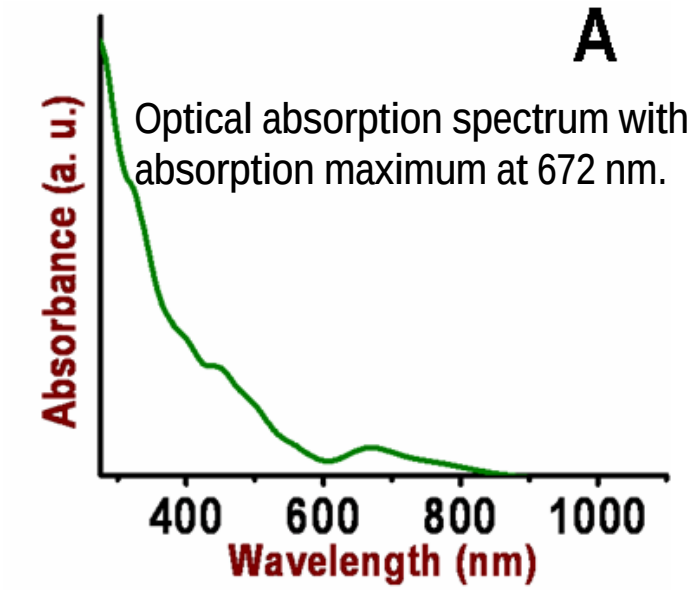
$Au_{25}SG_{18}$

Synthesis: Au_{25} clusters can be preferentially populated by dissociative excitation of larger precursors

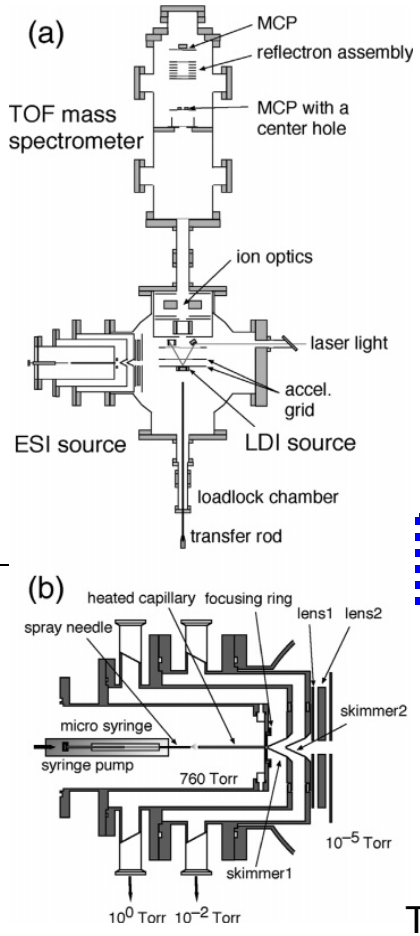


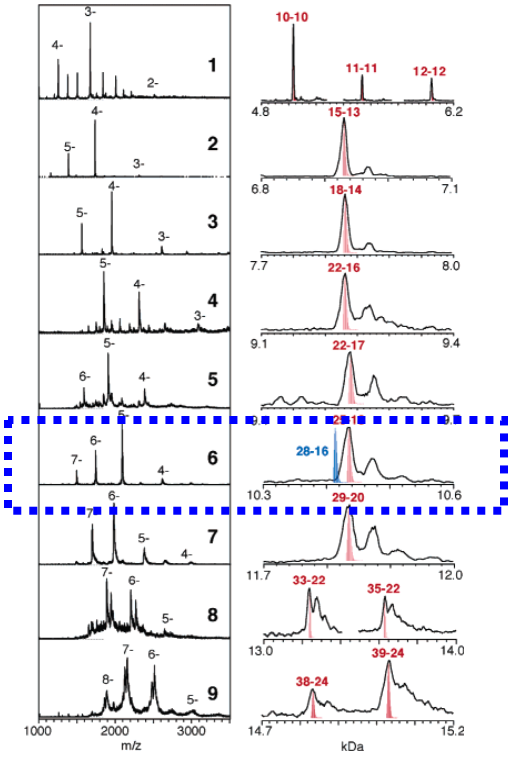
Scheme showing the synthesis of $Au_{25}SG_{18}$ clusters

Characterization of clusters

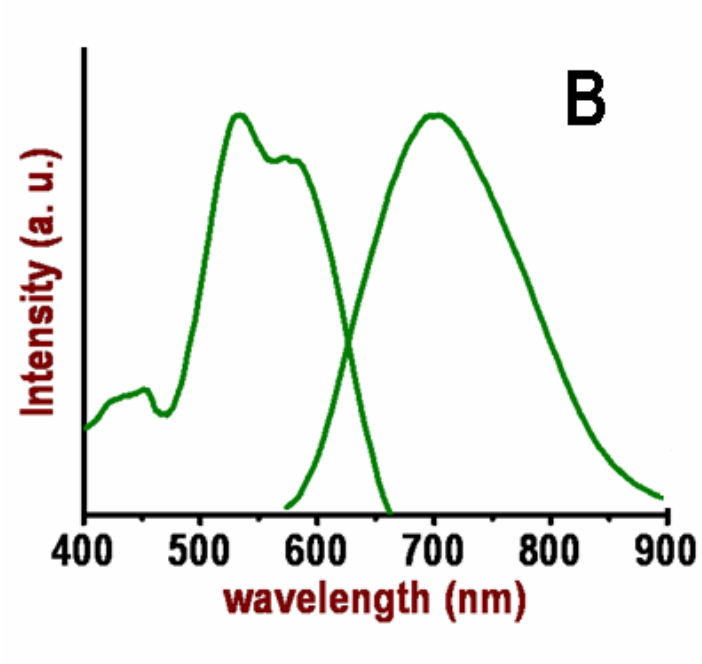


Optical absorption spectrum with an absorption maximum at 672 nm.



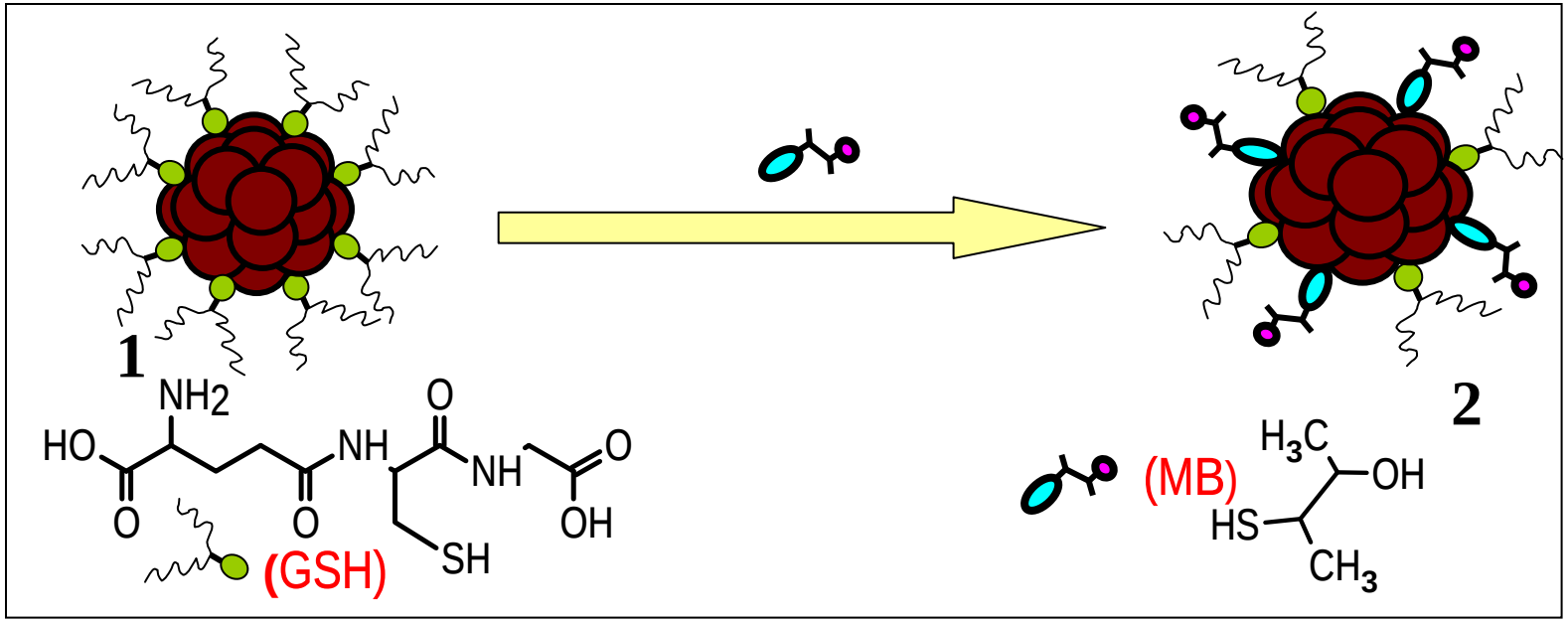


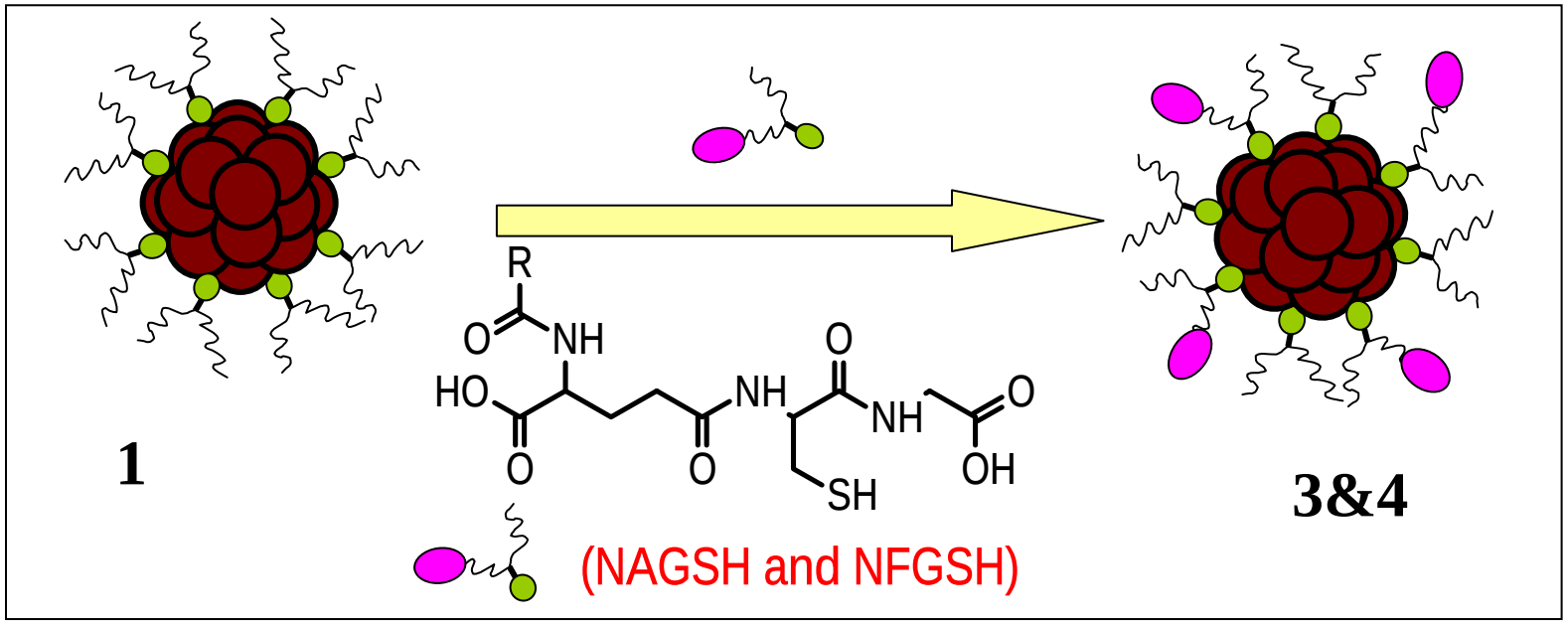
Tsukuda et. al. JACS 2005

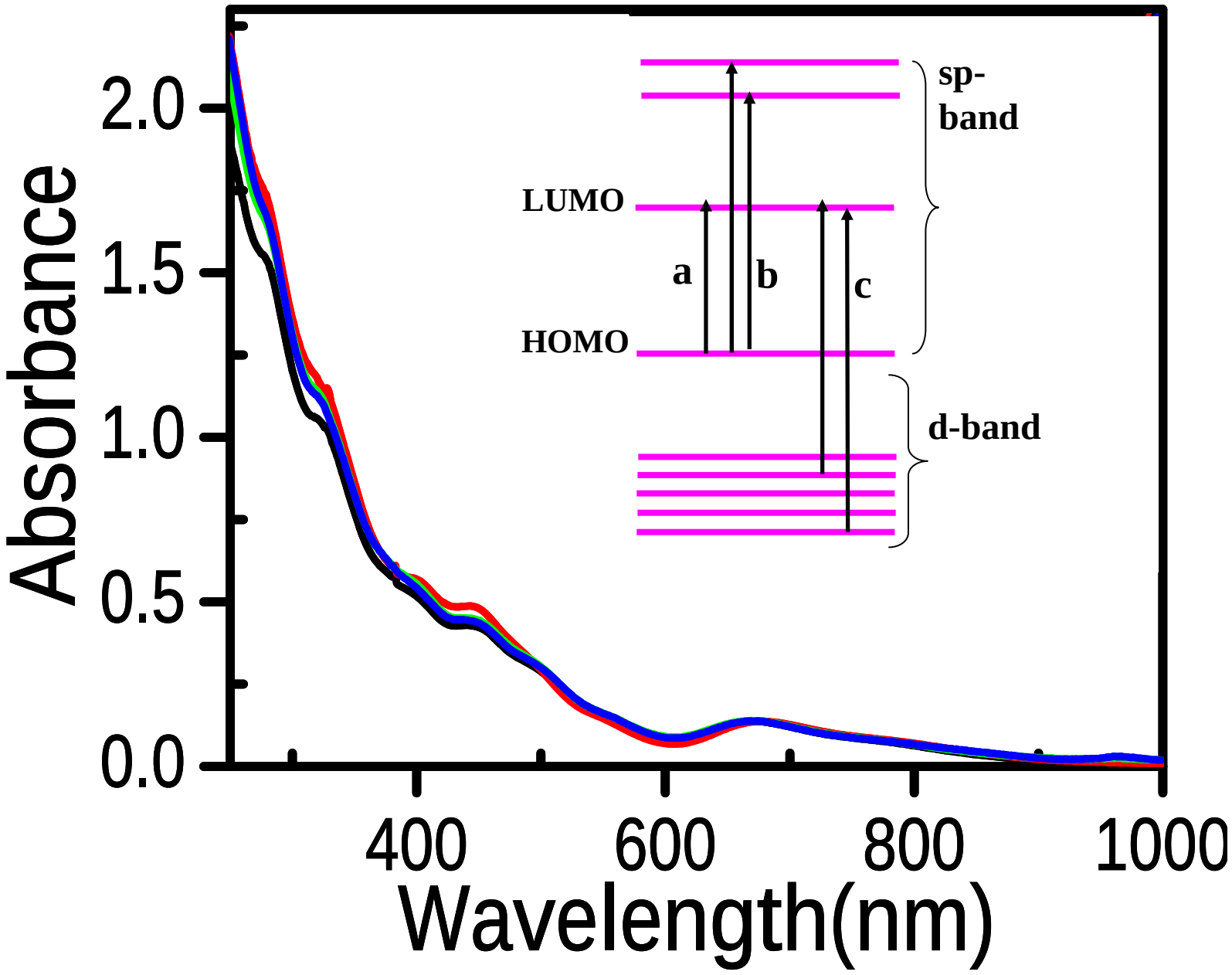


Photoluminescence profile with excitation and emission maxima at 535 and 700 nm, respectively.

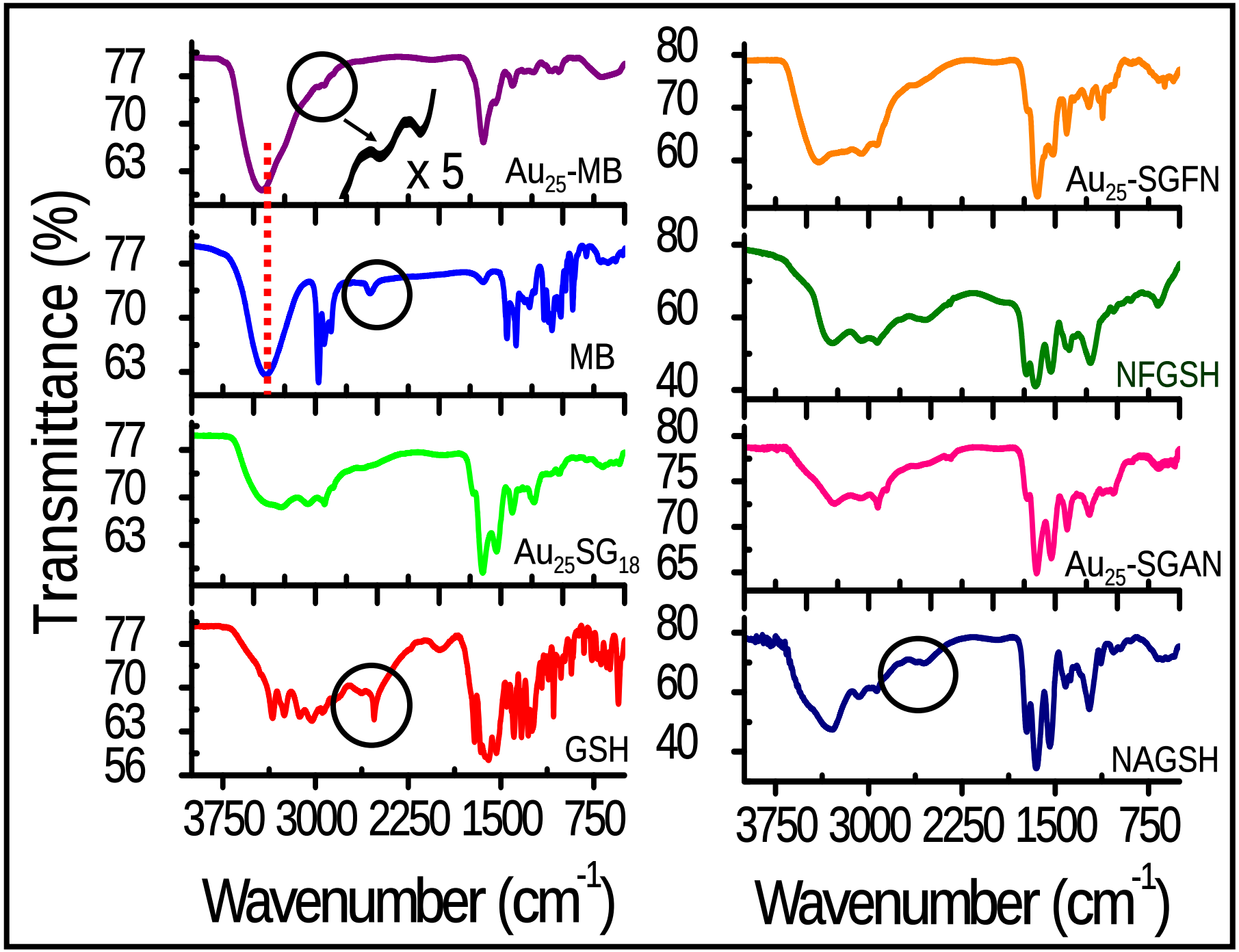
Ligand Exchange of Au_{25}

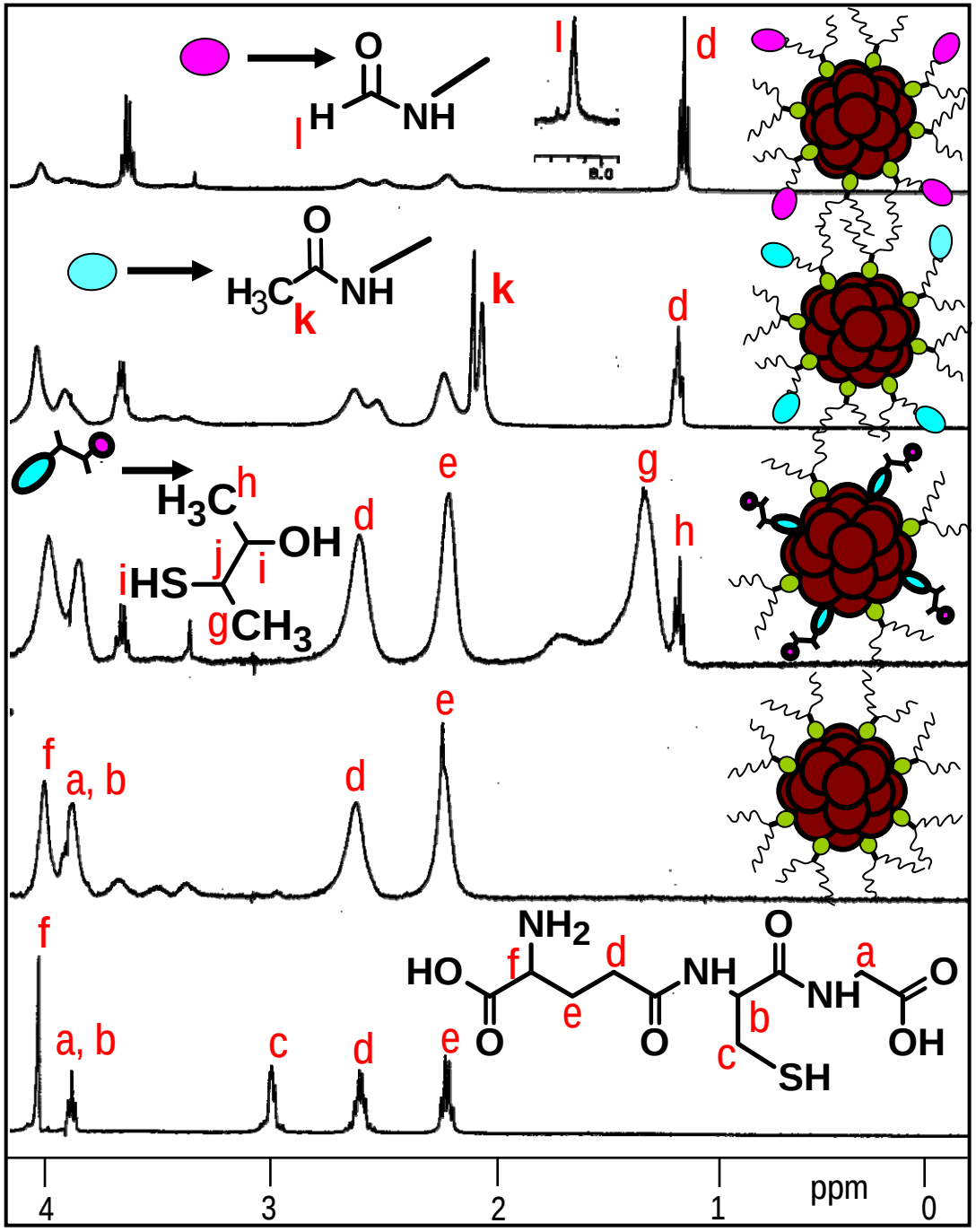


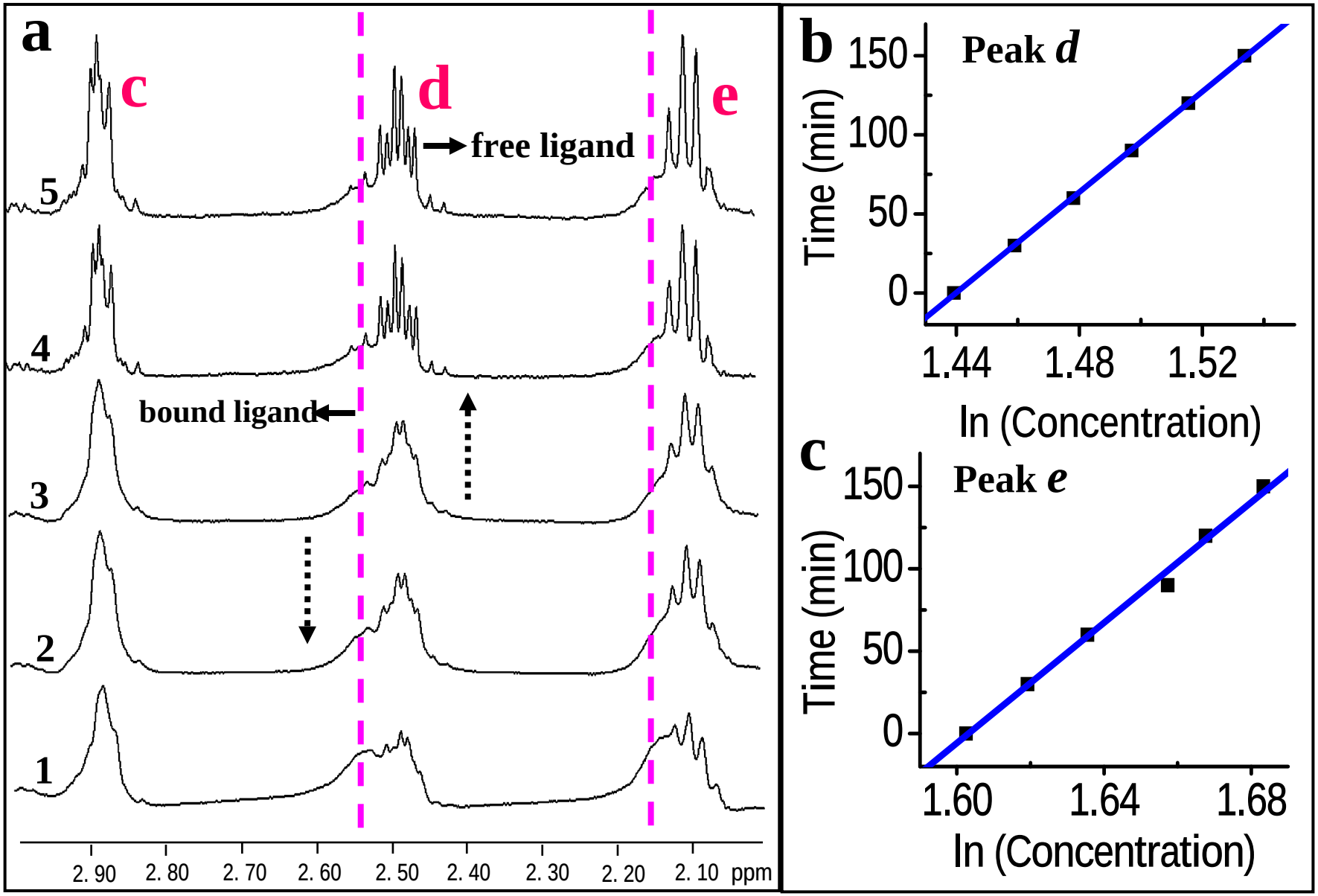


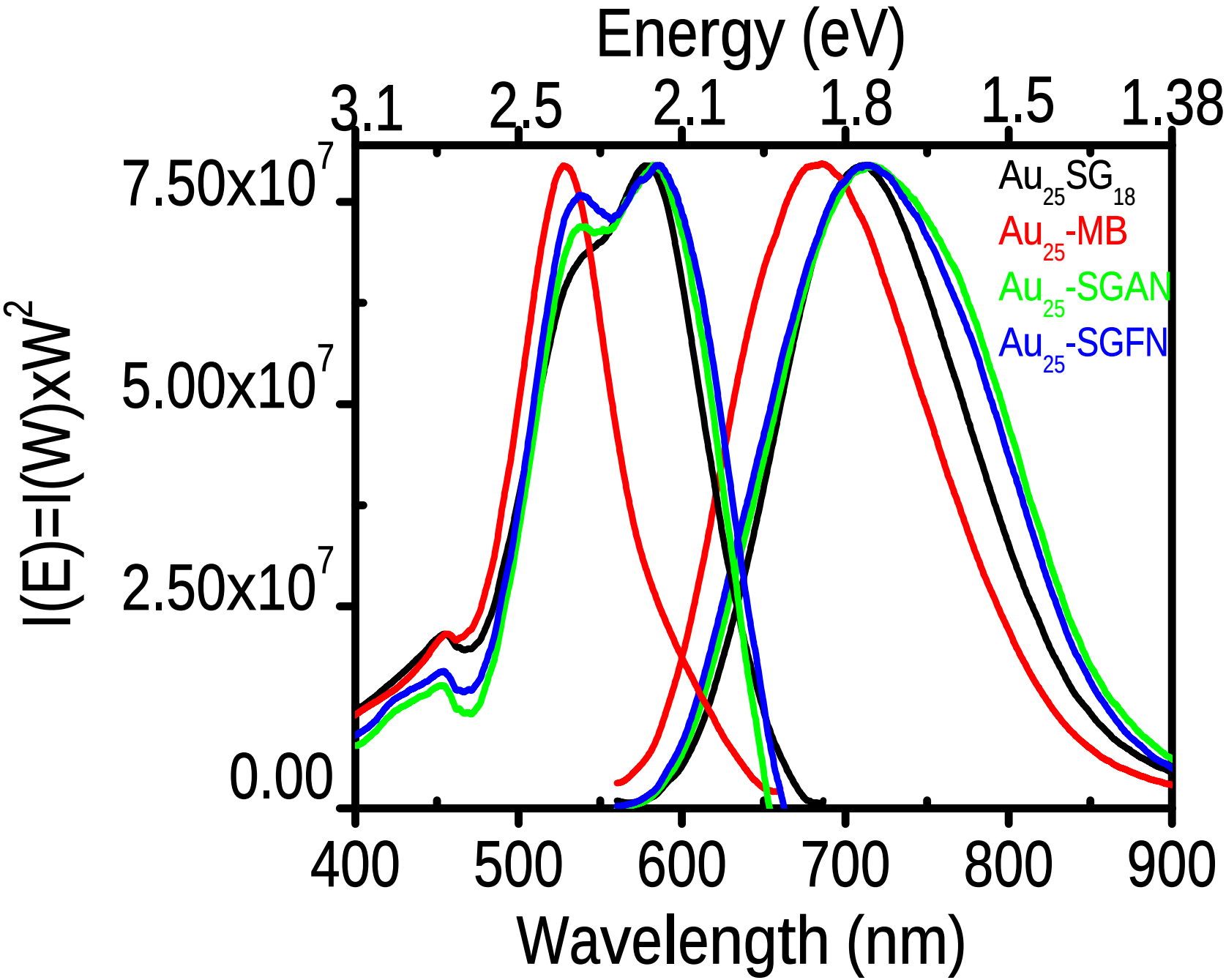


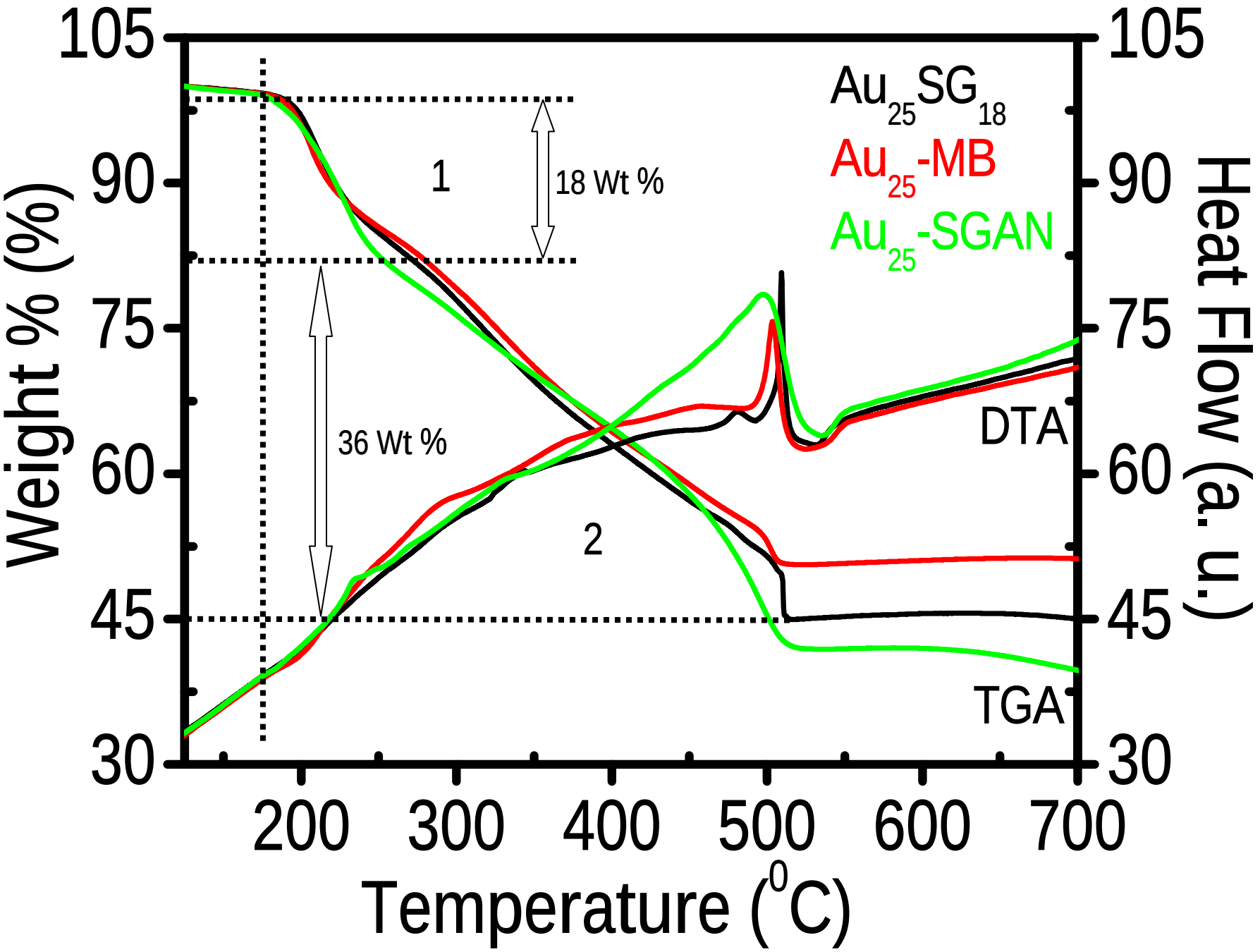
Shibu et al J.Phys. Chem. 2008

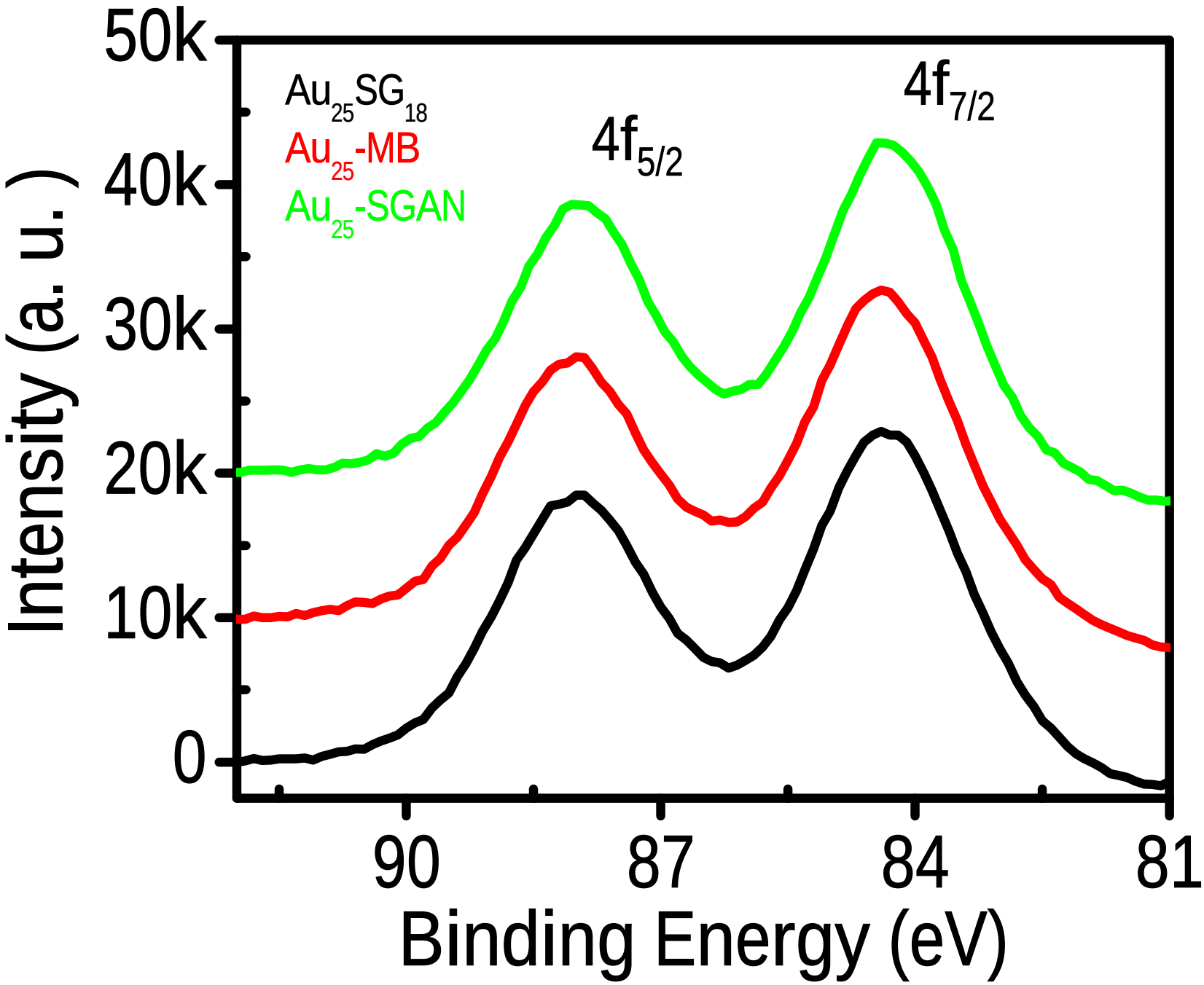

Transmittance (%)
77
70
63
x 5
Au25-MB
77
70
63
MB
77
70
63
Au25SG18
77
70
63
56
GSH
3750 3000 2250 1500 750
Wavenumber (cm-1)
80
70
60
Au25-SGFN
80
60
40
NFGSH
80
75
70
65
Au25-SGAN
80
60
40
NAGSH
3750 3000 2250 1500 750
Wavenumber (cm-1)


O
H
NH
l
l
d
O
H3C
NH
k
k
d
H3C
h
OH
j
i
iHS
gCH3
d
e
g
h
f
a, b
d
e
f
a, b
c
d
e
NH2
HO
f
d
NH
O
a
NH
O
e
O
O
b
c
SH
OH
4
3
2
1
ppm
0

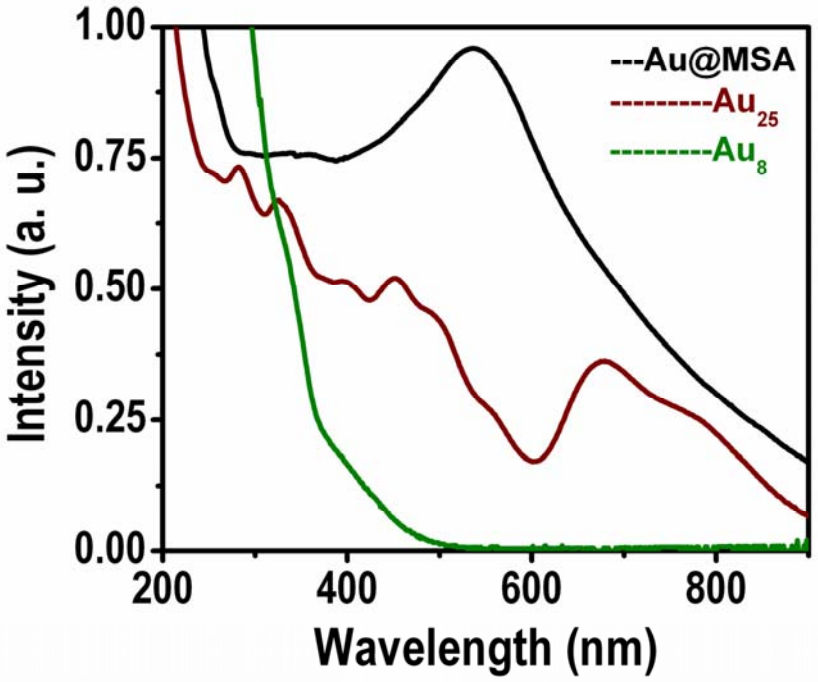

a
c
d
e
free ligand
bound ligand
5
4
3
2
1
2. 90
2. 80
2. 70
2. 60
2. 50
2. 40
2. 30
2. 20
2. 10
ppm
b
Peak d
Time (min)
150
100
50
0
1.44
1.48
1.52
ln (Concentration)
c
Peak e
Time (min)
150
100
50
0
1.60
1.64
1.68
ln (Concentration)


Energy (eV)
3.1
2.5
2.1
1.8
1.5
1.38
7.50x10^7
5.00x10^7
2.50x10^7
0.00
I(E)=I(W)xW^2
400
500
600
700
800
900
Wavelength (nm)
Au25SG18
Au25-MB
Au25-SGAN
Au25-SGFN

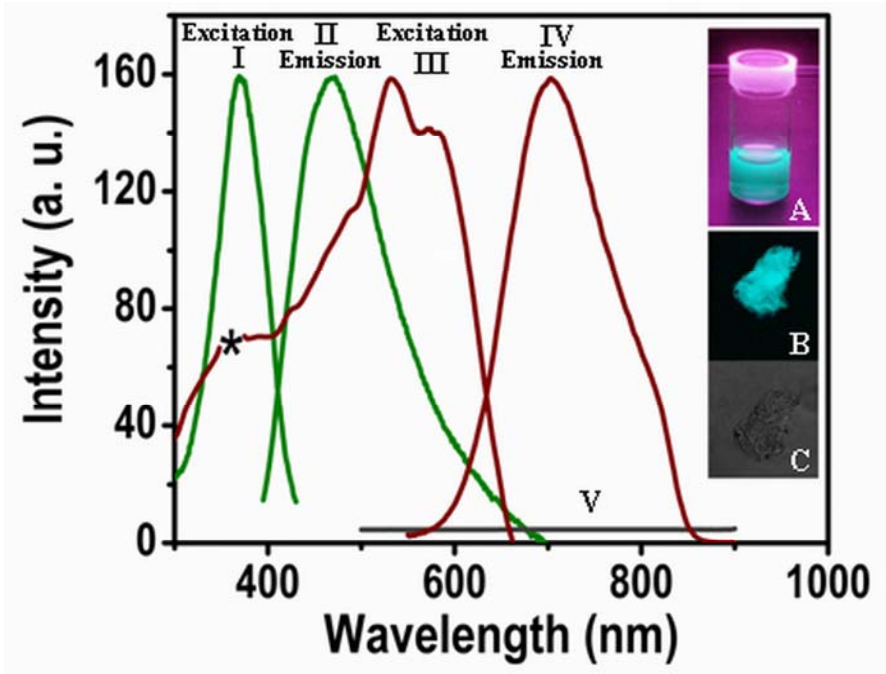

105
90
75
60
45
30
Weight % (%)
105
90
75
60
45
30
Heat Flow (a. u.)
200
300
400
500
600
700
Temperature (°C)
Au25SG18
Au25-MB
Au25-SGAN
1
18 Wt %
2
36 Wt %
DTA
TGA


50k
40k
30k
20k
10k
0
Intensity (a. u.)
90
87
84
81
Binding Energy (eV)
Au25SG18
Au25-MB
Au25-SGAN
4f5/2
4f7/2

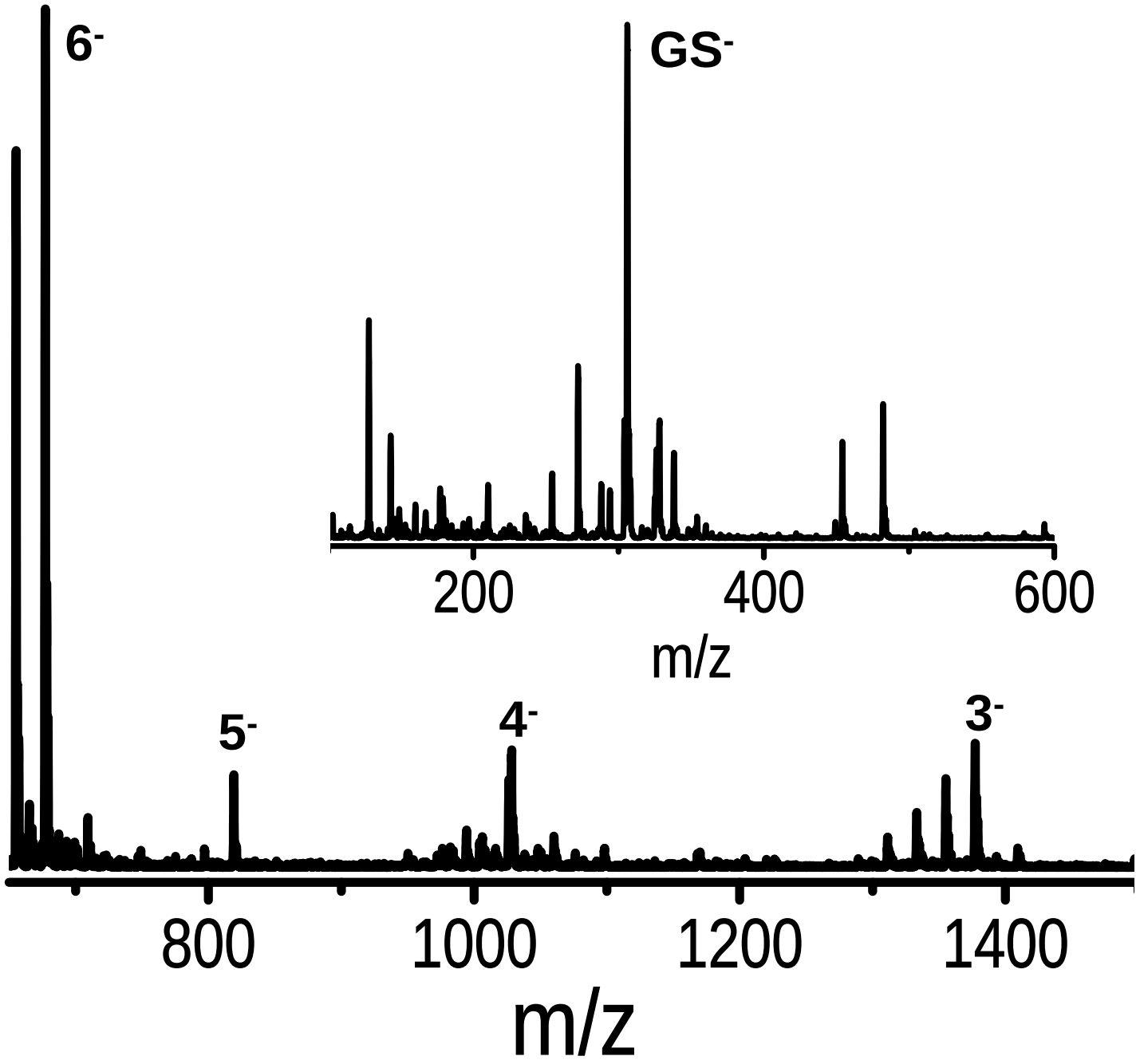
Au_8



Comparison of the optical absorption profiles of Au@MSA, Au_{25} and Au_8.



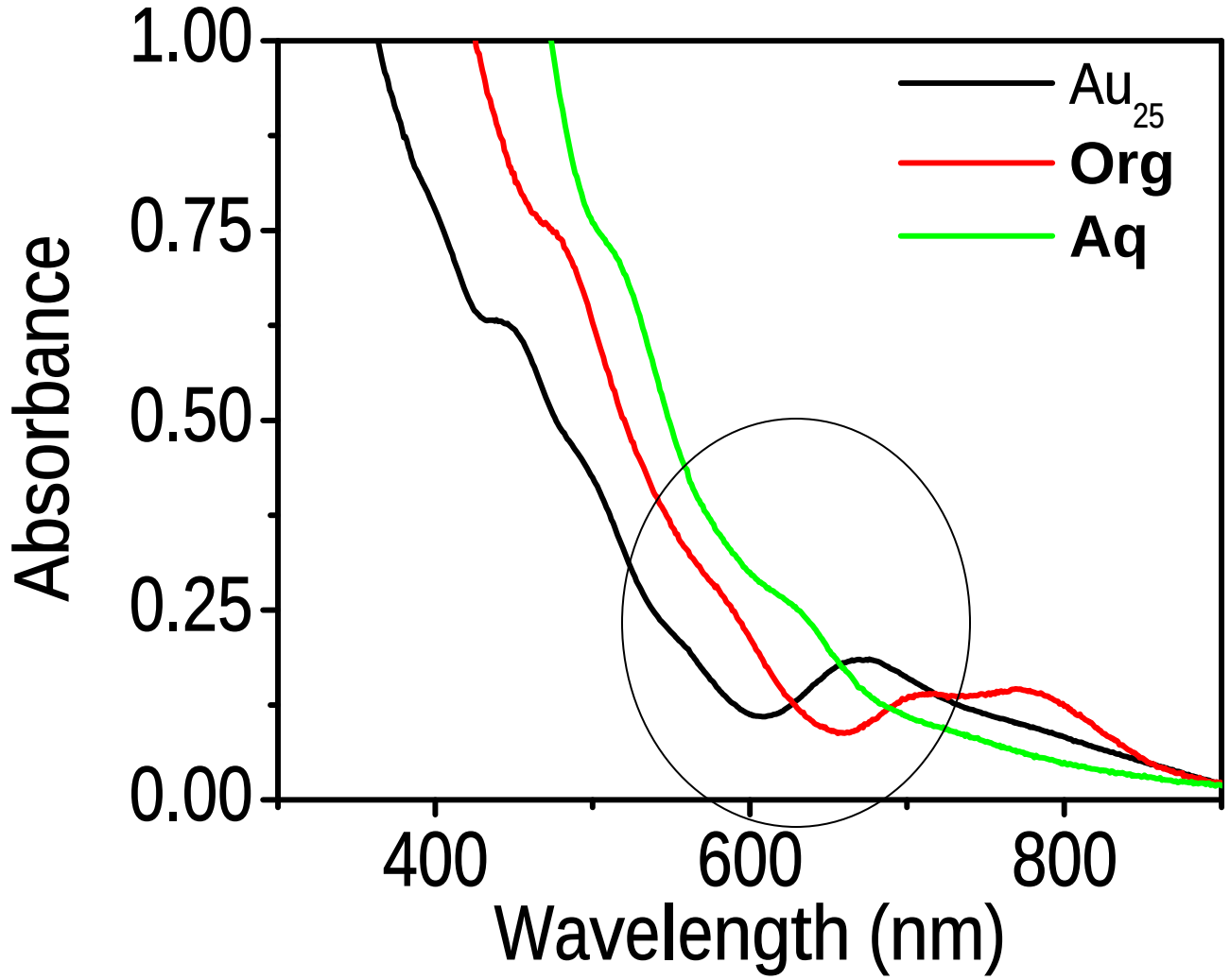
Comparison of the photoluminescence profiles of the clusters with Au@MSA. Traces I and II are the excitation and emission spectra of Au_8, respectively. Traces III and IV are the excitation and emission spectra of Au_{25}, respectively and trace V is the emission spectrum of Au@MSA.


6-
GS-
200
400
600
m/z
5-
4-
3-
800
1000
1200
1400
m/z

Interfacial Etching

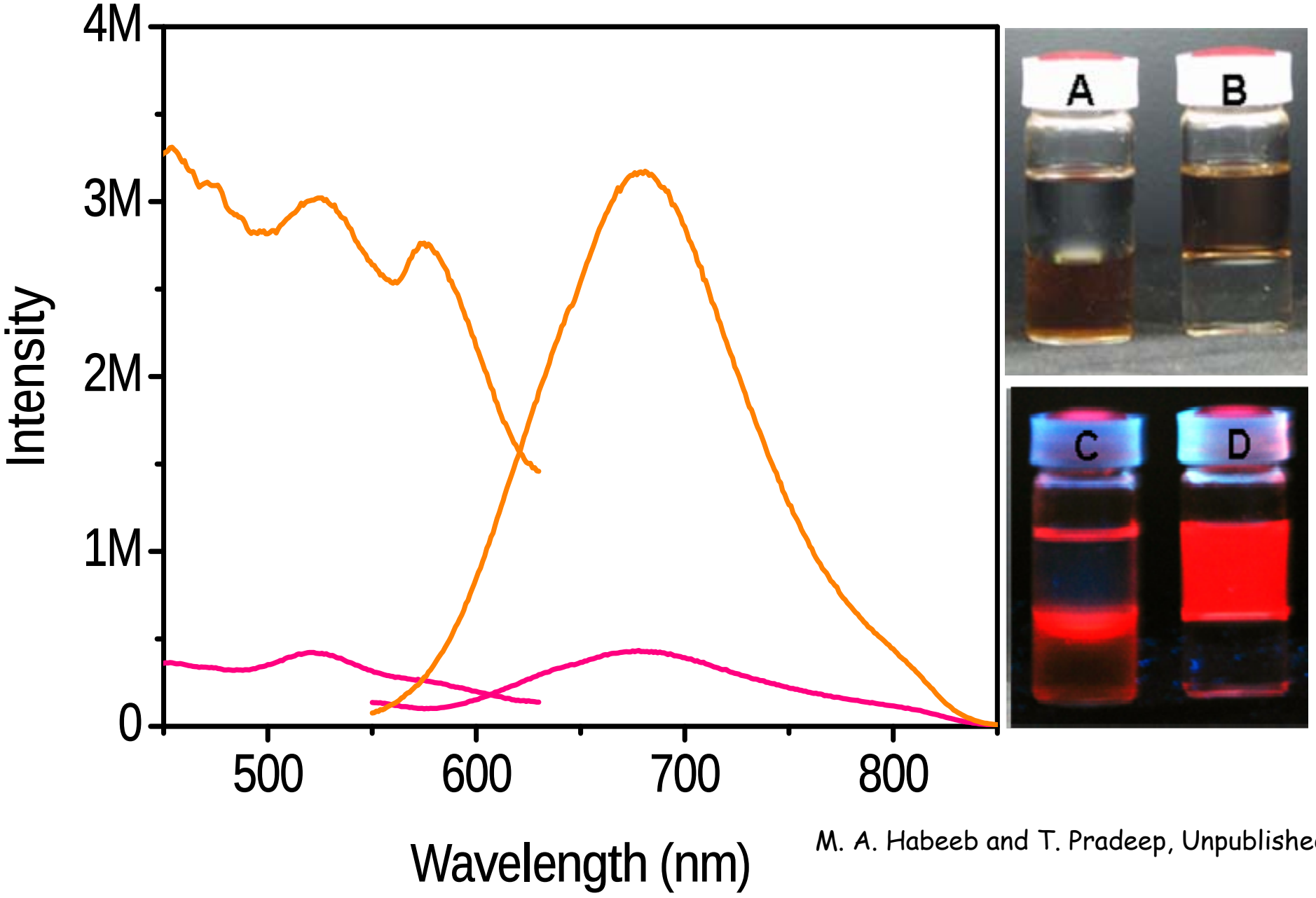
Schematic of the interfacial synthesis of red emitting clusters from $Au_{25}SG_{18}$.

Au_{22}, Au_{23} and Au_{33}



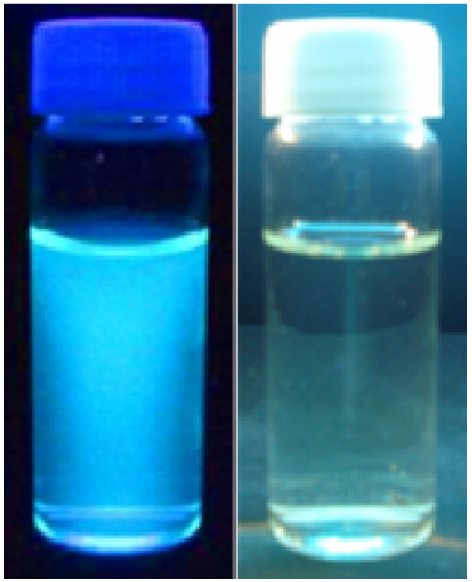
Comparison of the optical absorption spectra of $Au_{25}SG_{18}$ (black trace), red emitting cluster in aqueous (green trace) and organic layers (red trace).

Au_{23} can be phase transferred

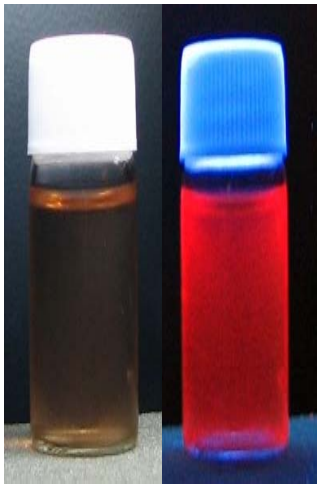


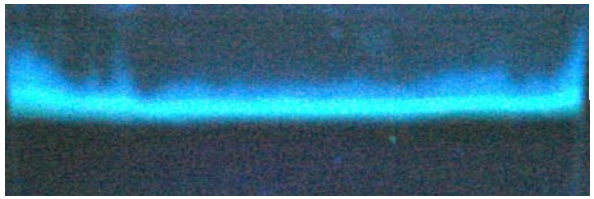
M. A. Habeeb and T. Pradeep, Unpublished

Au_8SG_8



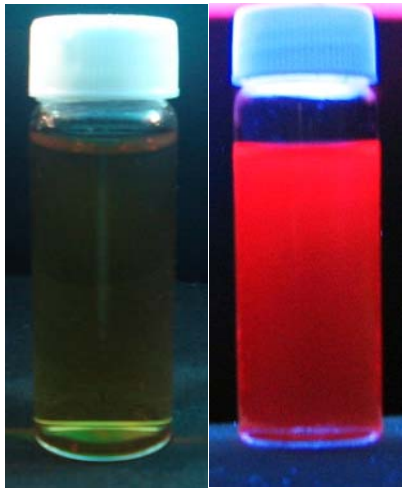
Organic soluble red emitting clusters



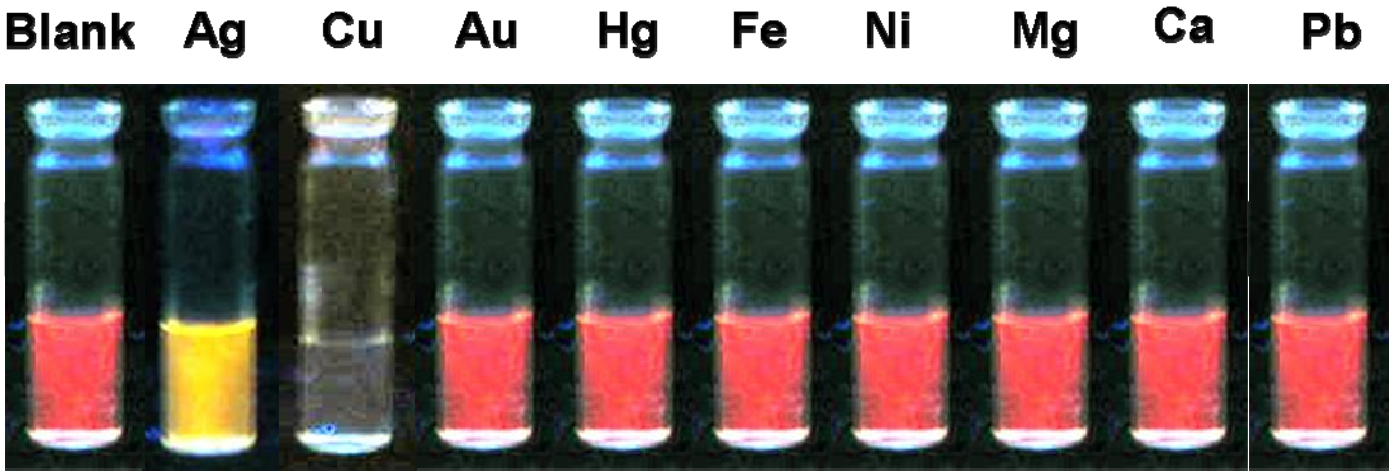


PAGE image of Au_8SG_8 cluster

Water soluble red emitting clusters

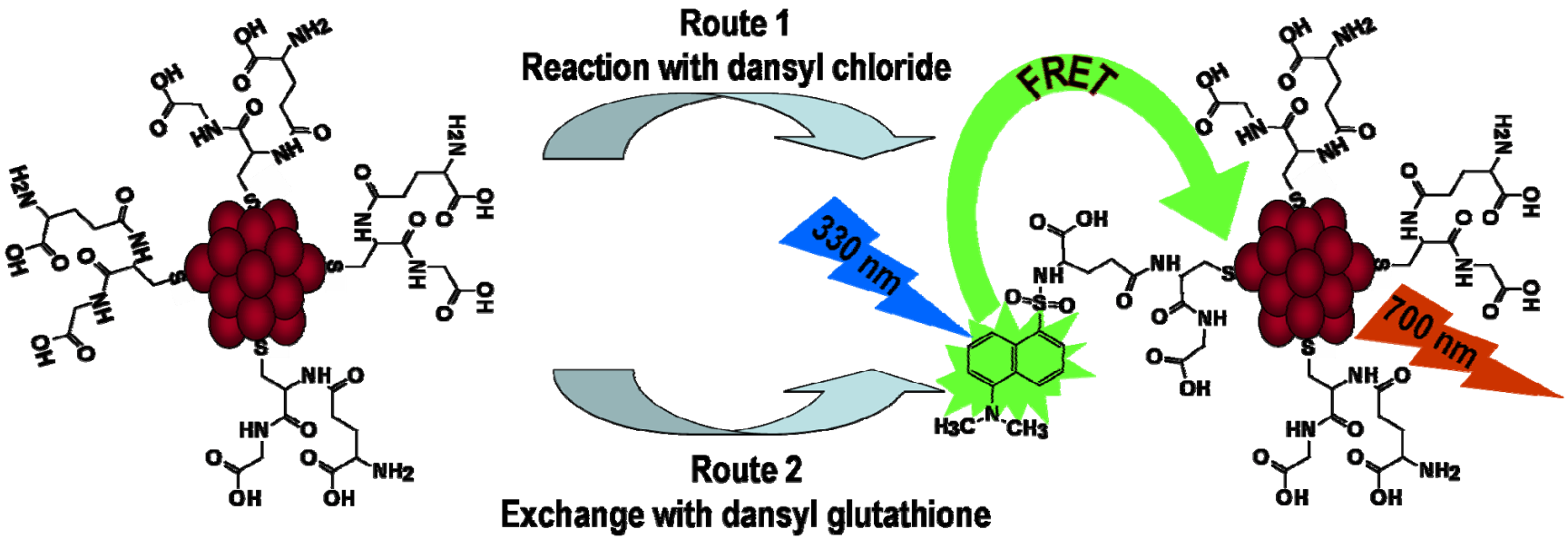


Au_{23} for metal ion detection



Water soluble red emitting clusters where treated with various metal ions with a final Concentration of 25 ppm. The emission was shifted to lower wavelength in case of silver ions and quenched completely in case of copper ions. The emission was an altered in case of other ions.

FRET between Au_{25} and Dansyl Chromophore

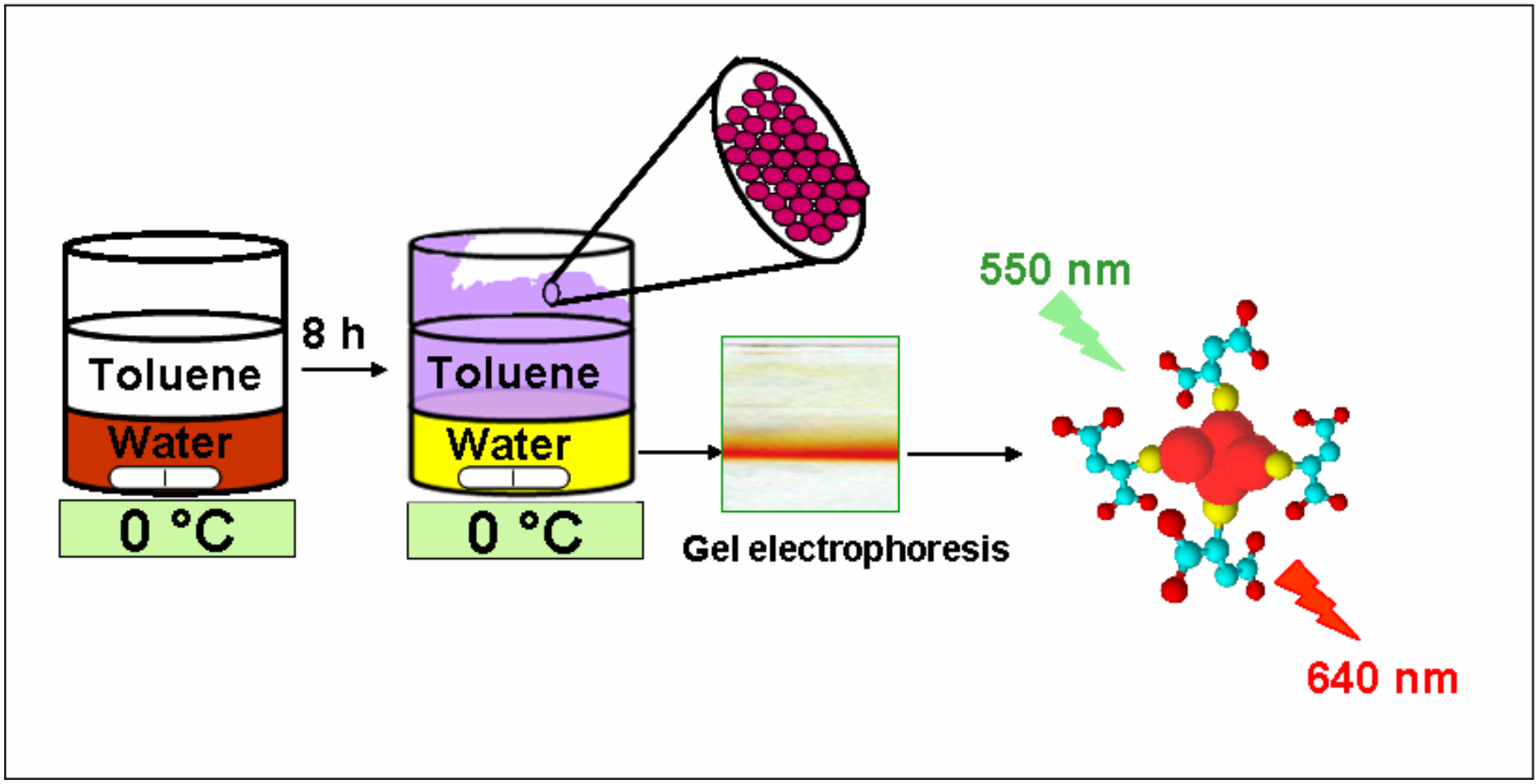


Approaches Used for the Functionalization of Dansyl Chromophore on the Au_{25} Cluster.

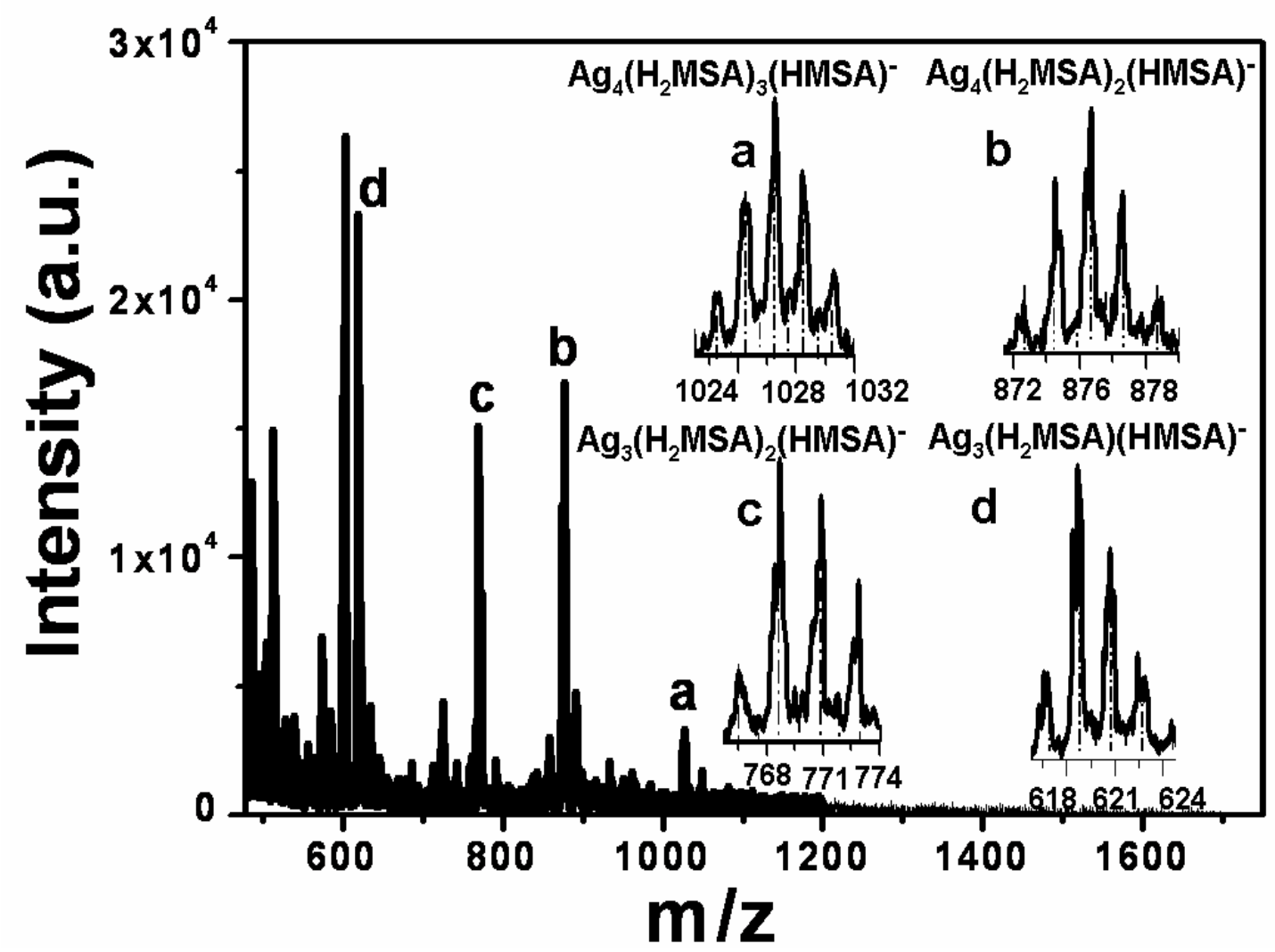
Habeeb et al J.Phys. Chem. 2008

Silver clusters

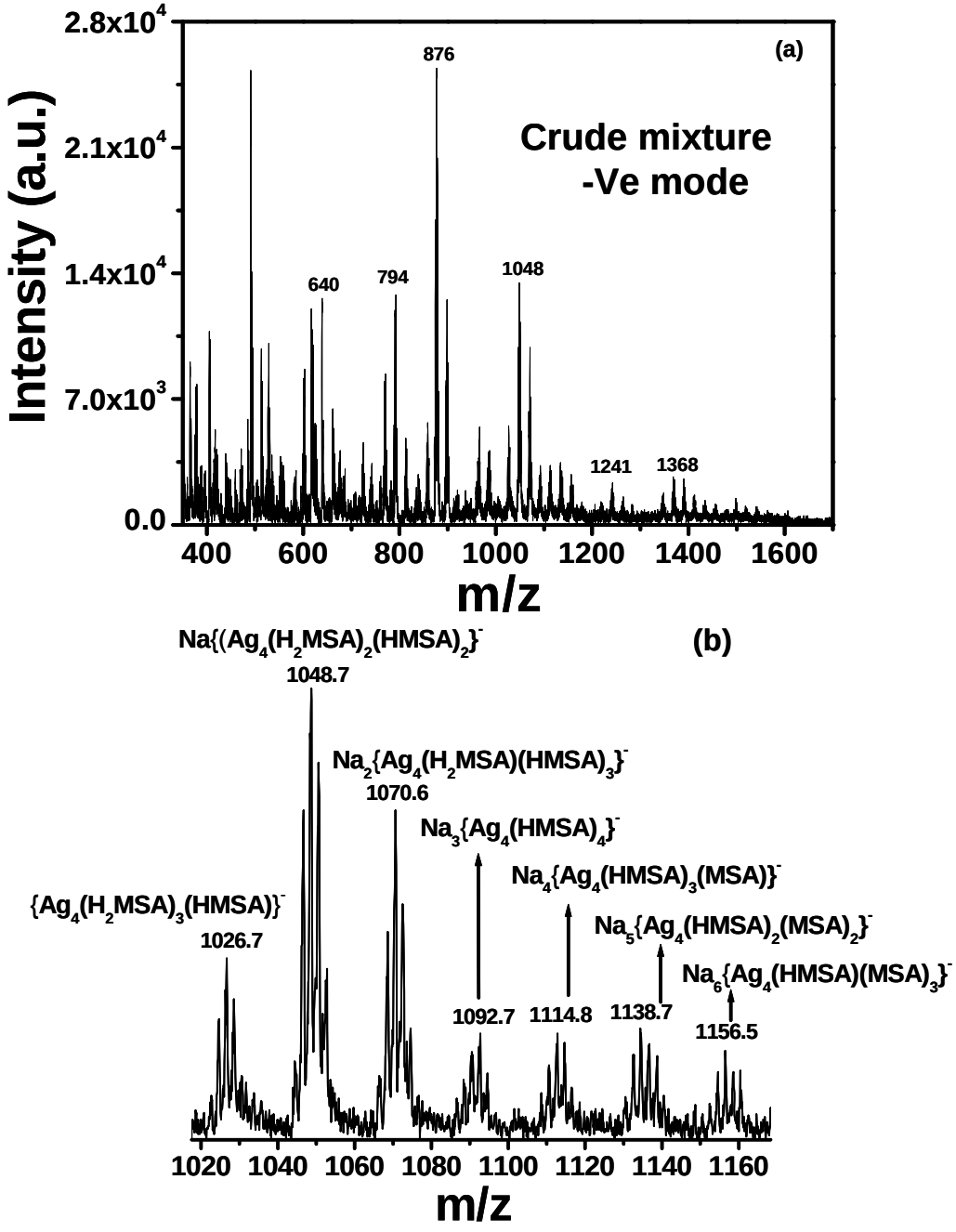
Interfacial etching

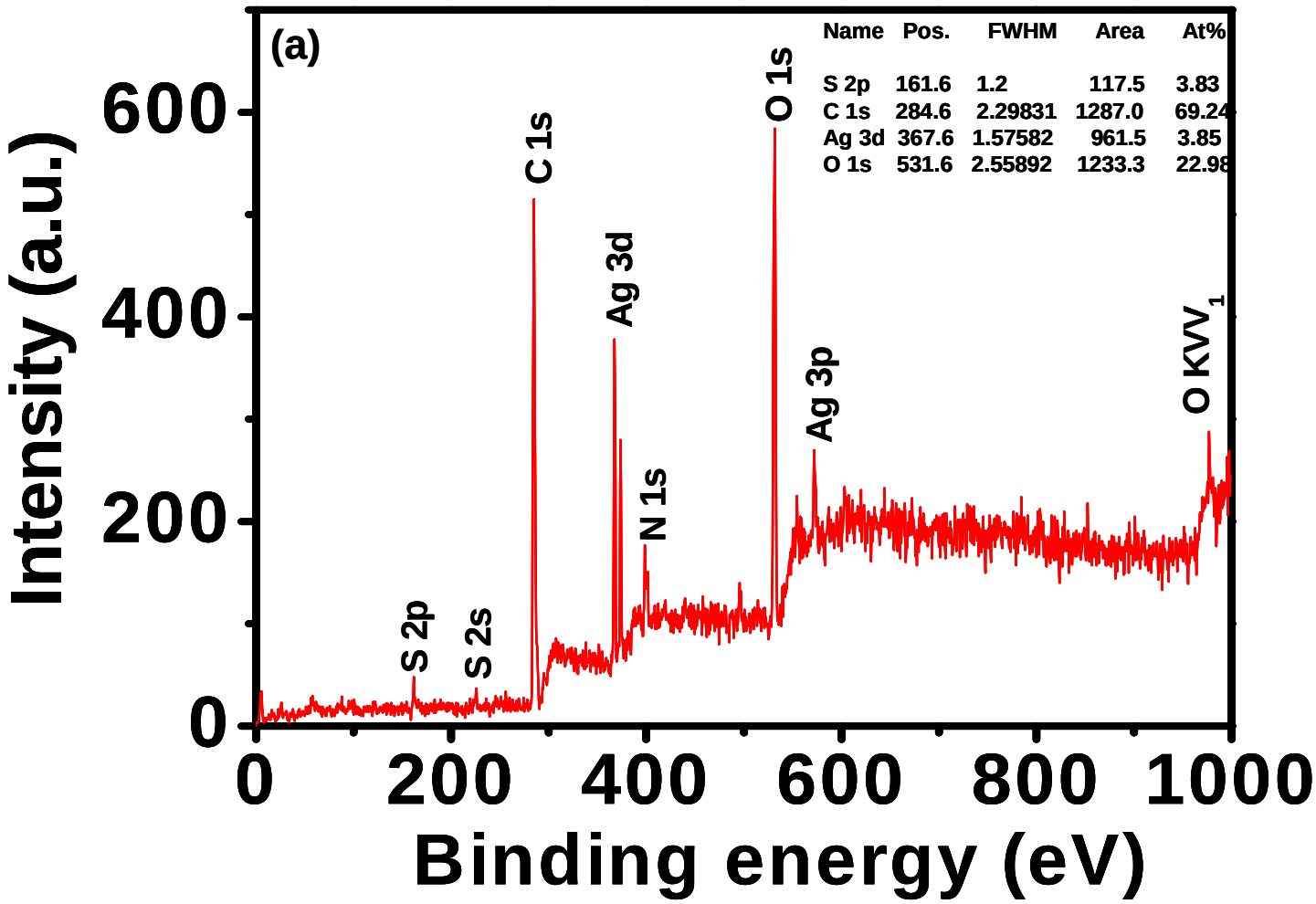


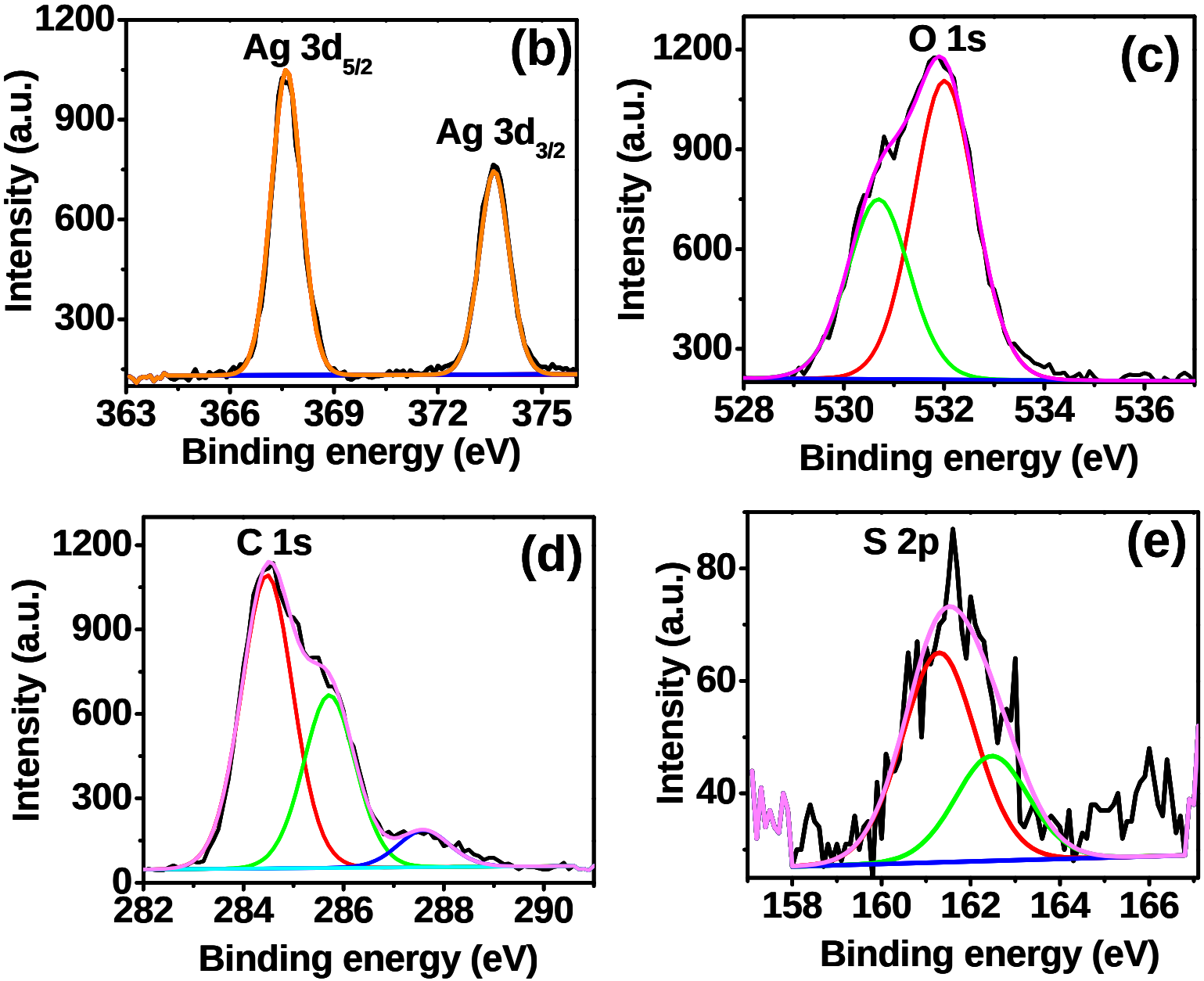
Ag_4MSA_4

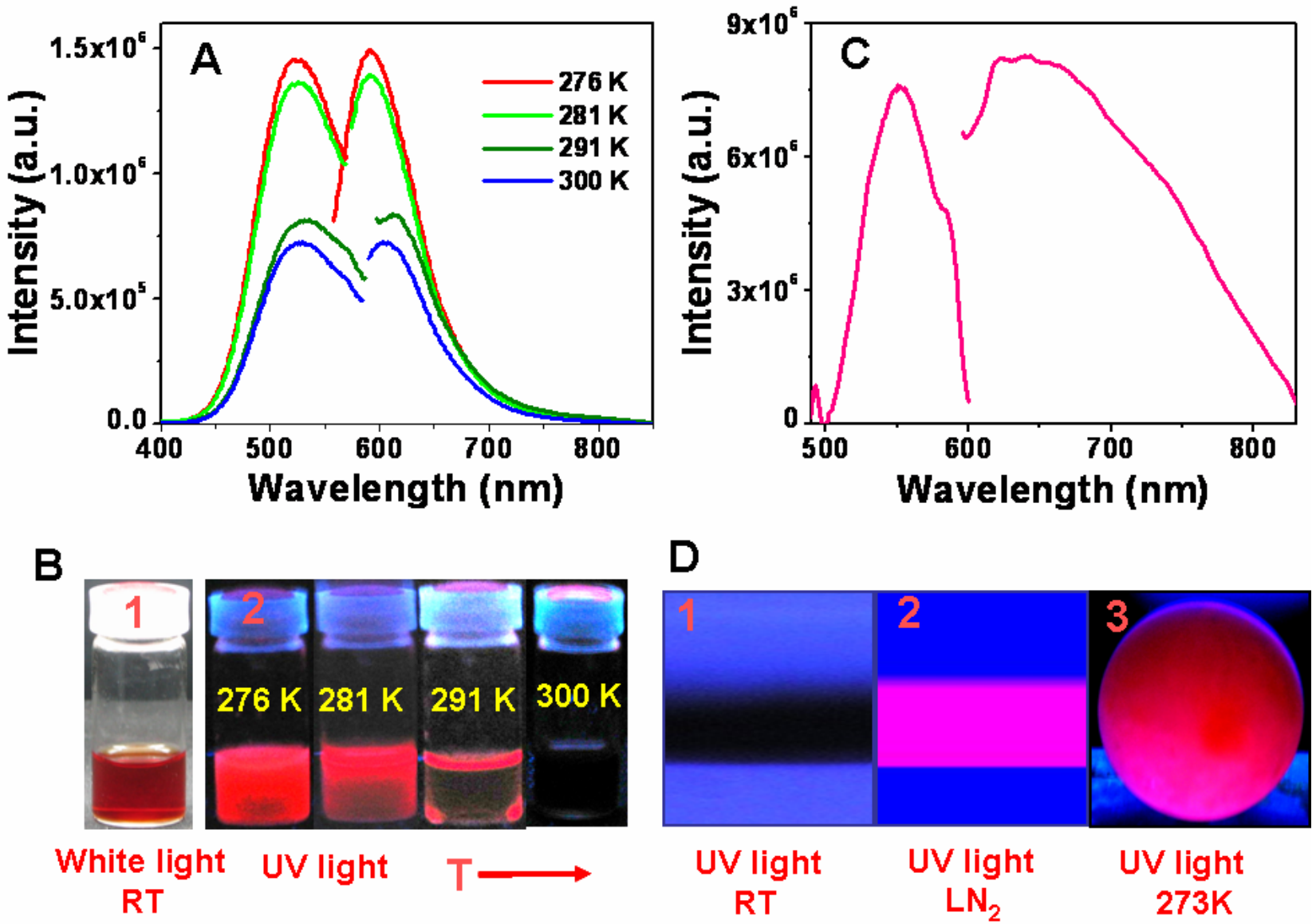


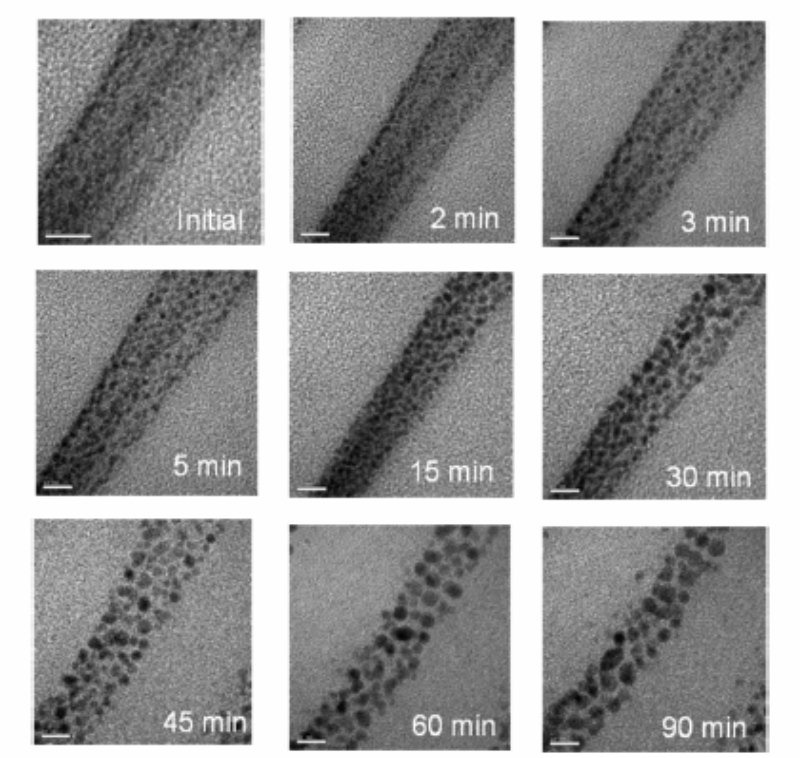
Unpublished

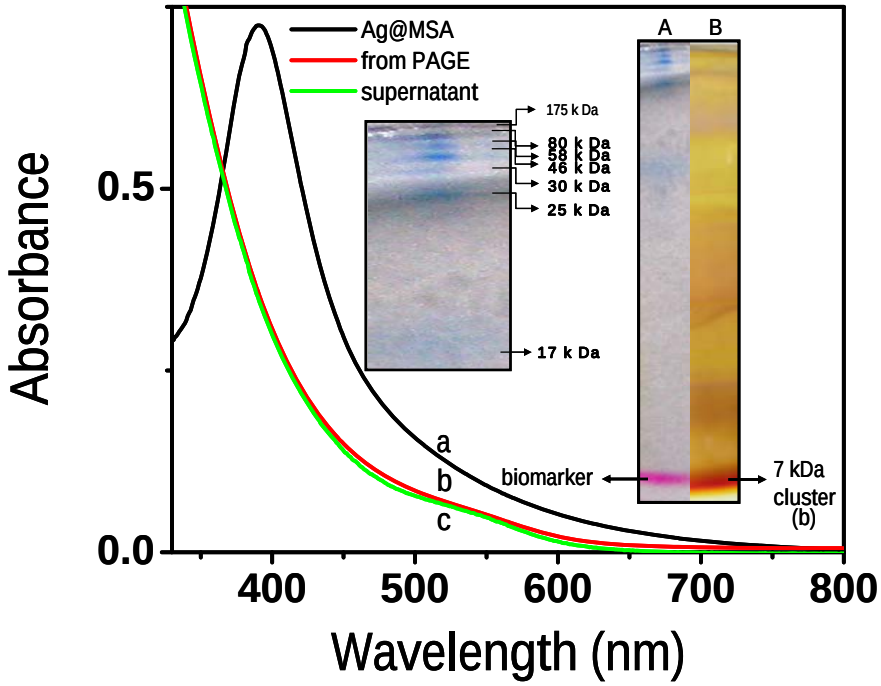

(a)
Crude mixture
-Ve mode
Intensity (a.u.)
2.8x10^4
2.1x10^4
1.4x10^4
7.0x10^3
0.0
876
640
794
1048
1241
1368
400
600
800
1000
1200
1400
1600
m/z
(b)
Na{(Ag4(H2MSA)2(HMSA)2}-
1048.7
Na2{Ag4(H2MSA)(HMSA)3}-
1070.6
Na3{Ag4(HMSA)4}-
Na4{Ag4(HMSA)3(MSA)}-
Na5{Ag4(HMSA)2(MSA)2}-
Na6{Ag4(HMSA)(MSA)3}-
{Ag4(H2MSA)3(HMSA)}-
1026.7
1092.7
1114.8
1138.7
1156.5
1020
1040
1060
1080
1100
1120
1140
1160
m/z


(a)
Name Pos. FWHM Area At%
S 2p 161.6 1.2 117.5 3.83
C 1s 284.6 2.29831 1287.0 69.24
Ag 3d 367.6 1.57582 961.5 3.85
O 1s 531.6 2.55892 1233.3 22.98
S 2p
S 2s
C 1s
Ag 3d
N 1s
O 1s
Ag 3p
O KVV1
Intensity (a.u.)
0
200
400
600
0
200
400
600
800
1000
Binding energy (eV)


(b)
Ag 3d5/2
Ag 3d3/2
Intensity (a.u.)
Binding energy (eV)
(c)
O 1s
(d)
C 1s
(e)
S 2p


A
Intensity (a.u.)
1.5x10^6
1.0x10^6
5.0x10^5
0.0
400
500
600
700
800
Wavelength (nm)
276 K
281 K
291 K
300 K
C
Intensity (a.u.)
9x10^6
6x10^6
3x10^6
0
500
600
700
800
Wavelength (nm)
B
1
2
276 K
281 K
291 K
300 K
White light
RT
UV light
T
D
1
2
3
UV light
RT
UV light
LN2
UV light
273K





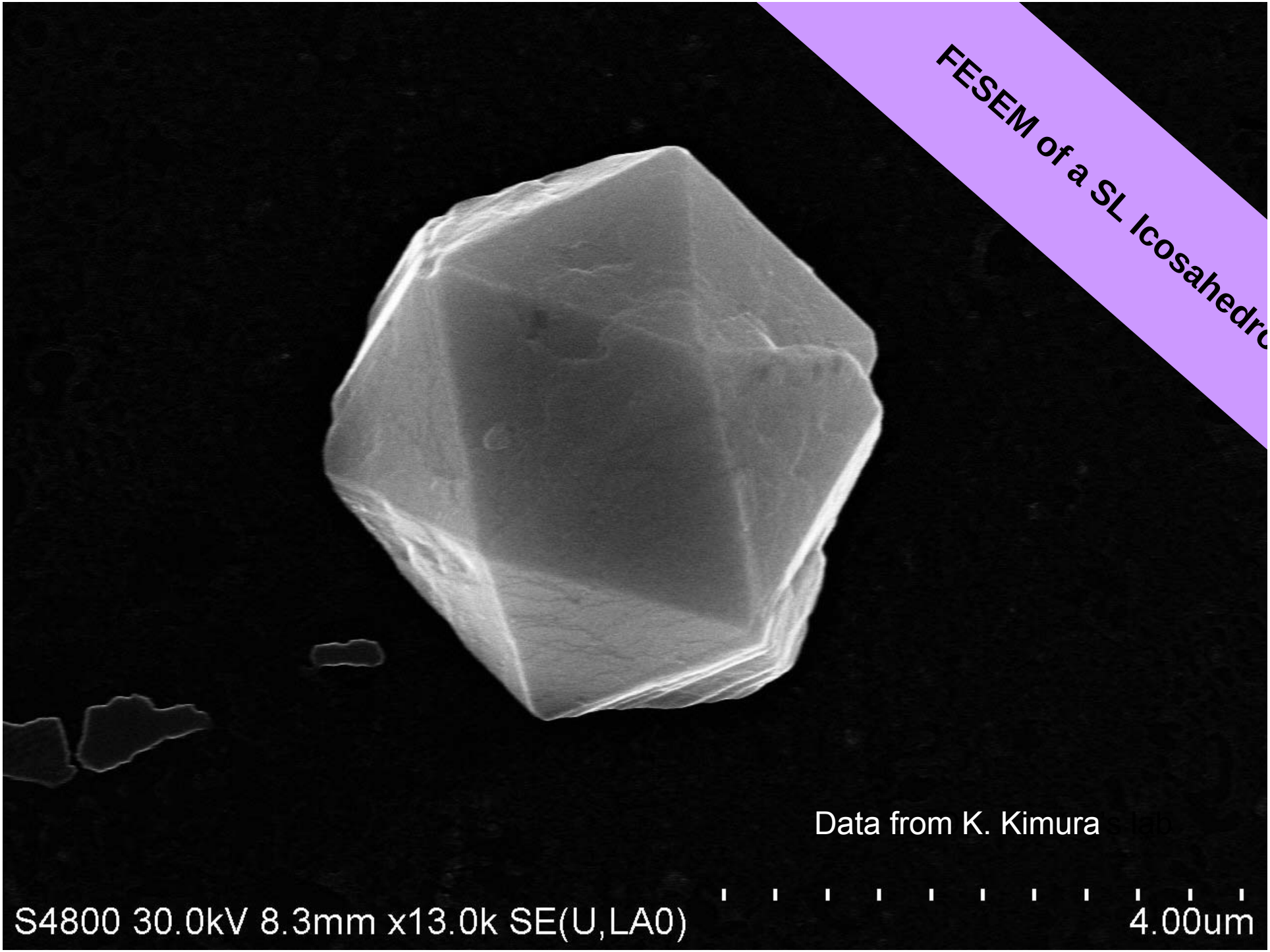
7 kDa clusters of silver

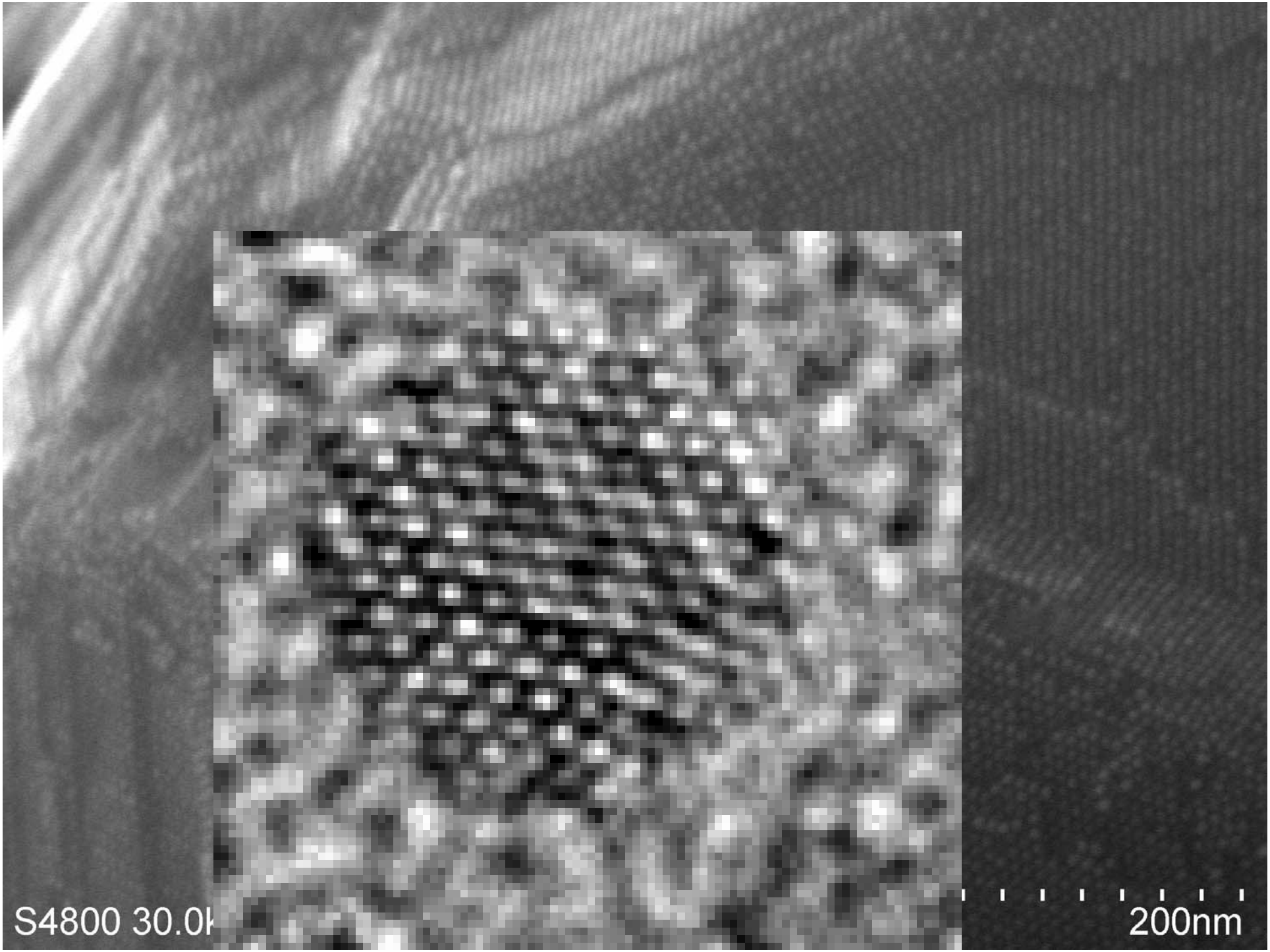
J. Mater. Chem. 2009

Metal nanoparticle superlattices

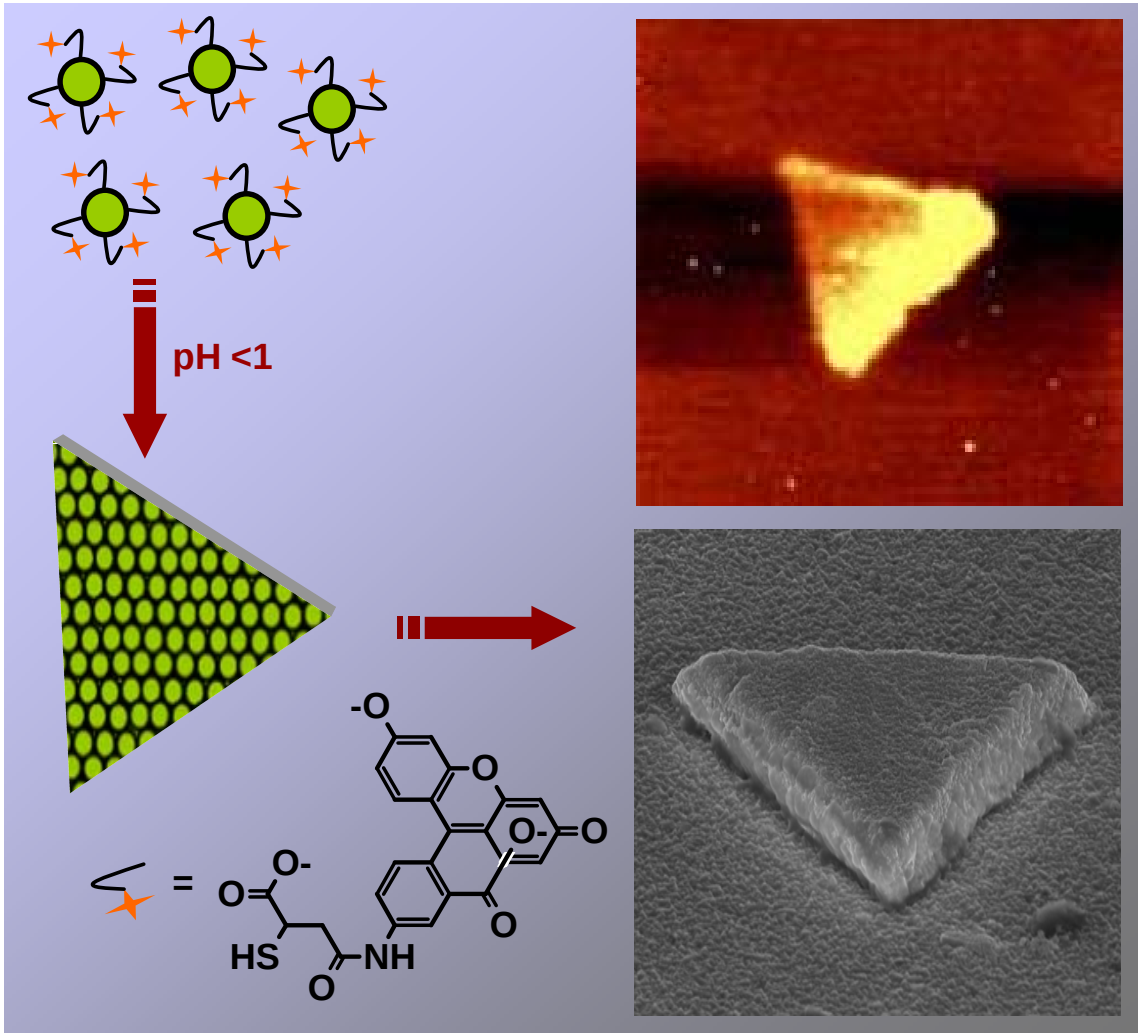
Particle crystals
Multiple periodicity
Particles may not have orientational order
Unit cells of a few nm

New applications


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

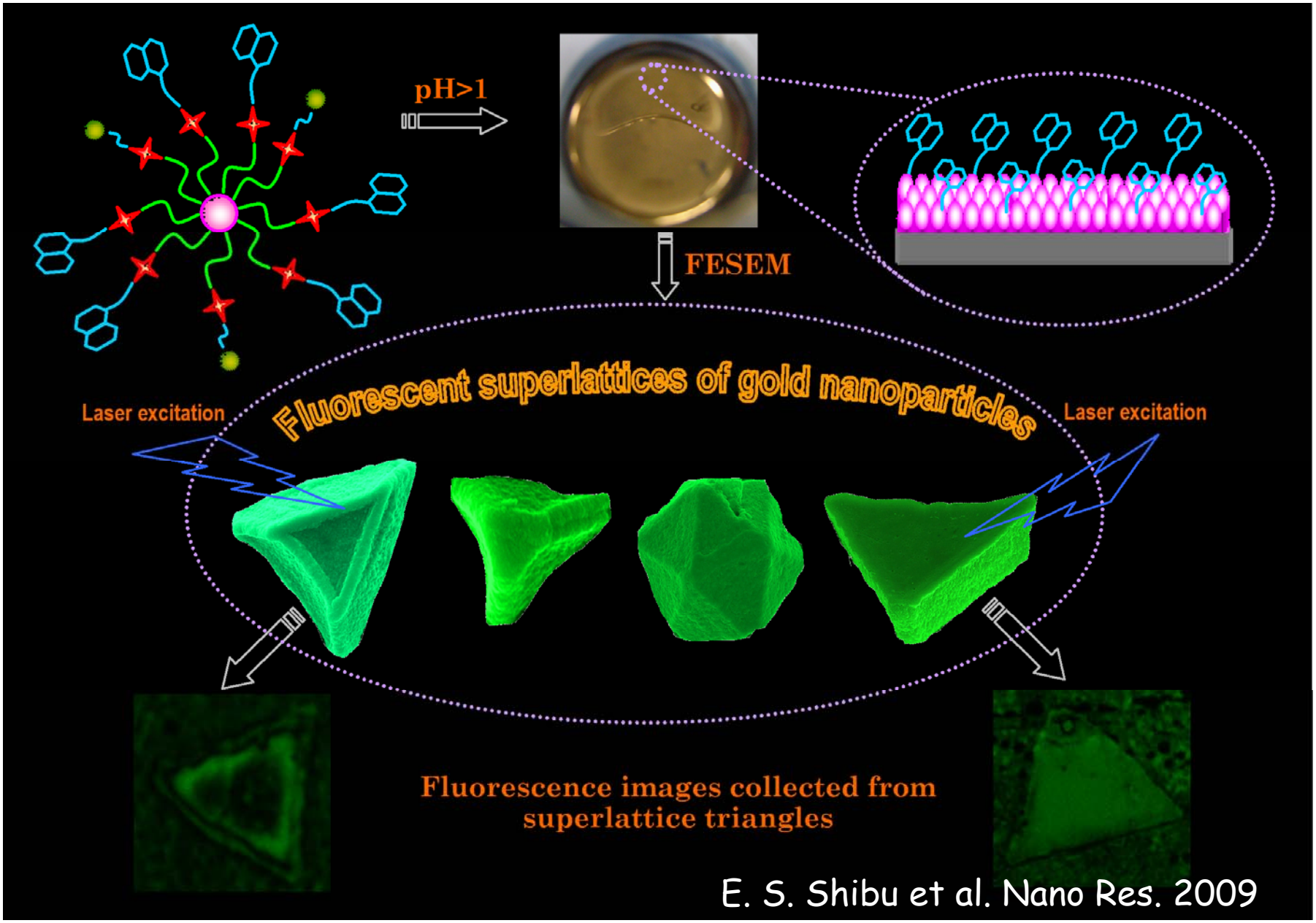

S4800 30.0k
200nm

SAMSA-Functionalized SLs



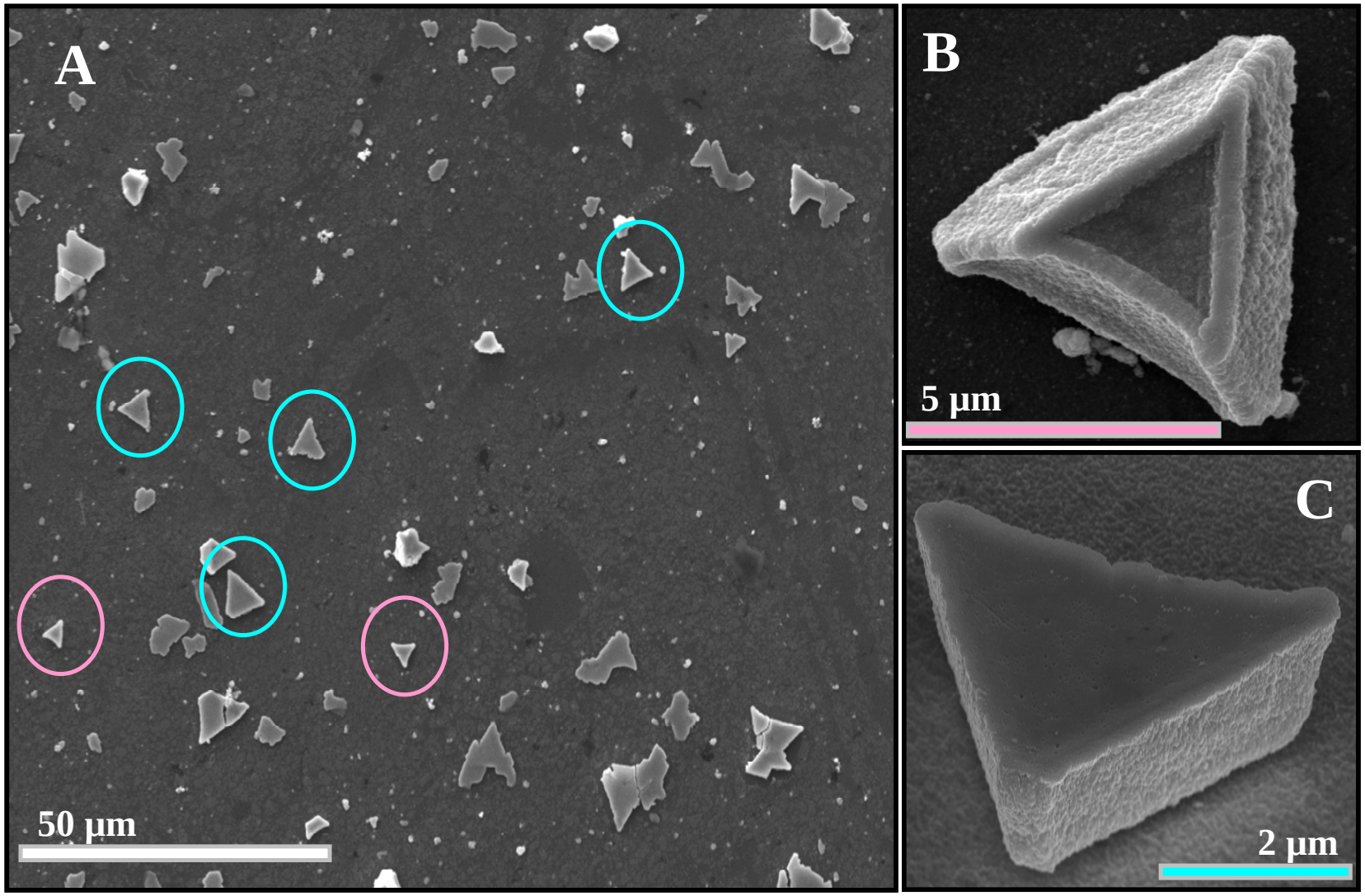
Shibu et al. Adv. Mat. 2008

Fluorescent superlattices



E. S. Shibu et al. Nano Res. 2009

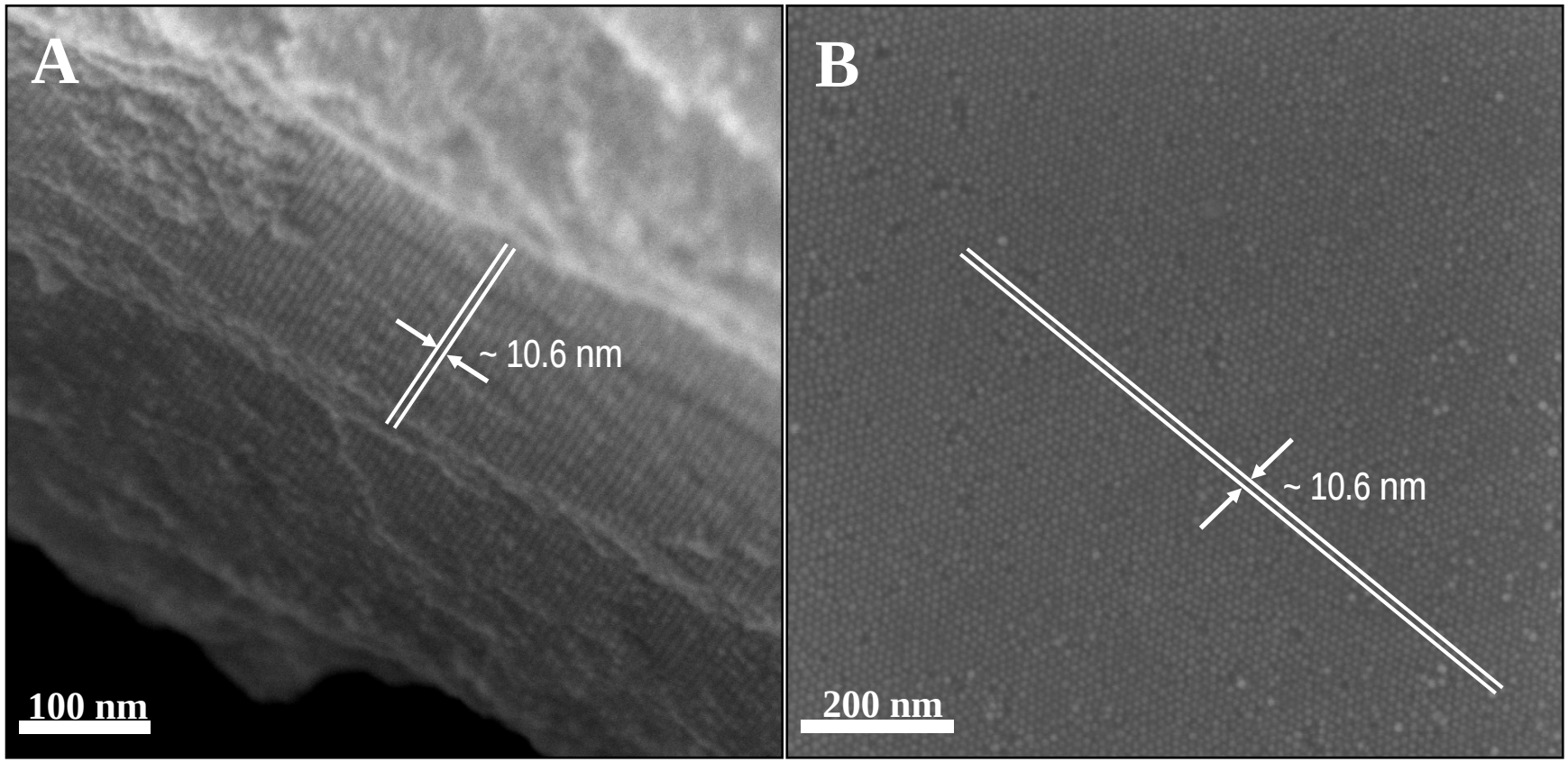
TWO DIFFERENT TRIANGLES



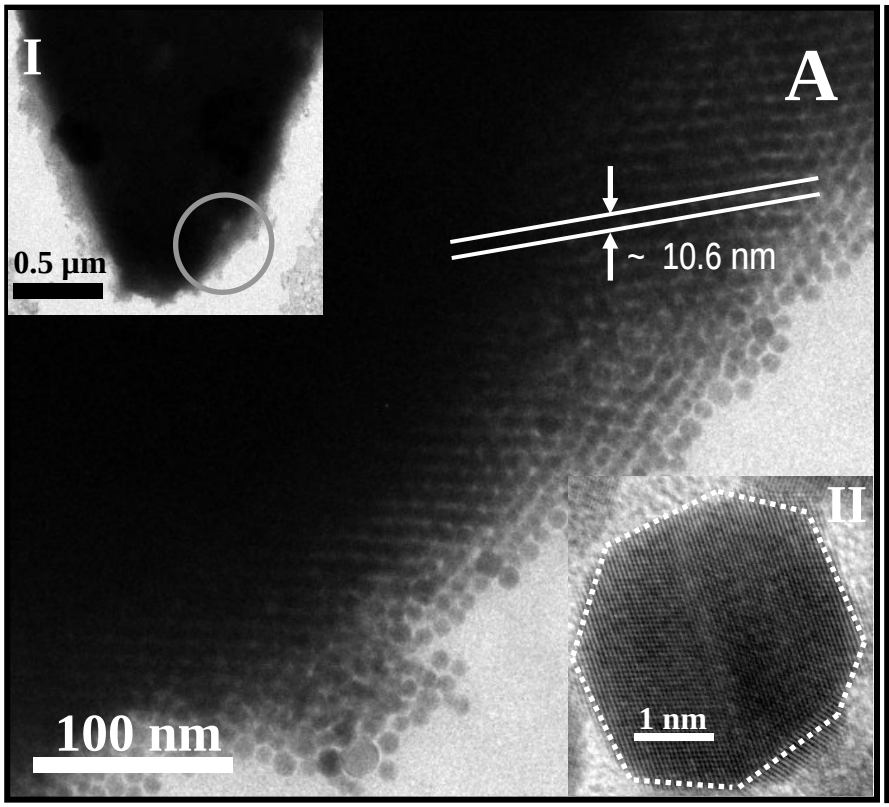
FESEM images – G.U. Kulkarni

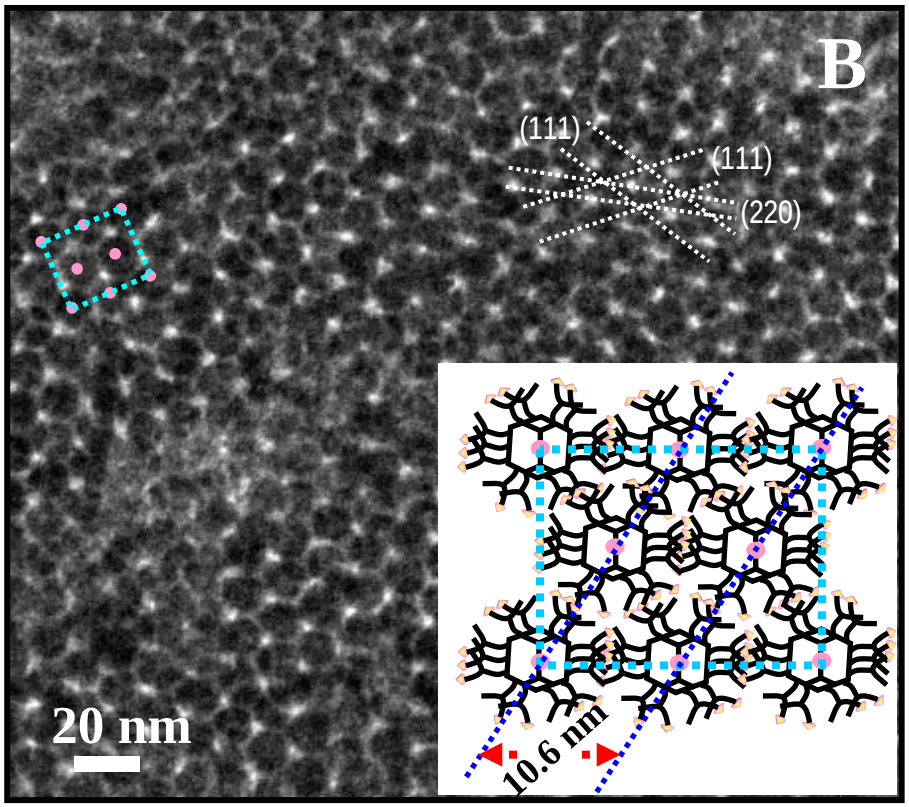
Shibu et al. Nano Research 2009

LARGE AREA FESEM

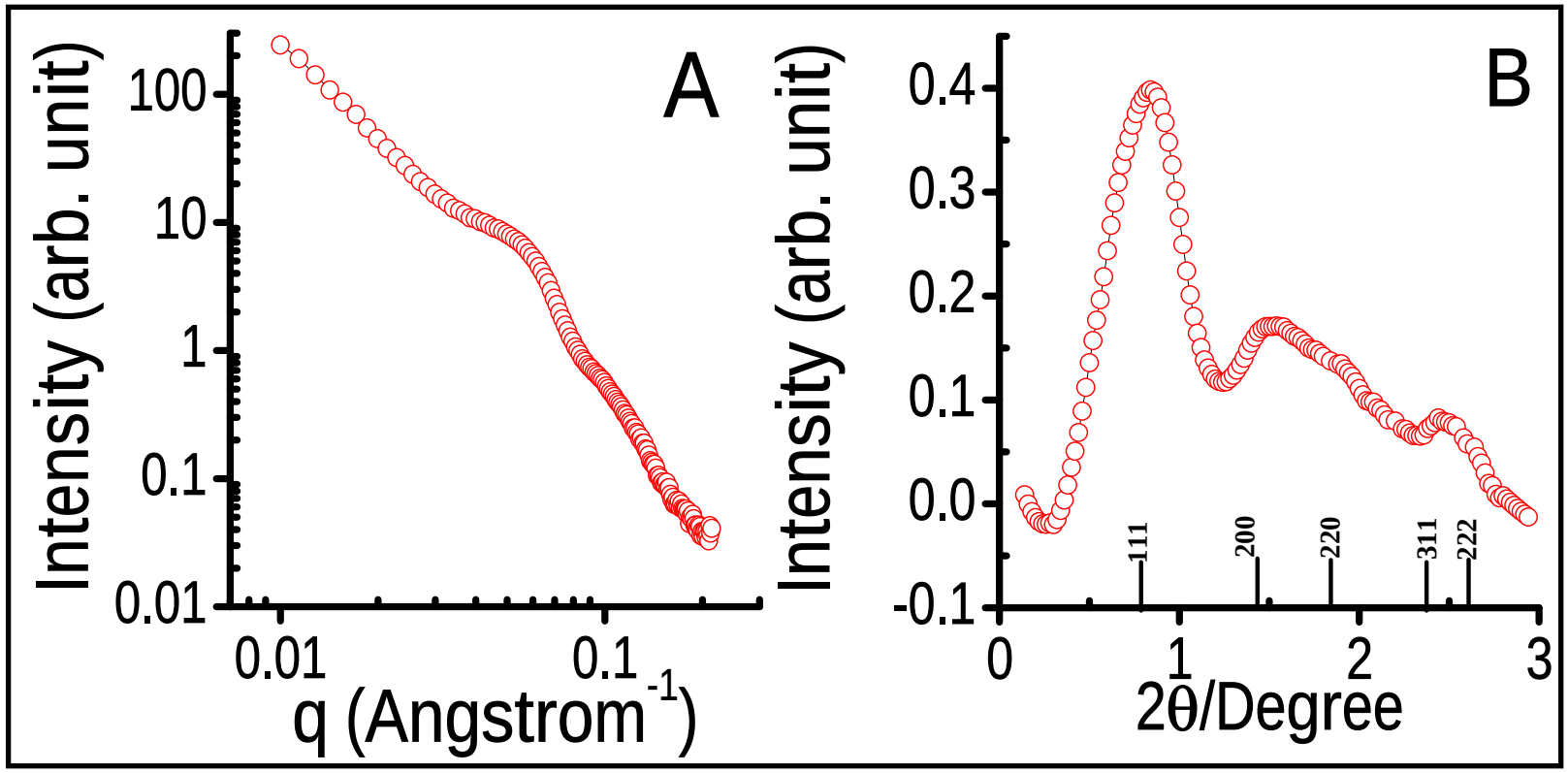


HR TEM-Images



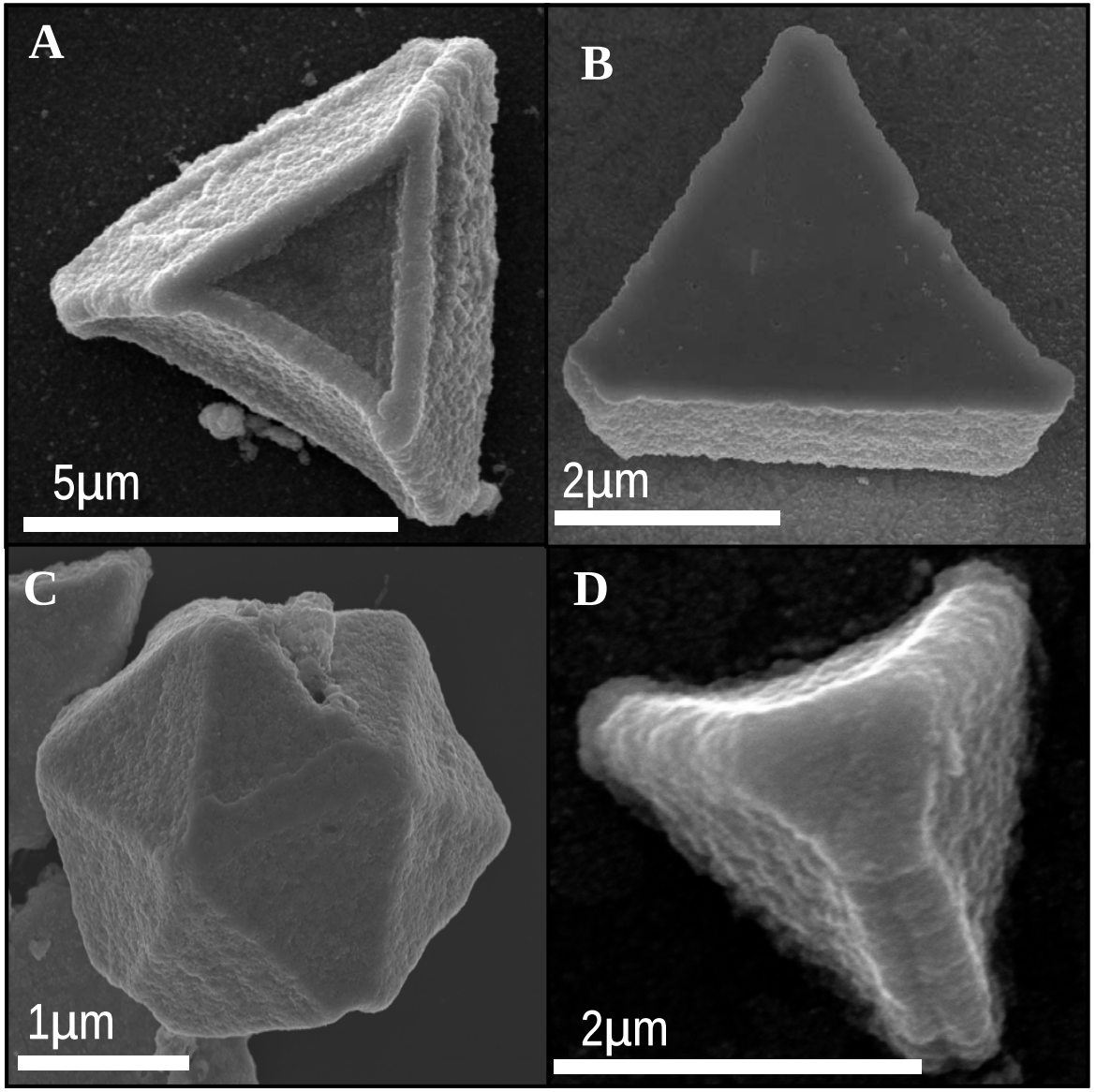


SAXS

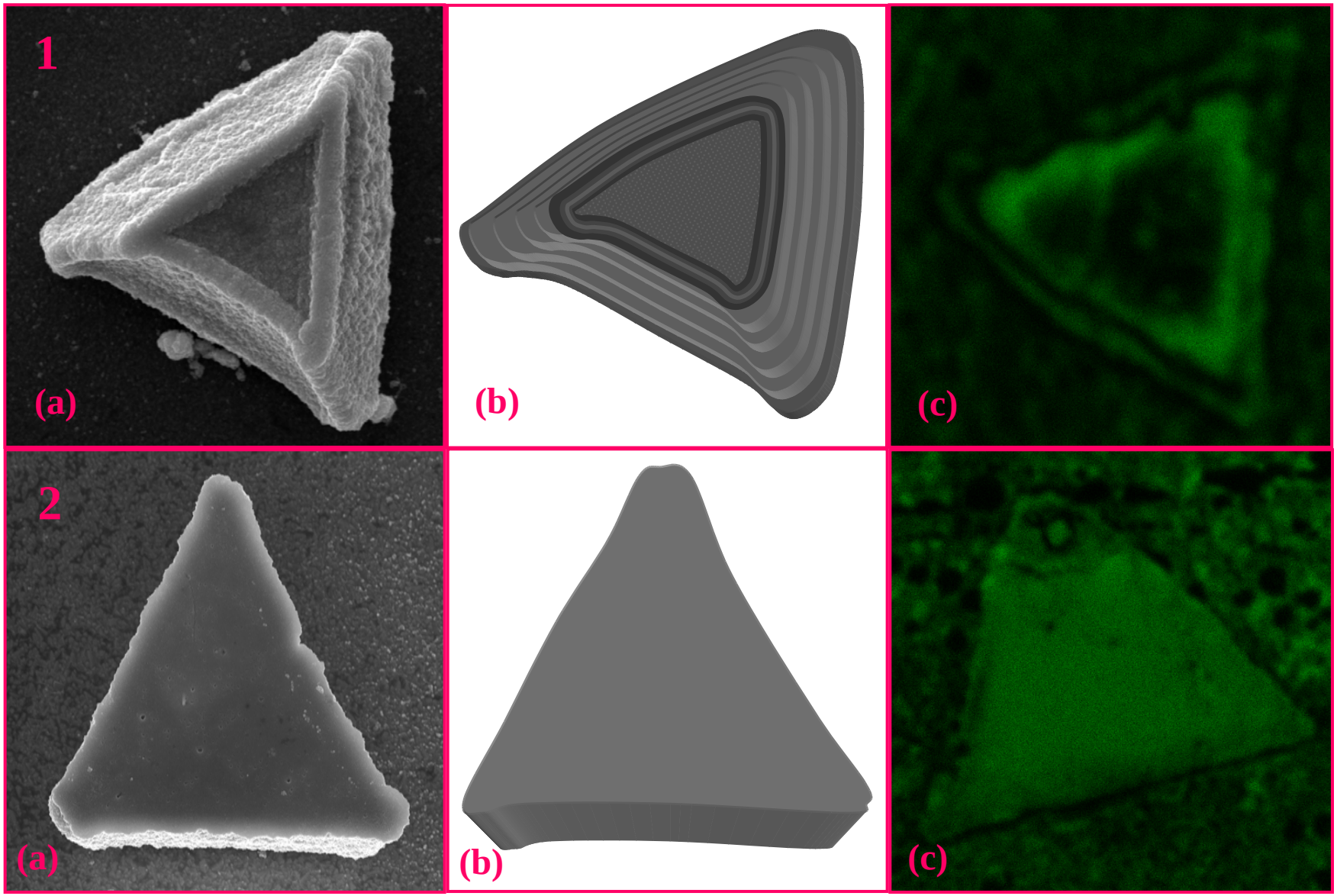


Measured in Prof. C. N. R. Rao's Lab

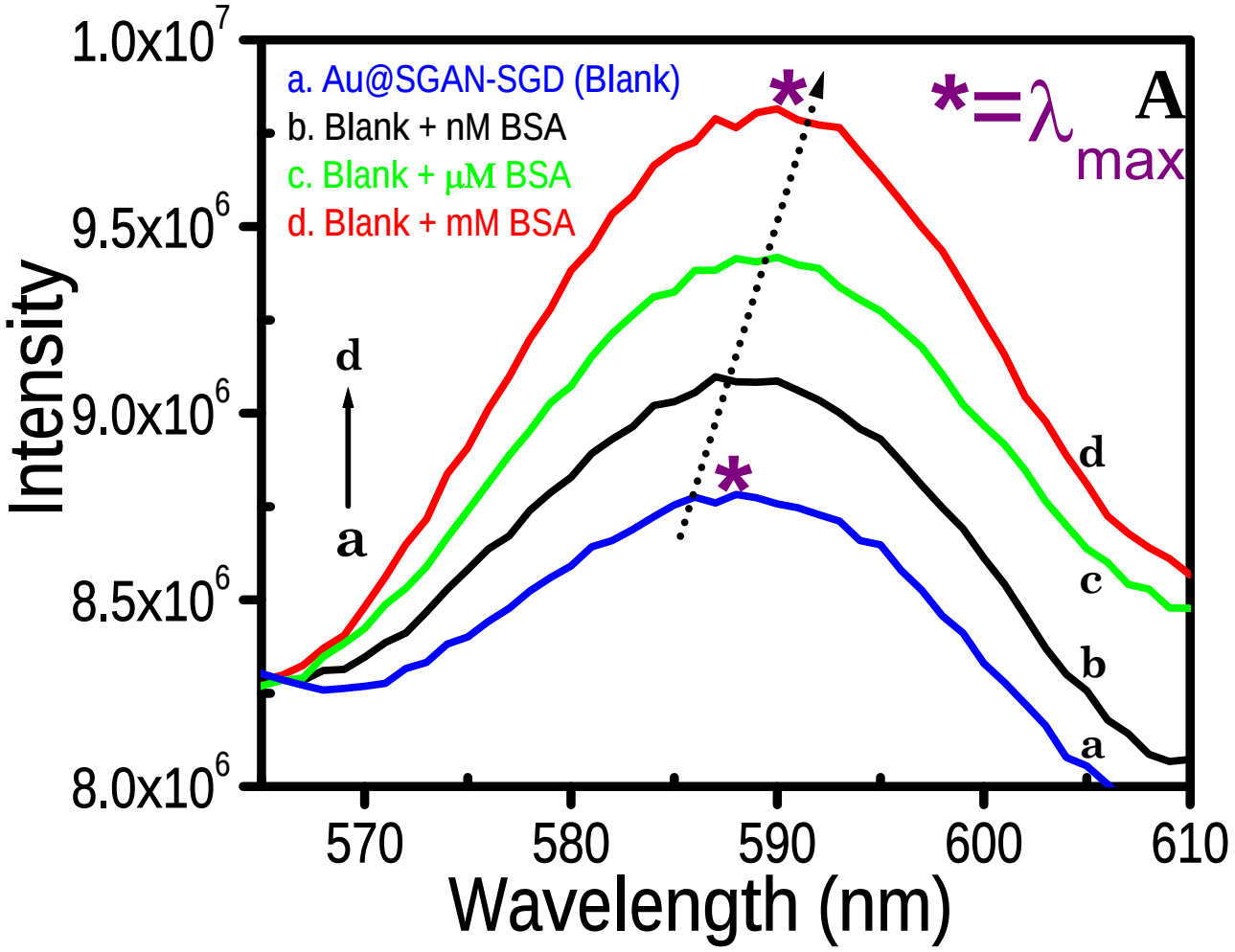
OTHER MORPHOLOGIES

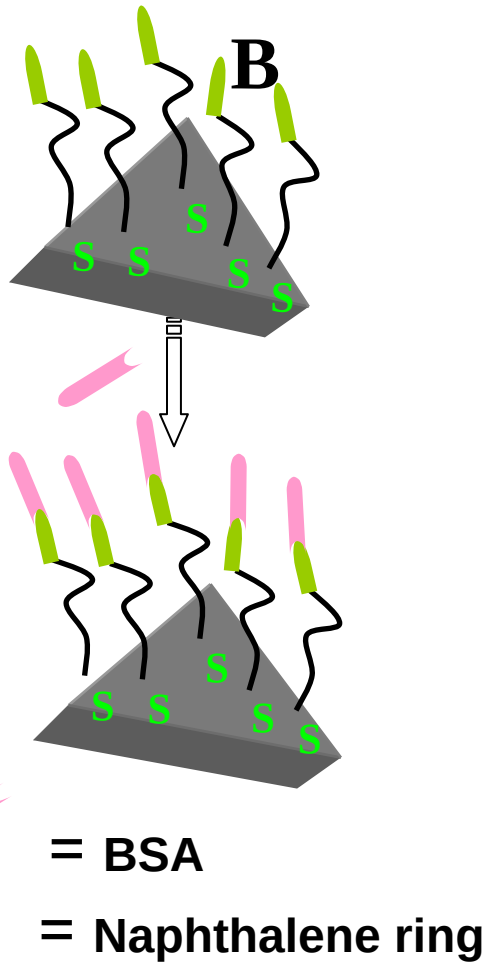


Investigation of crystal fluorescence

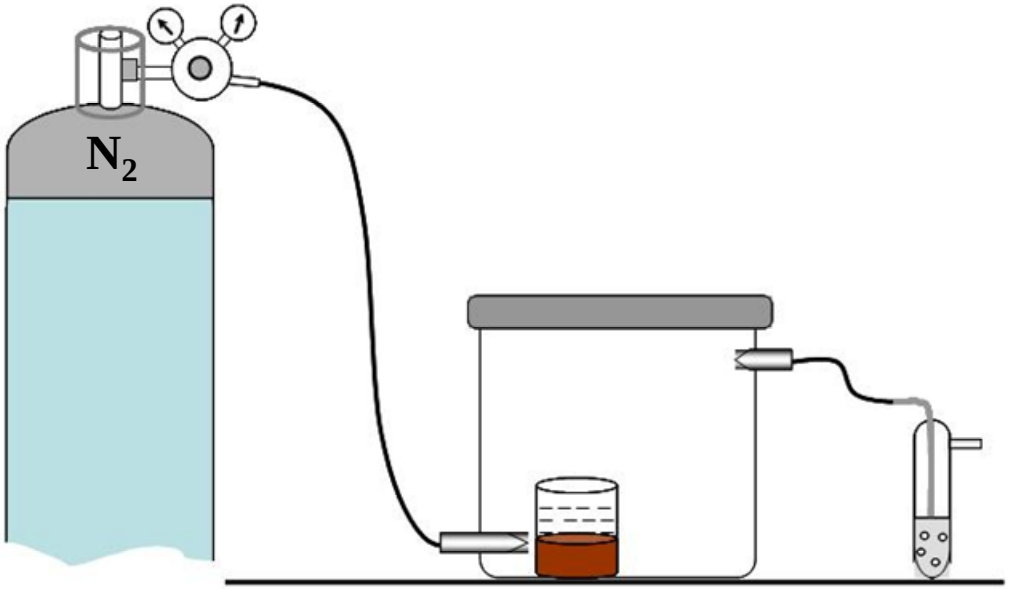


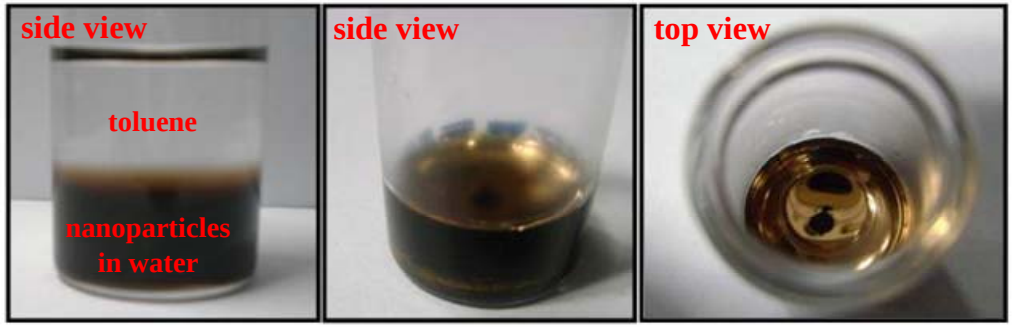
Selective detection of BSA using dansylglutathione SLs





Interfacial synthesis – superlattices in one day

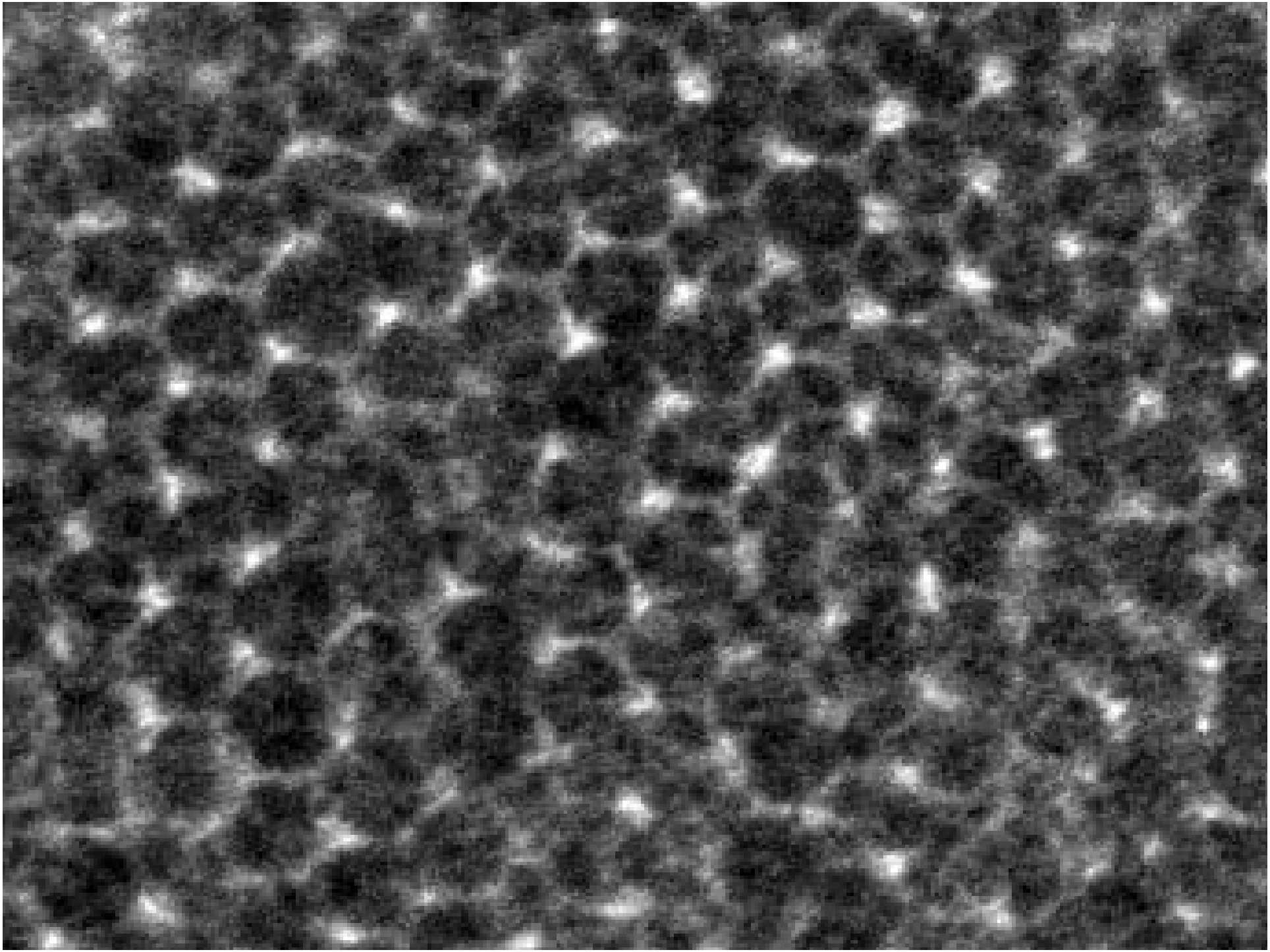




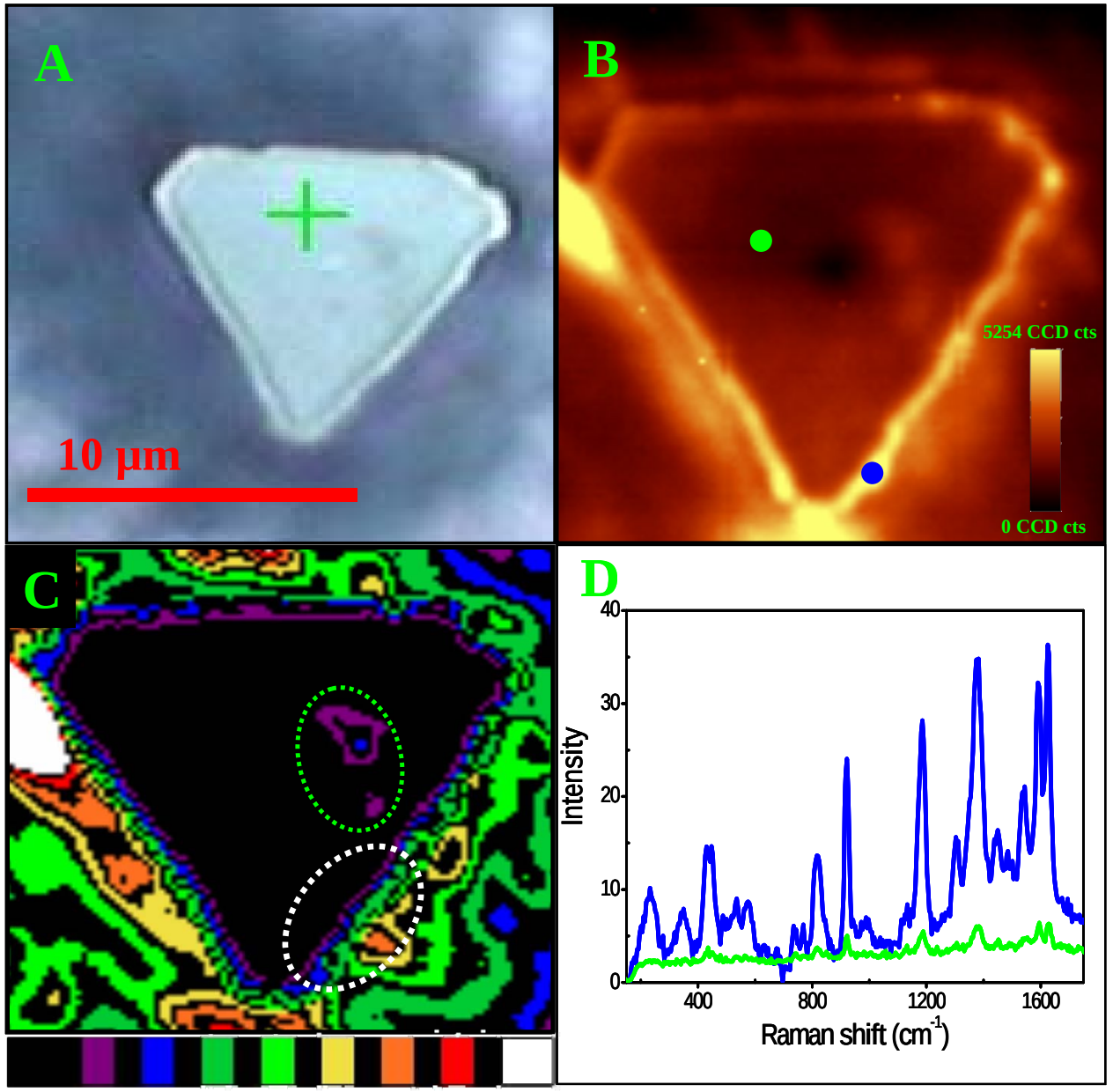
Stage 1 Stage 2 Stage 3

E. S. Shibu and T. Pradeep, Submitted

PHOTOGRAPH OF THE SET-UP

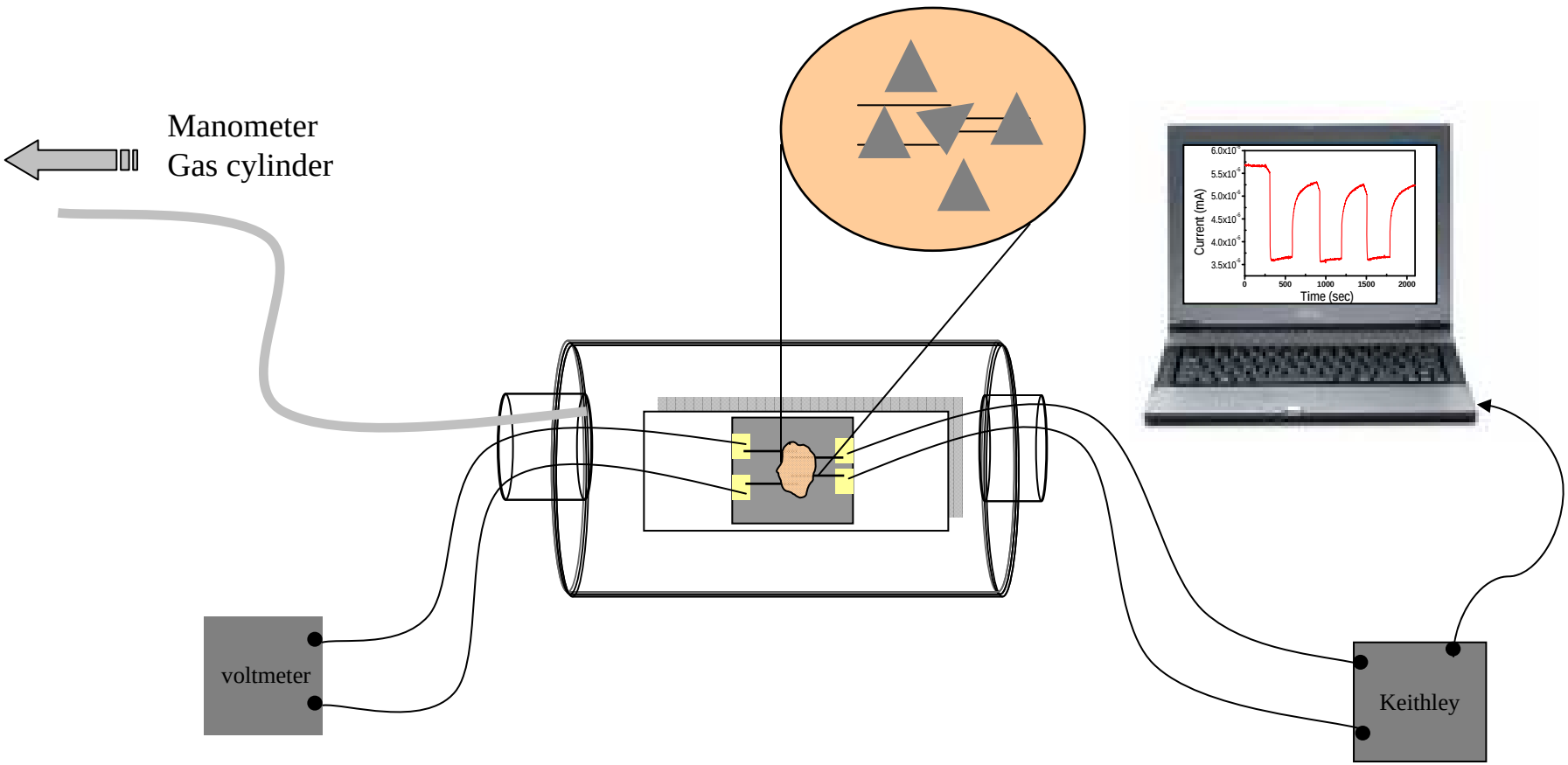


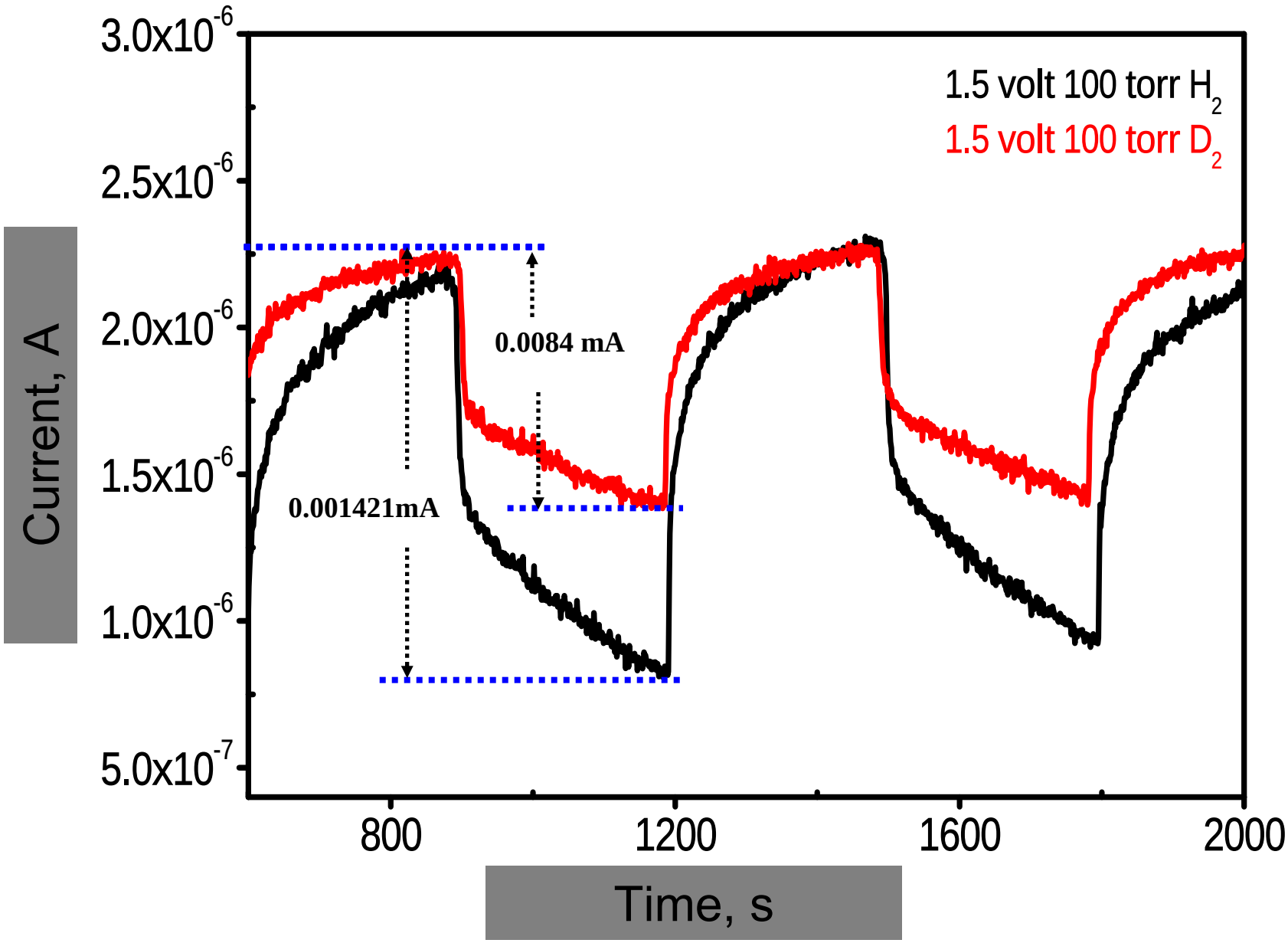
RAMAN MAPPING

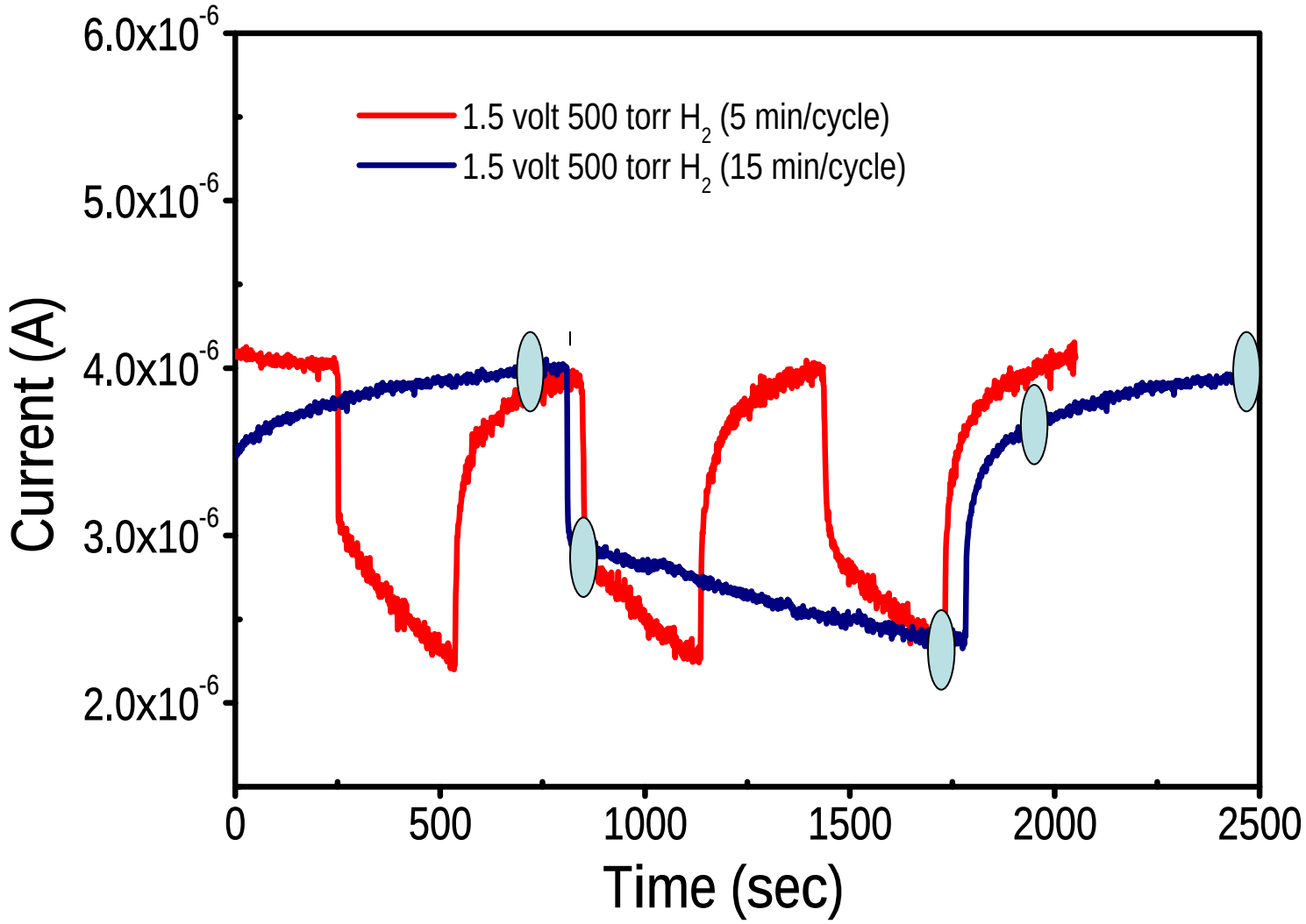


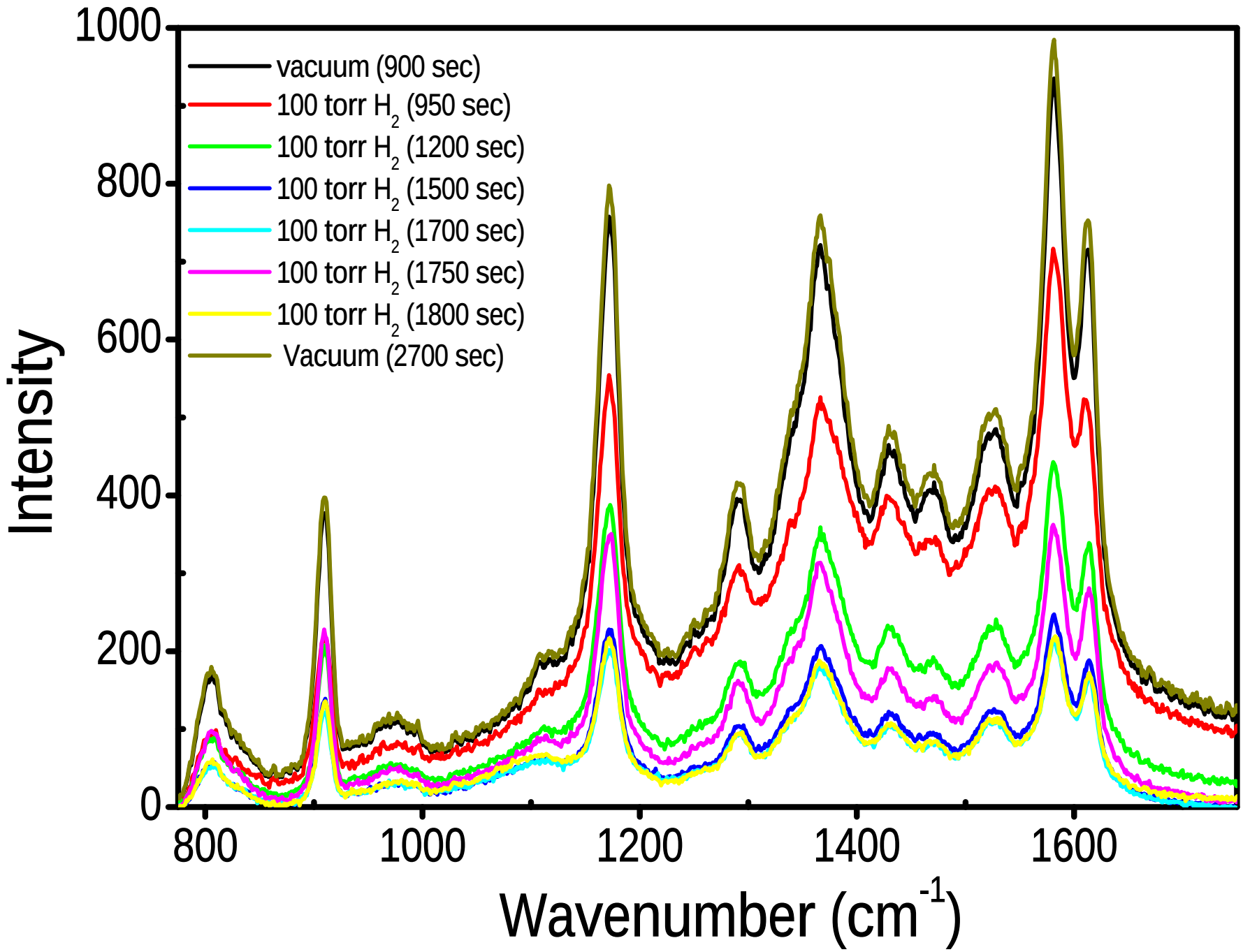
Au@MSA SL Triangles

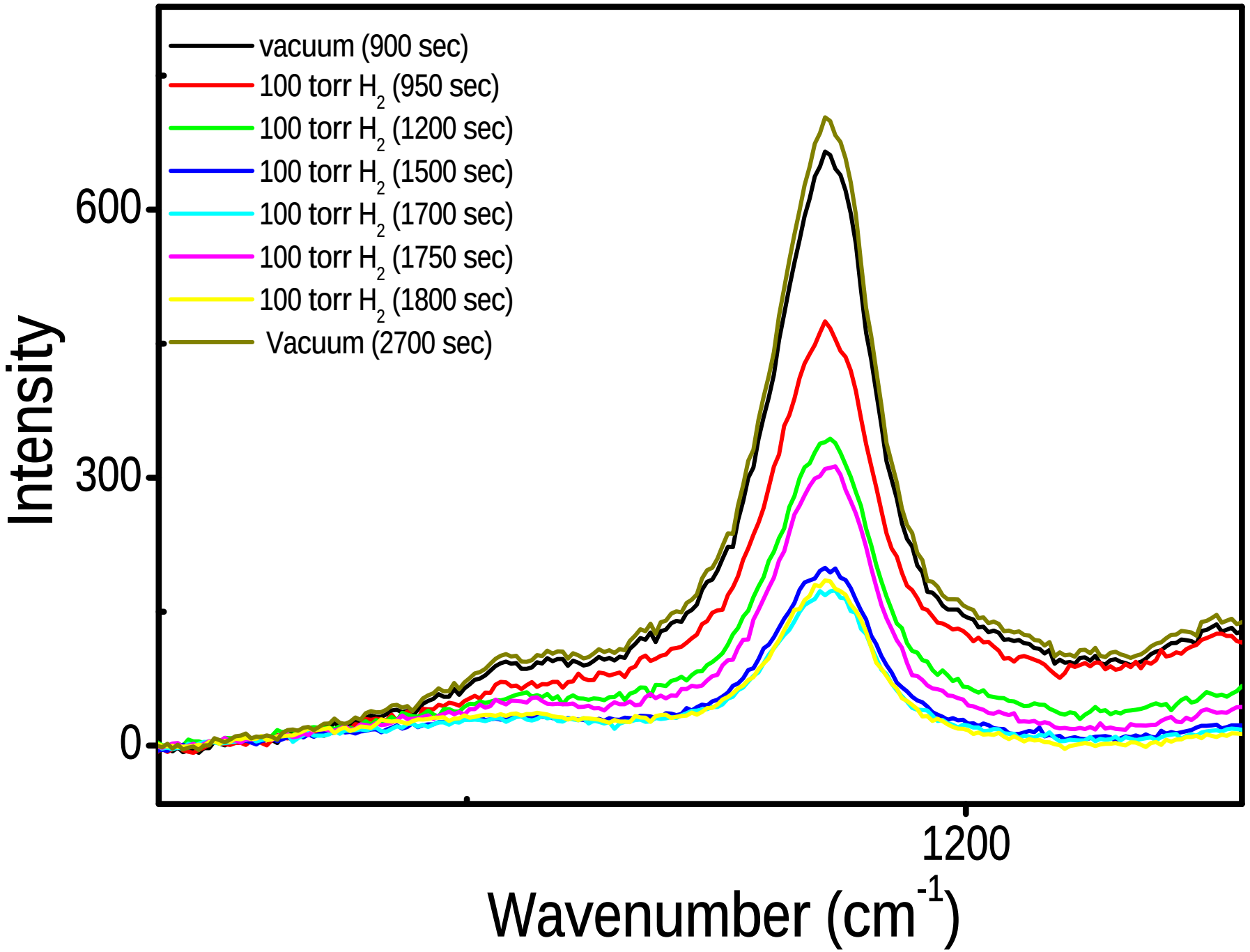
E. S. Shibu and T. Pradeep, Submitted

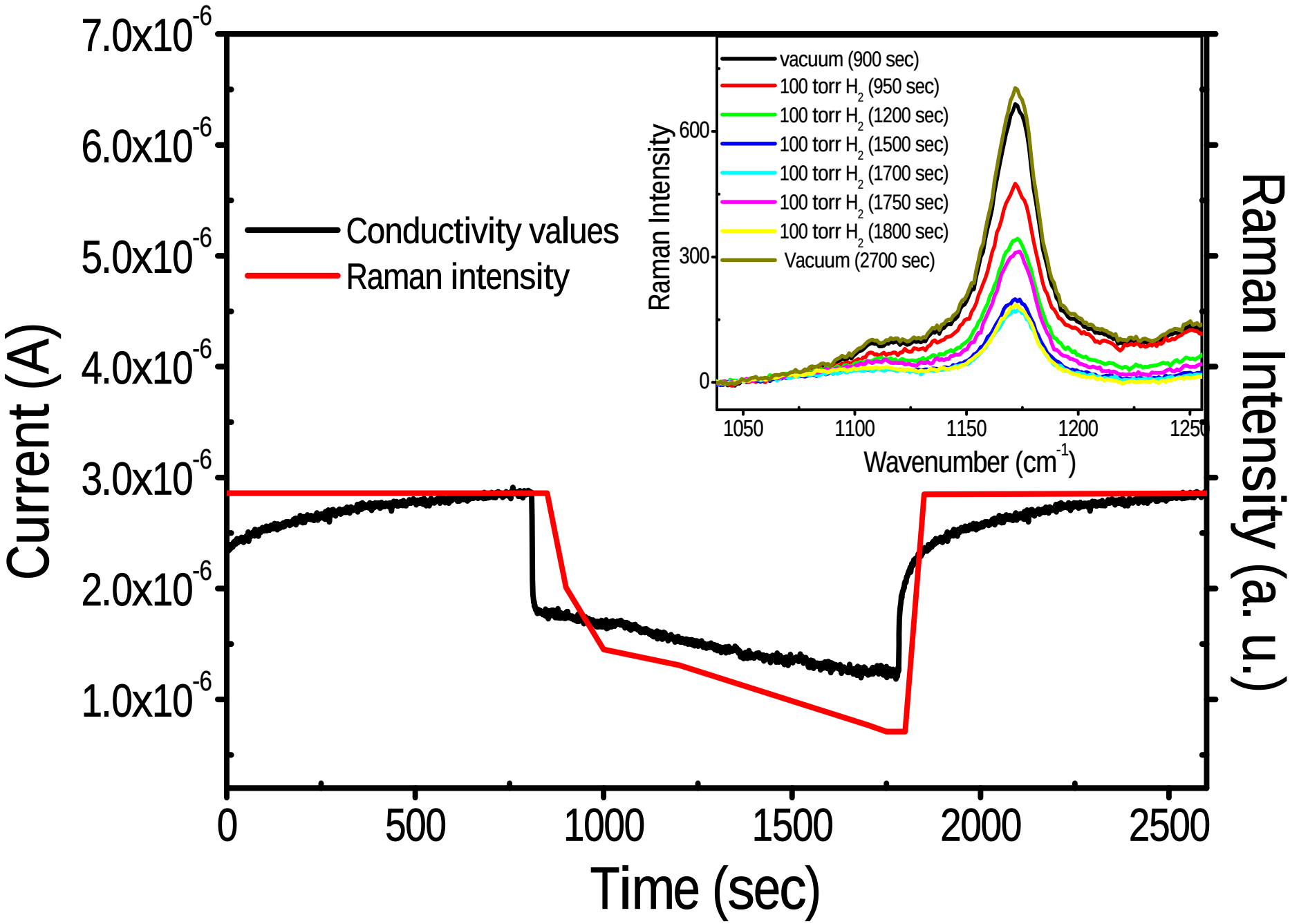

Manometer
Gas cylinder
voltmeter
Keithley
Current (mA)
Time (sec)


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)


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
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)

Sub-nano clusters of gold and silver are now available in tens of milligram scale. They offer new possibilities:
electroluminescence, cellular imaging, delivery, single molecule spectroscopy, sensors, etc.…

Nanoparticle superlattices are new solids, available in milligram scale. Novel properties of these systems worth collaborative exploration.

Ongoing examples of collaboration

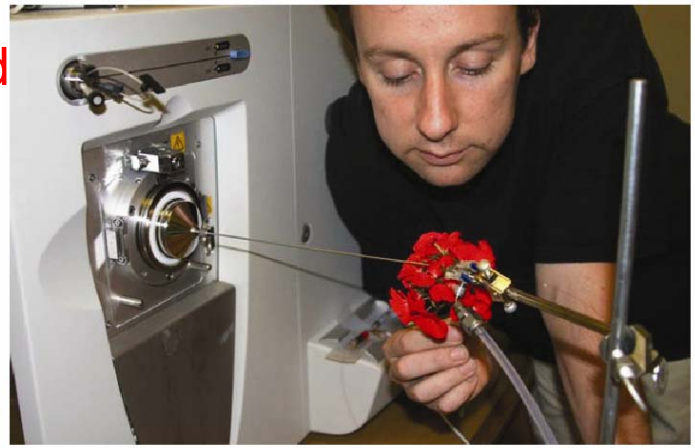
Studies on ice surfaces

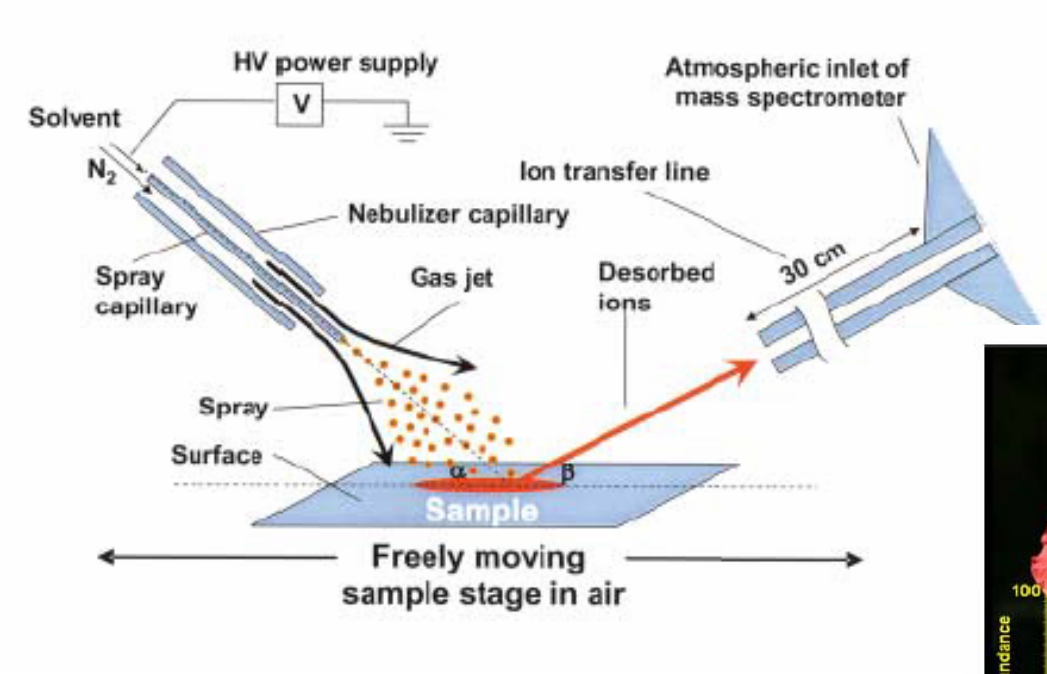
Low energy ion scattering spectrometer

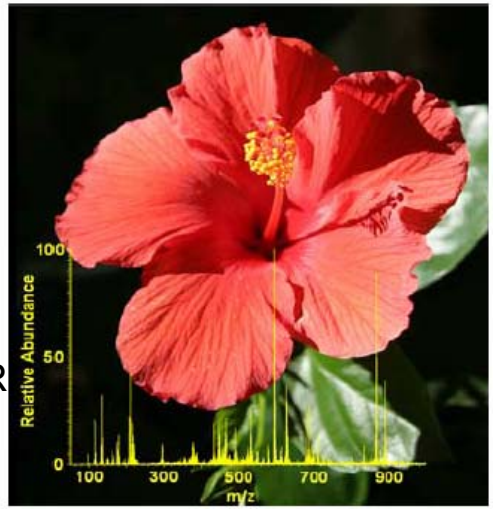
Jobin Cyriac et al. Chem. Rev. 2009

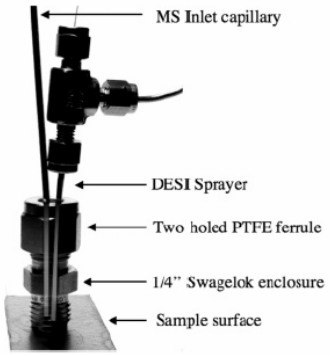
Jobin and Pradeep, J. Phys. Chem. C 2007a, 2007b, 2008

An advanced mass spectrometry has arrived



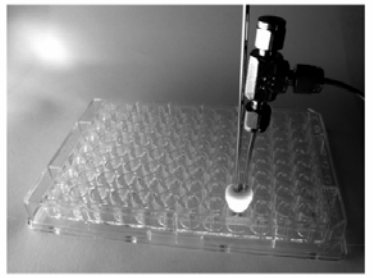




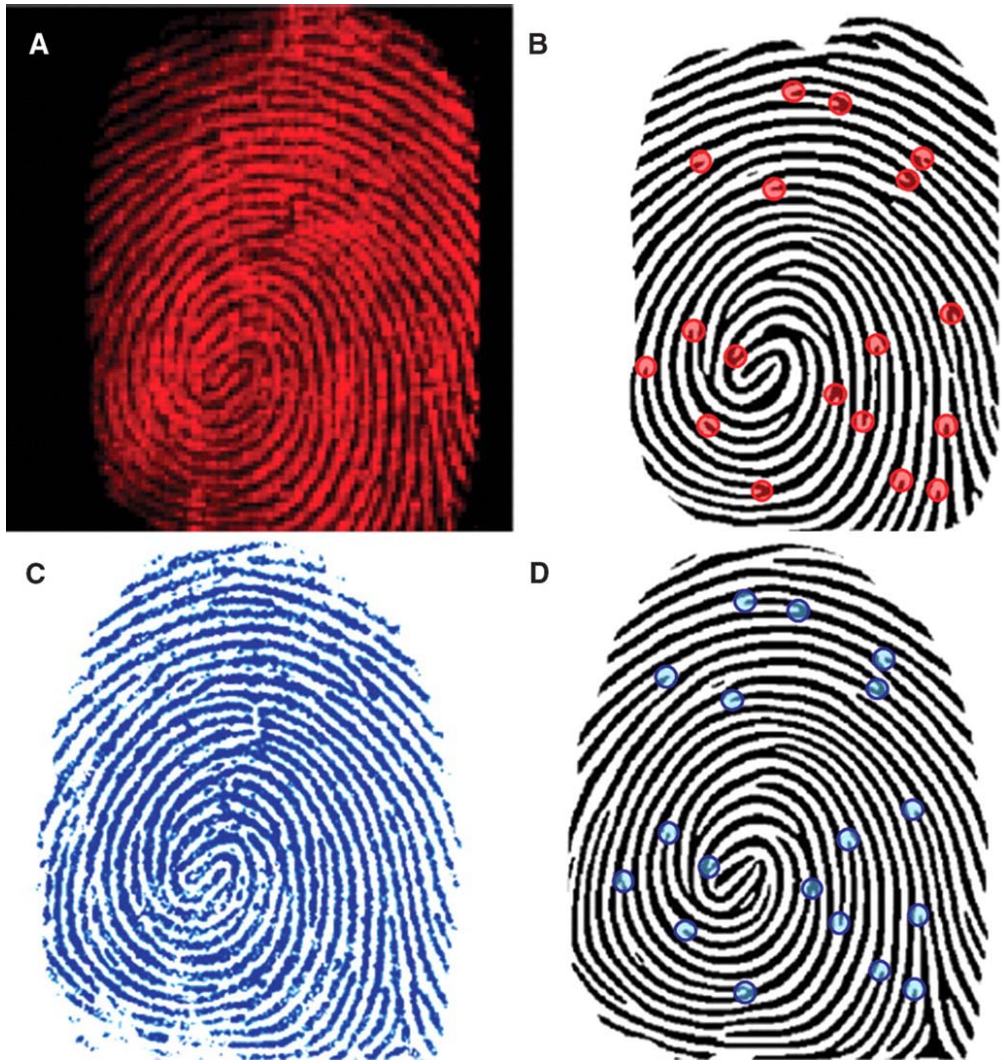


Zoltan Taka´ts, Justin M. Wiseman, Bogdan Gologan, R
Graham Cooks ***Science*, 306, 471, 2004**

Schematic of typical DESI experiment. The sample solution was deposited from solution and dried onto a PTFE surface, and methanol-water (1:1 containing 1% acetic acid or 0.1% aqueous acetic acid solution) was sprayed at a flow rate of 3 to 15 µl/min under the influence of a high (4 kV) voltage. The nominal linear velocity of the nebulizing gas was set to 350 m/s.

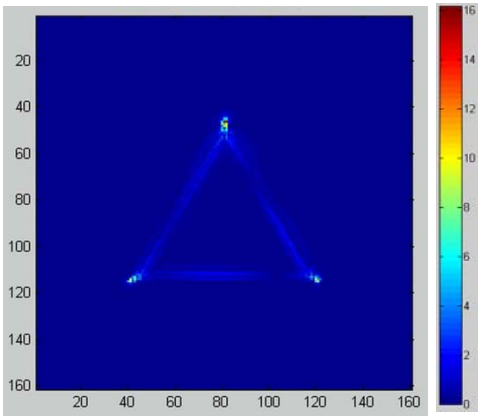


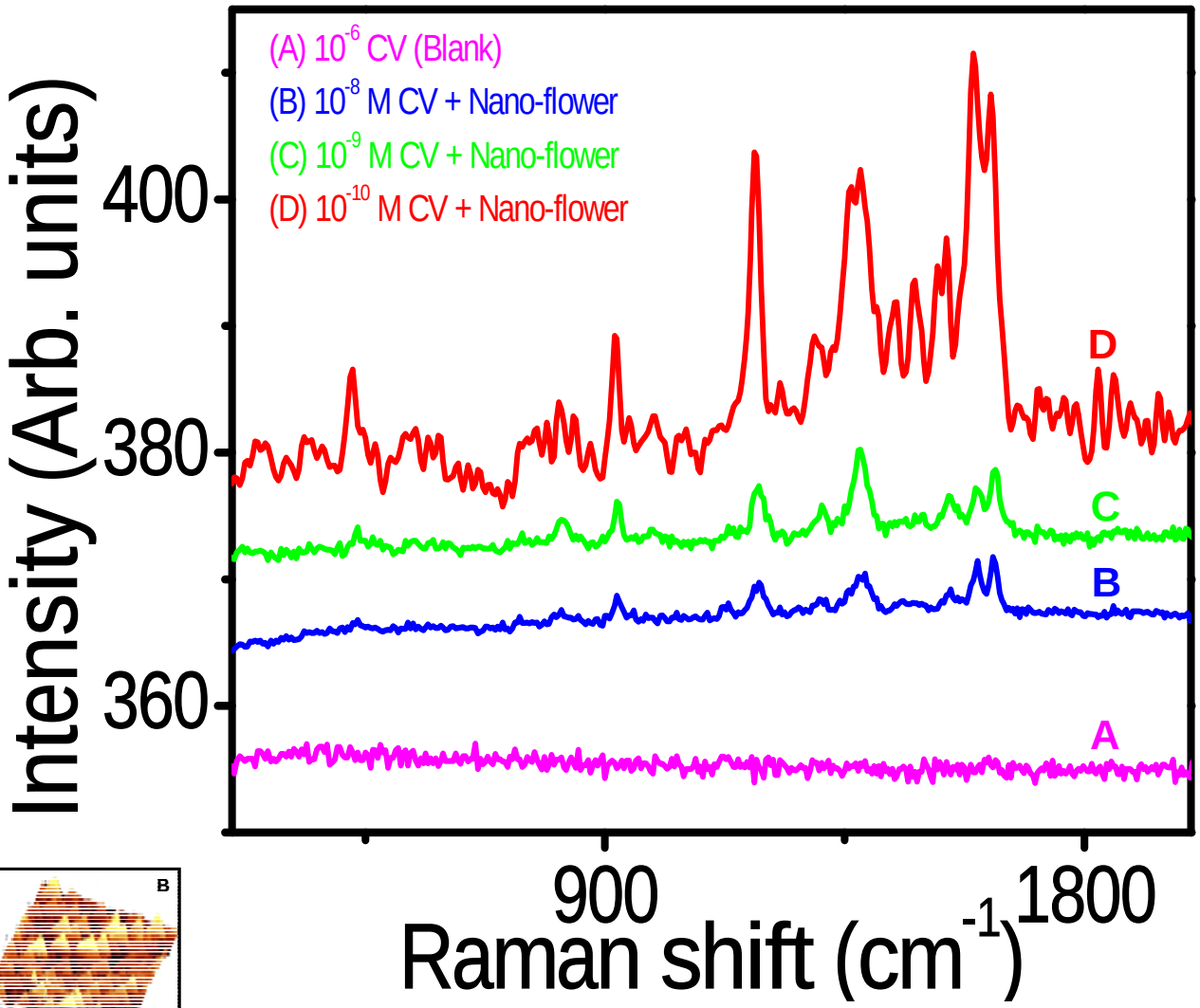
Cooks, 2007 & 2008

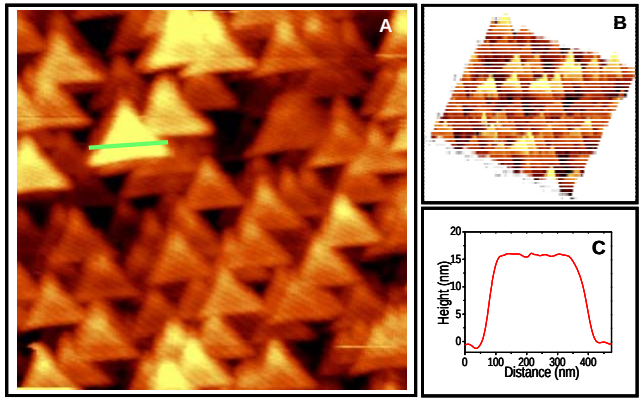


(**A**) DESI image of distribution of cocaine on a LFP blotted on glass. (**B**) Computer-generated fingerprint from DESI image. (**C**) Ink fingerprint blotted on paper and optically scanned. (**D**) Computer-generated fingerprint from optical image. Some of the automatically detected points of interest (minutiae) are represented by dots in (B) and (D).

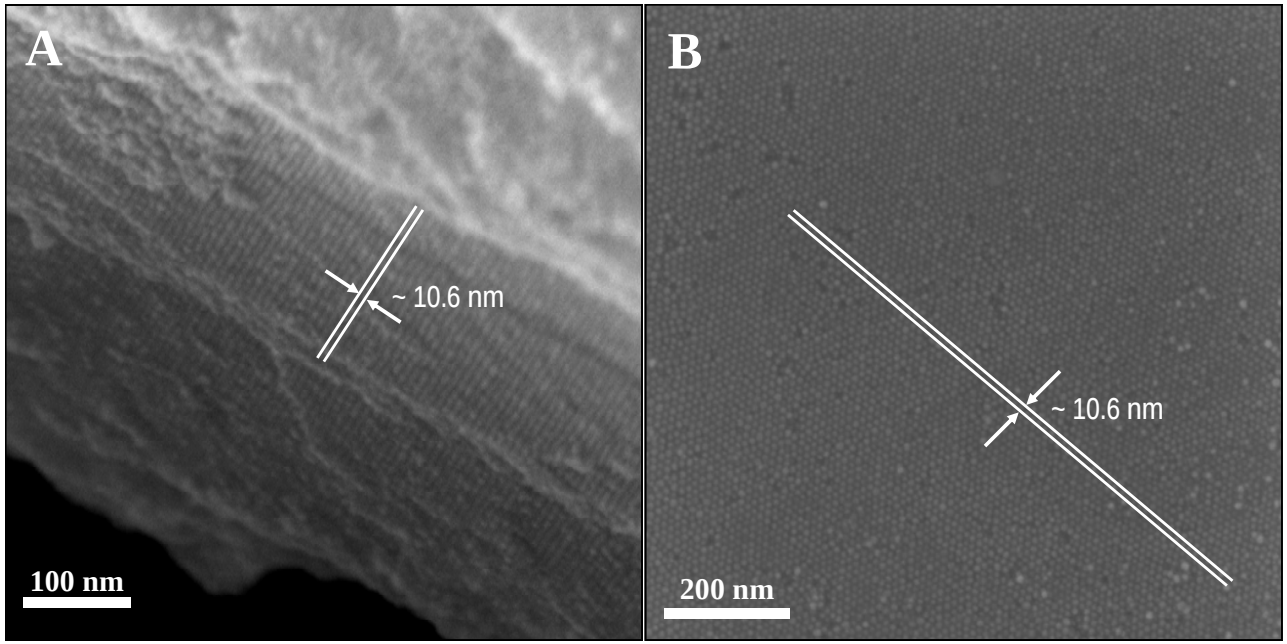
D. R. Ifa, N. E. Manicke, A. L. Dill and R. G. Cooks, Science , 2008 , 321, 805-805,

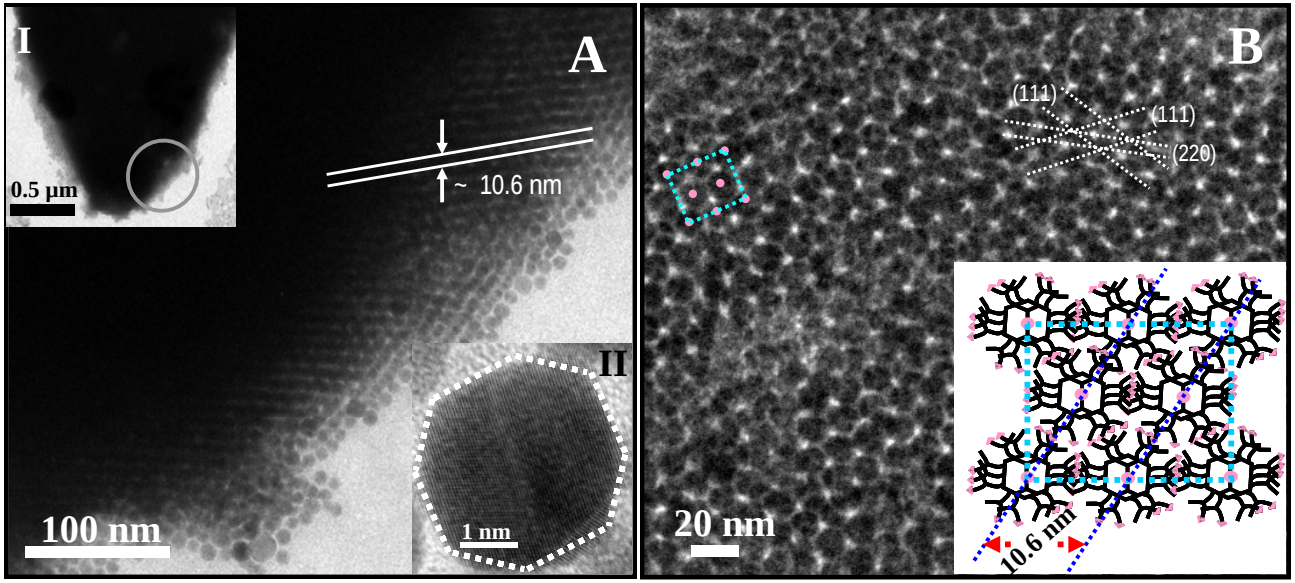






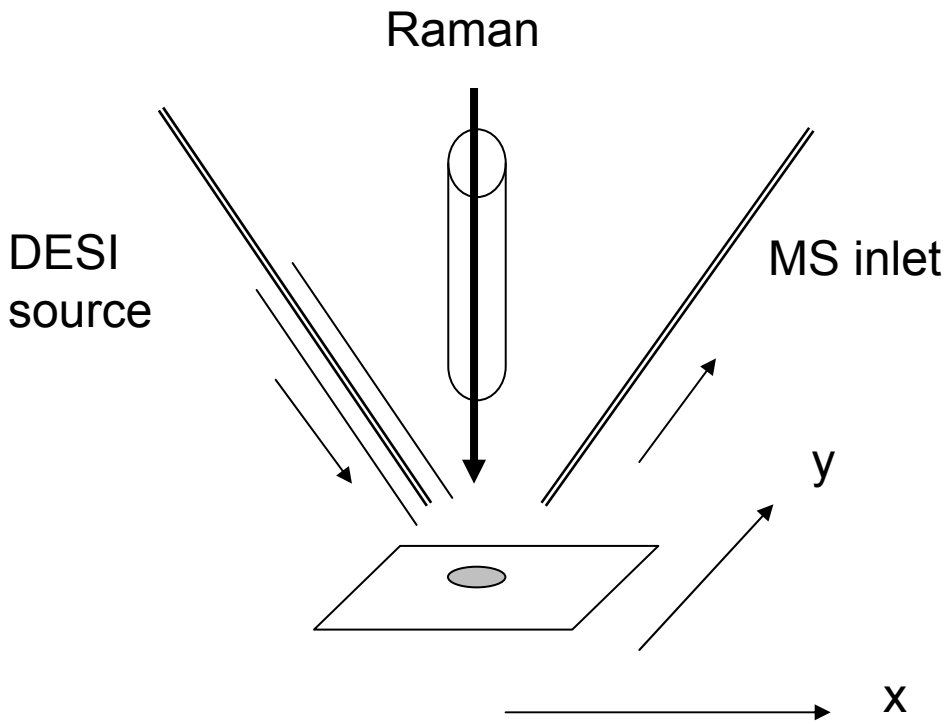
P. R. Sajanlal and T. Pradeep, Advanced Materials, 2008



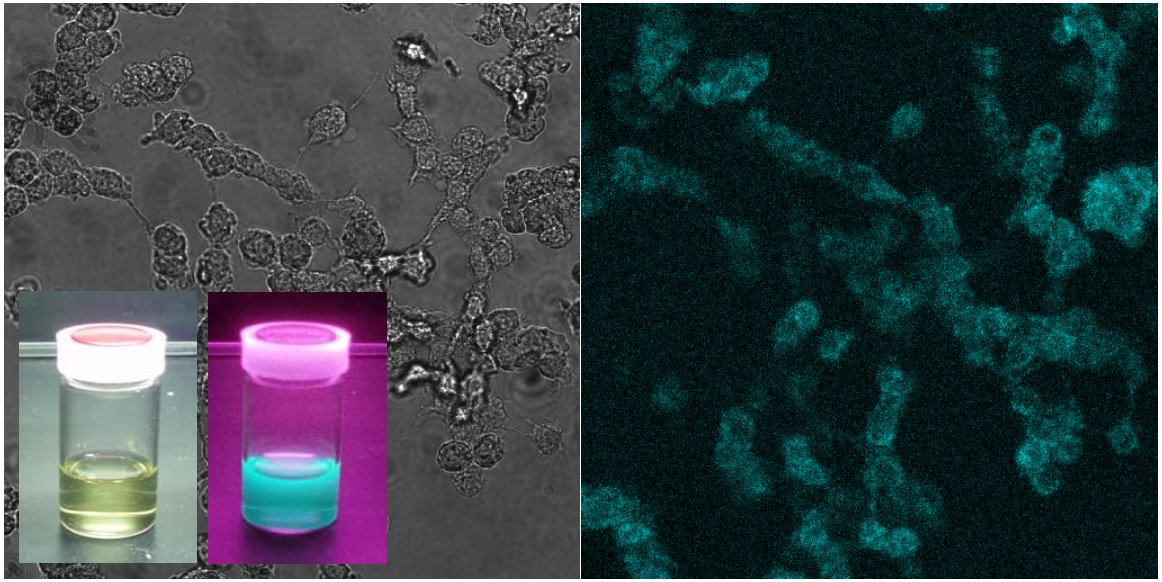


Nanoparticle superlattices

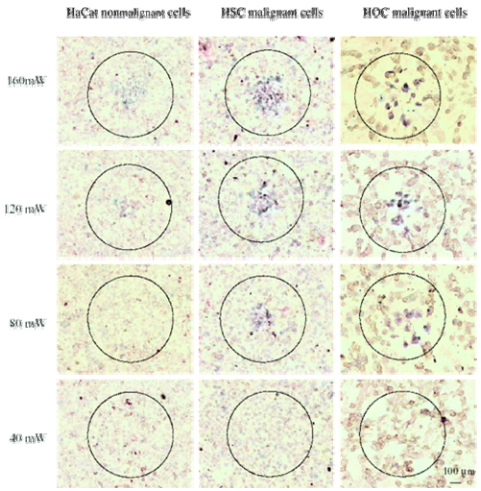
Shibu and Pradeep, Submitted


Raman
DESI
source
MS inlet
y
x

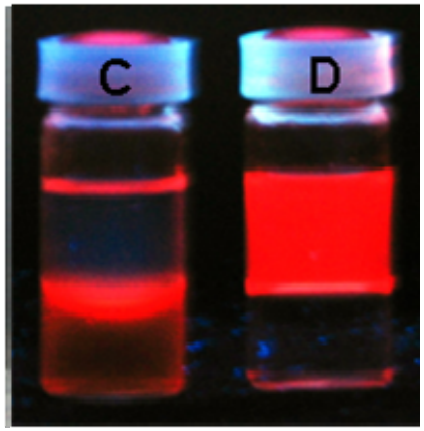
Nano-Bio Confluence: FRET Based Imaging Using Clusters

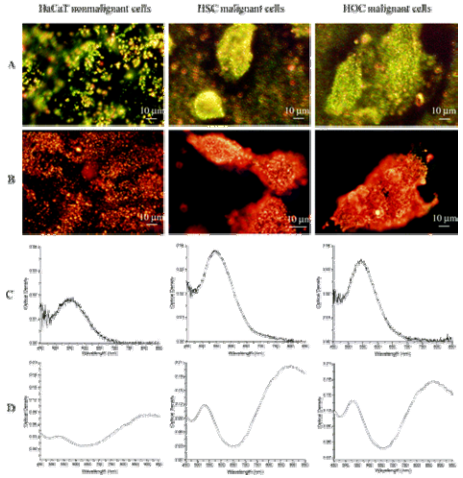


Habeeb Muhammed et al. Nano Res. 2008



Selective photothermal therapy of cancer cells with anti-EGFR/Au nanorods incubated, MA El-Sayed et al, J. Am. Chem. Soc., 128, 2006, 2115 -2120





Light scattering images of (A) anti-EGFR/Au nanospheres post-incubation (B) anti-EGFR/Au nanorods post-incubation. Average extinction spectra of (C) anti-EGFR/Au nanospheres (D) anti-EGFR/Au nanorods , MA El-Sayed et al, J. Am. Chem. Soc., 128, 2006, 2115 -2120

Nano Mission, DST

Nano Mission, Department of Science and Technology

IIT Madras

Thank you all

All my friends in DST