New kinds of sensors with nanoparticles, nanotubes and superlattices

…and clusters

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Three new kinds of sensors

Mesoflowers
Nanoparticle-nanotube composites
Nanoparticle superlattices

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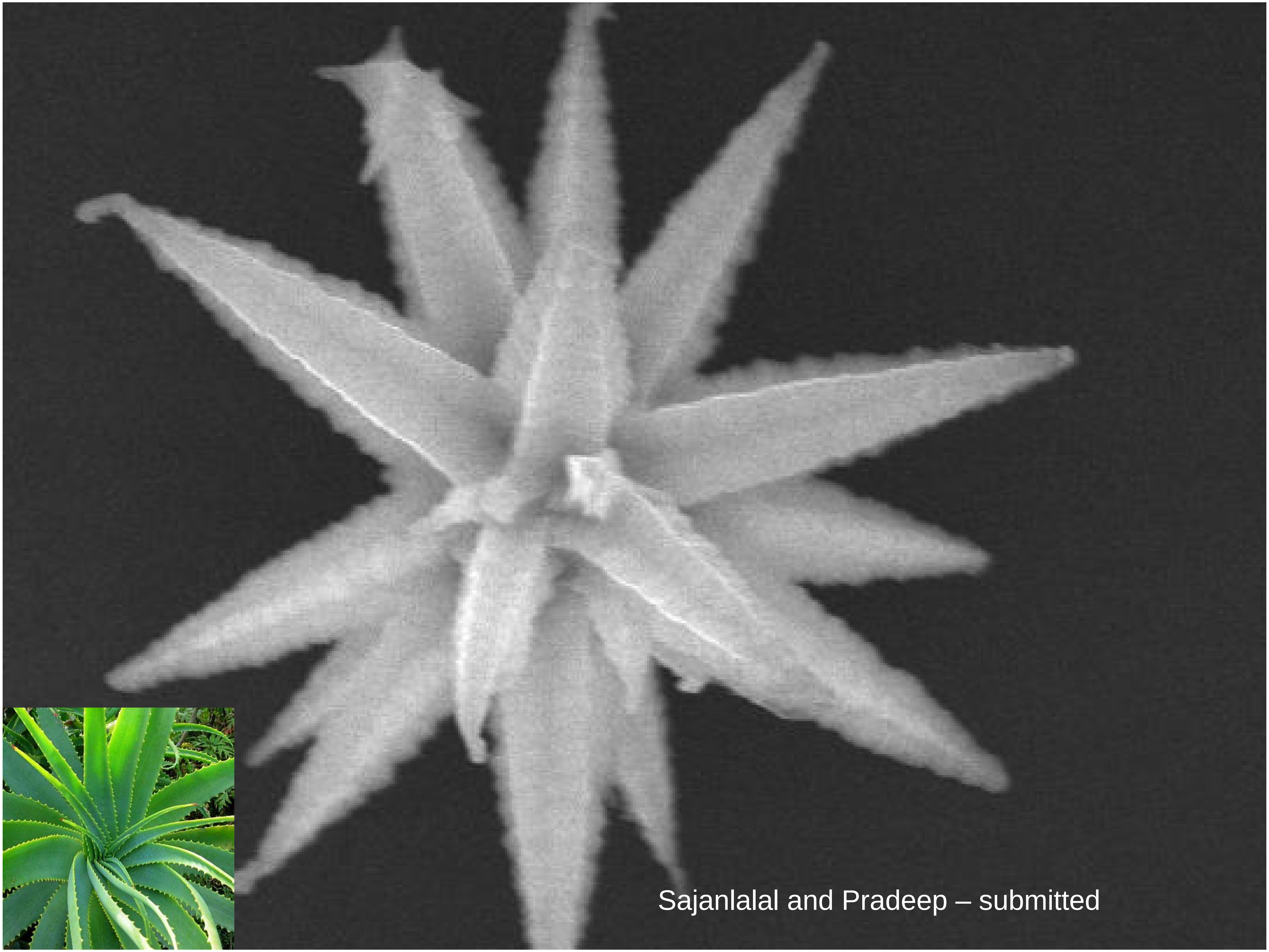
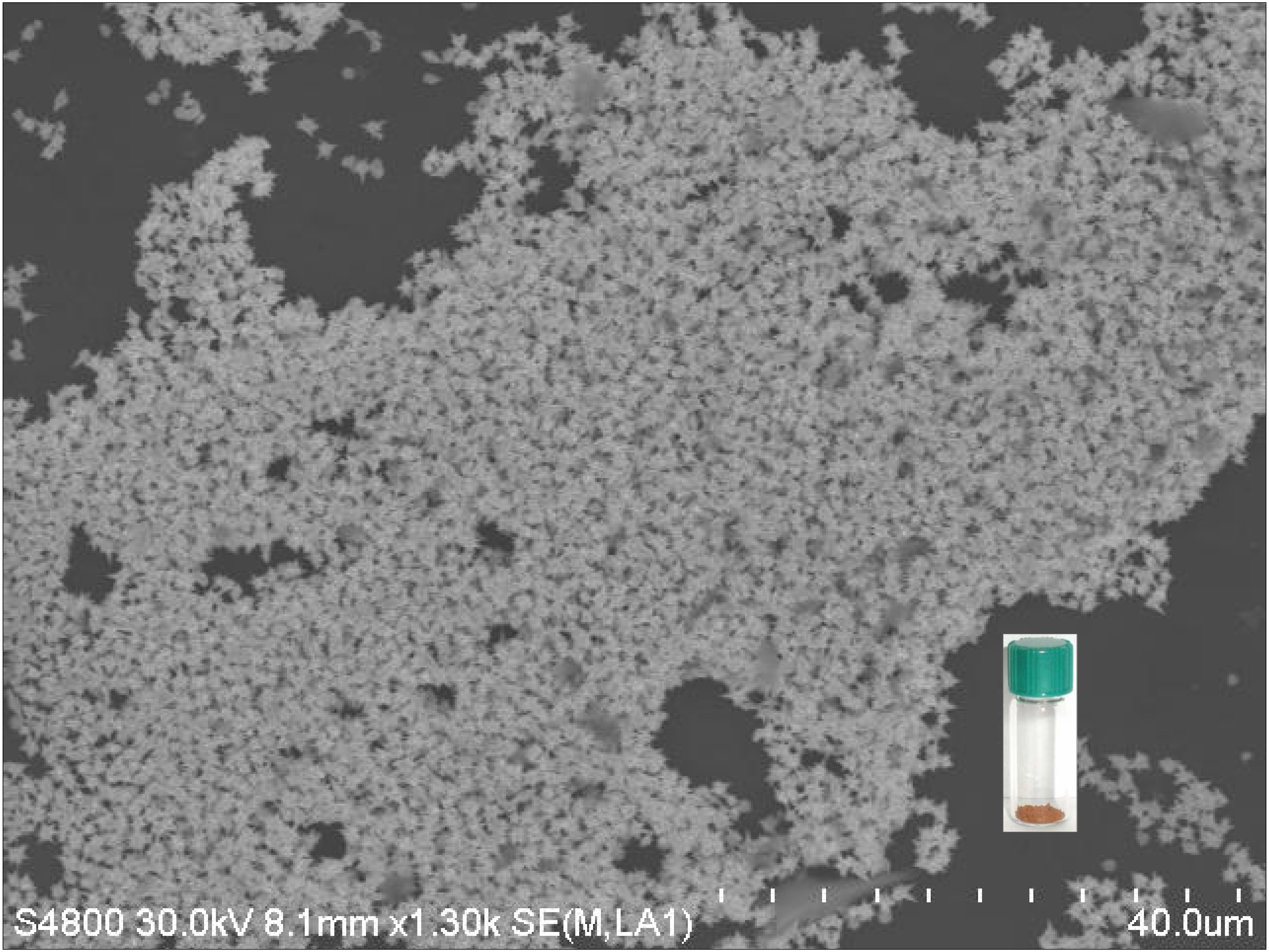
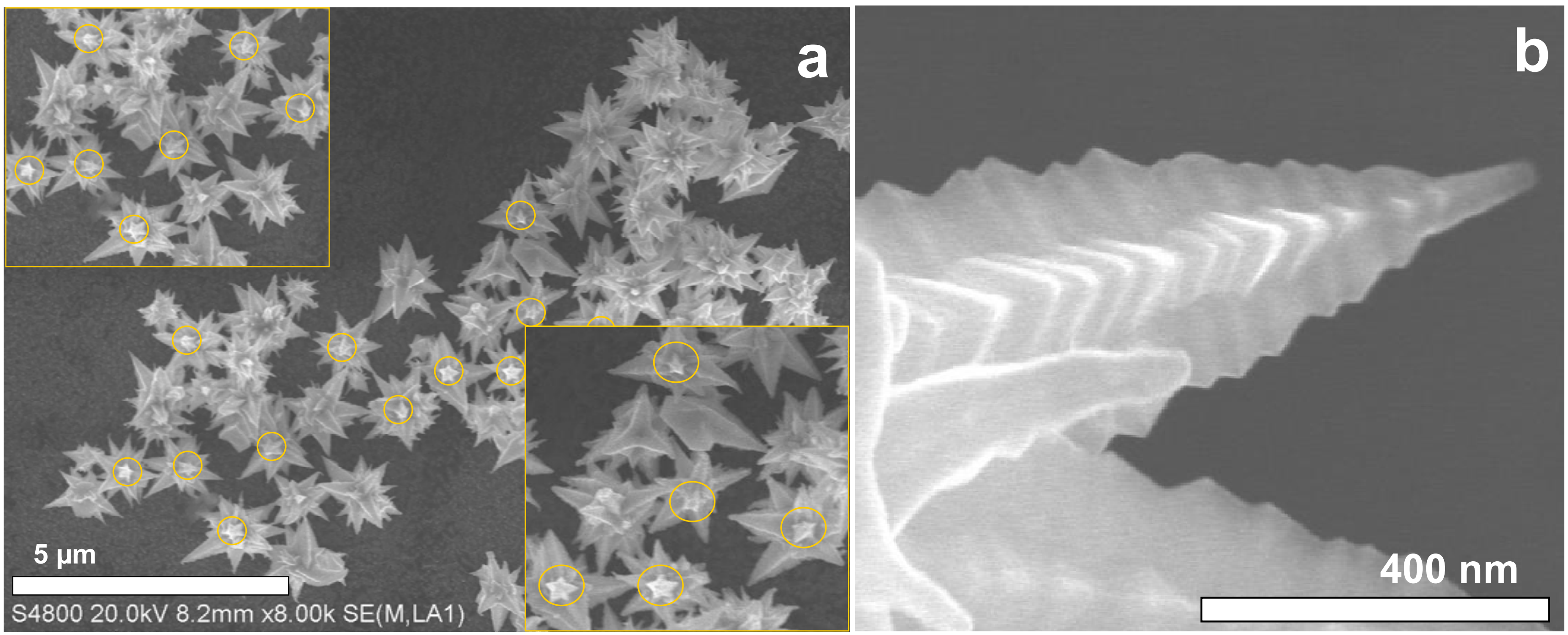
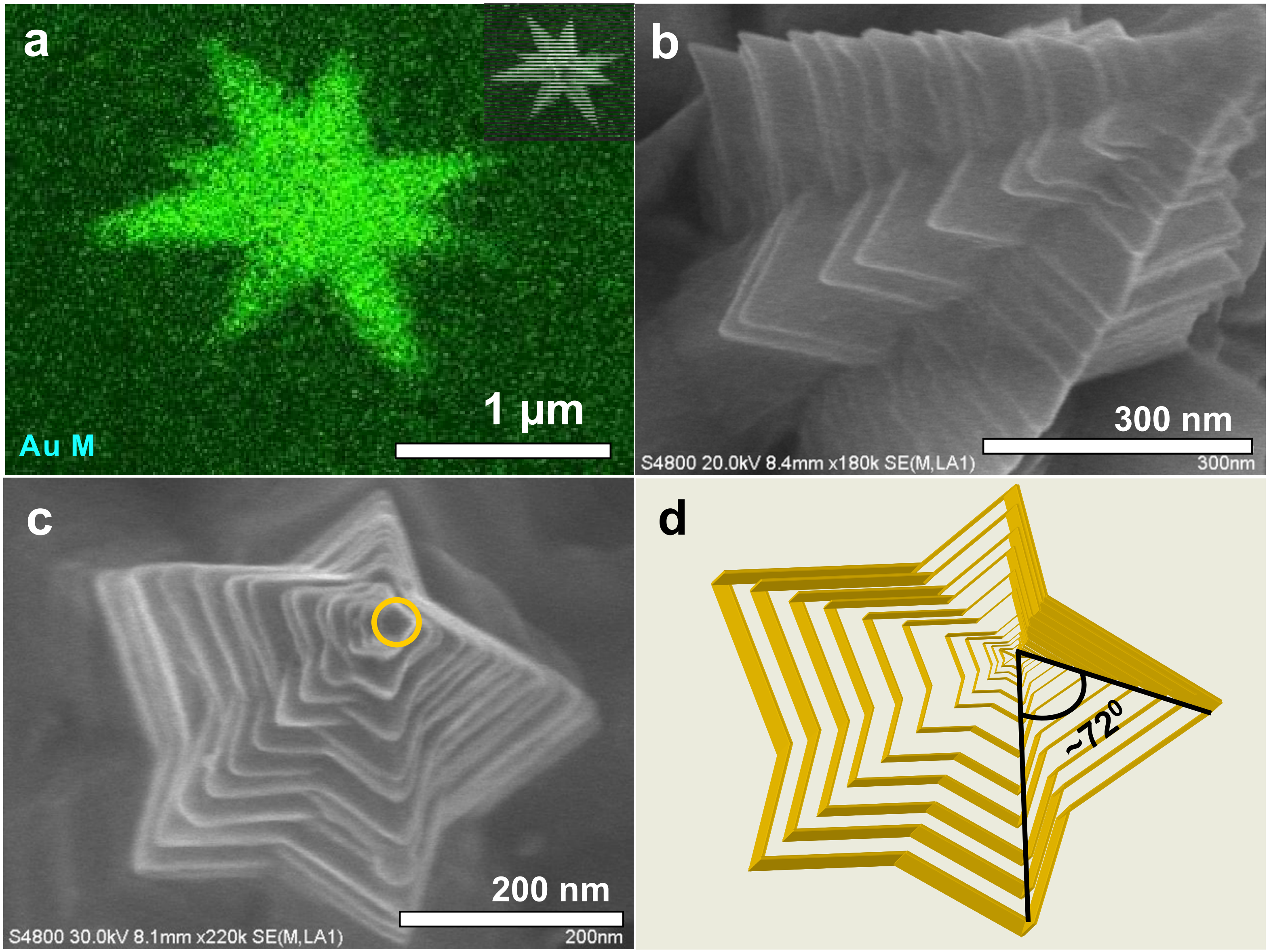
1

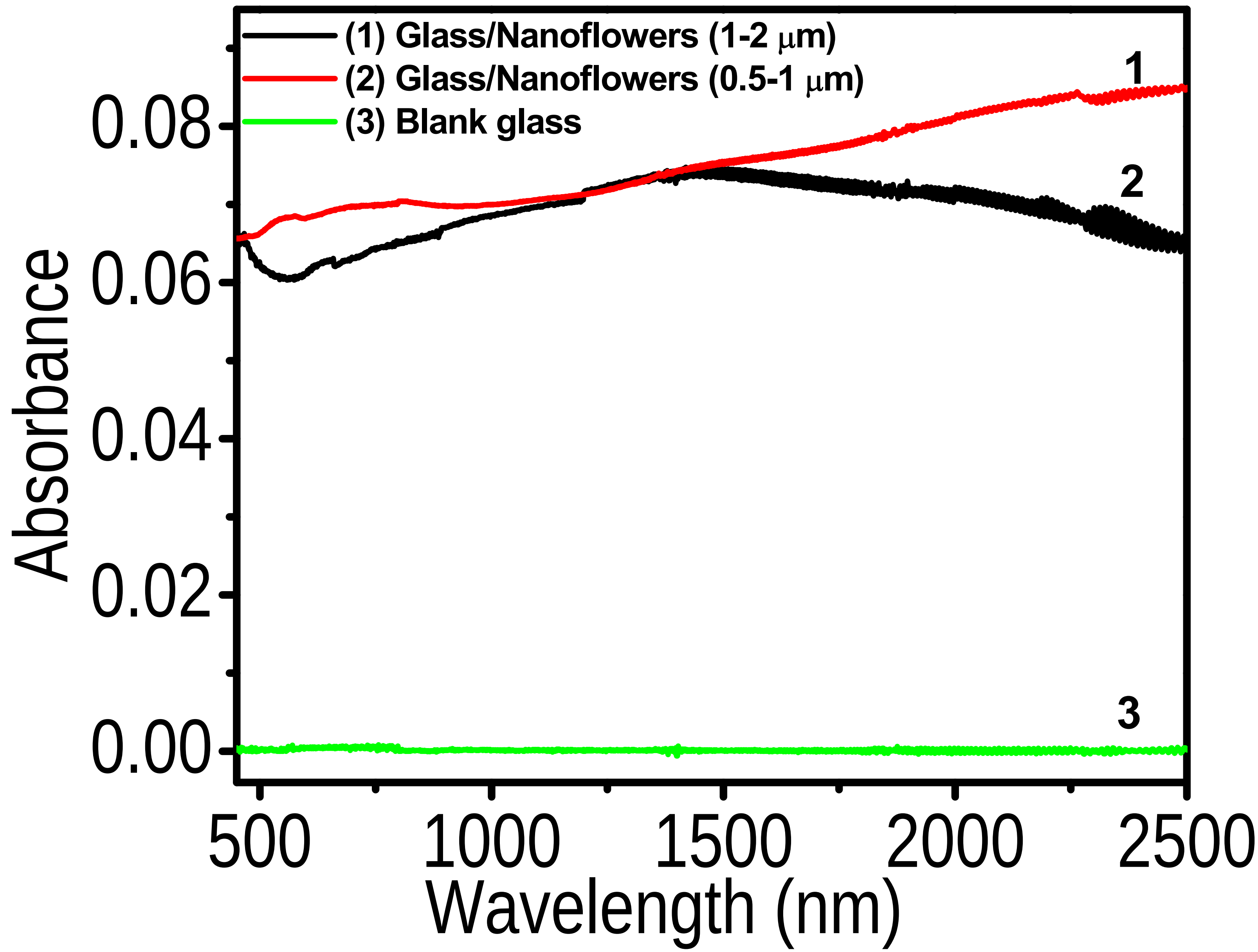
Mesoflowers


Sajanlalal and Pradeep – submitted

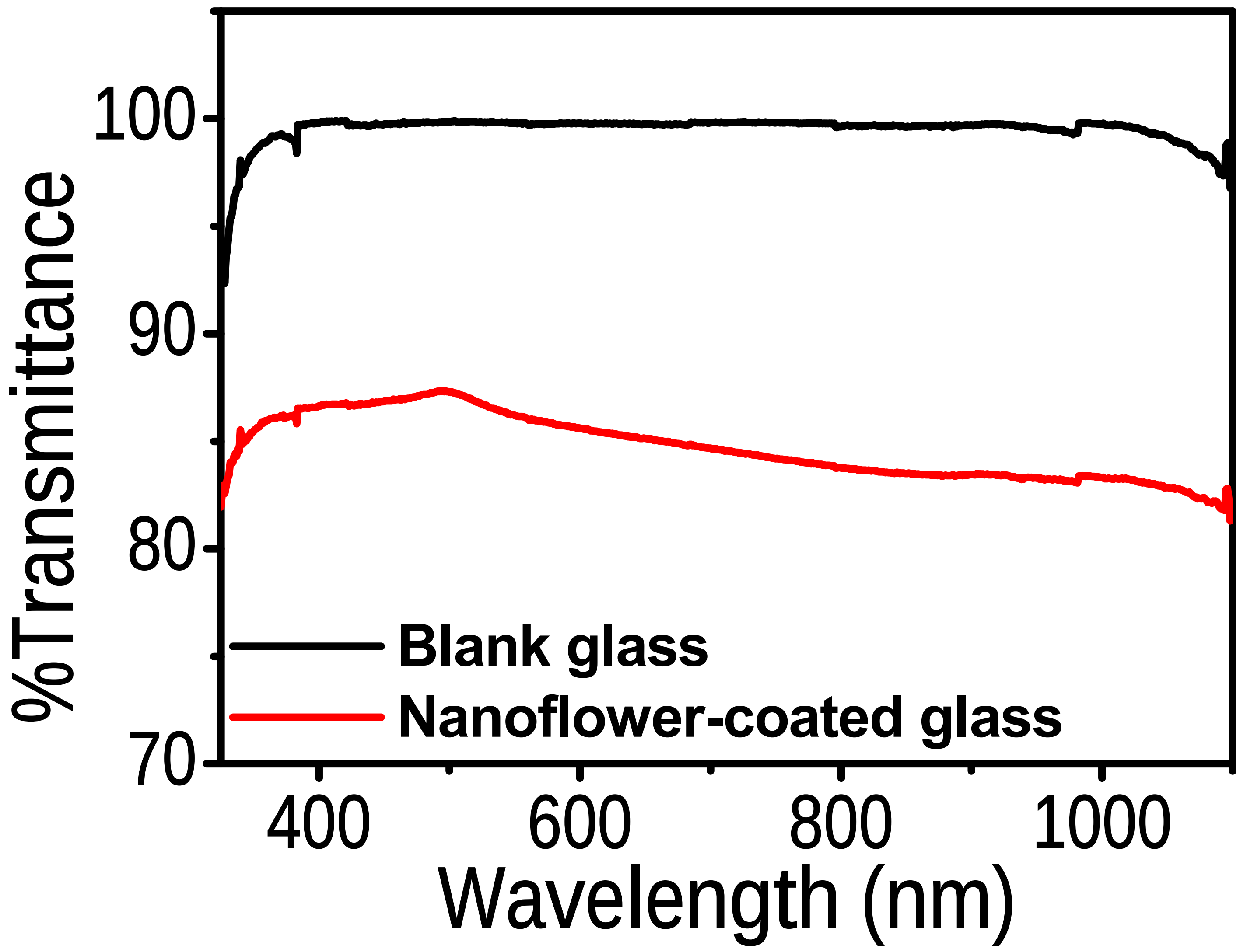

S4800 30.0kV 8.1mm x1.30k SE(M,LA1)
40.0um


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

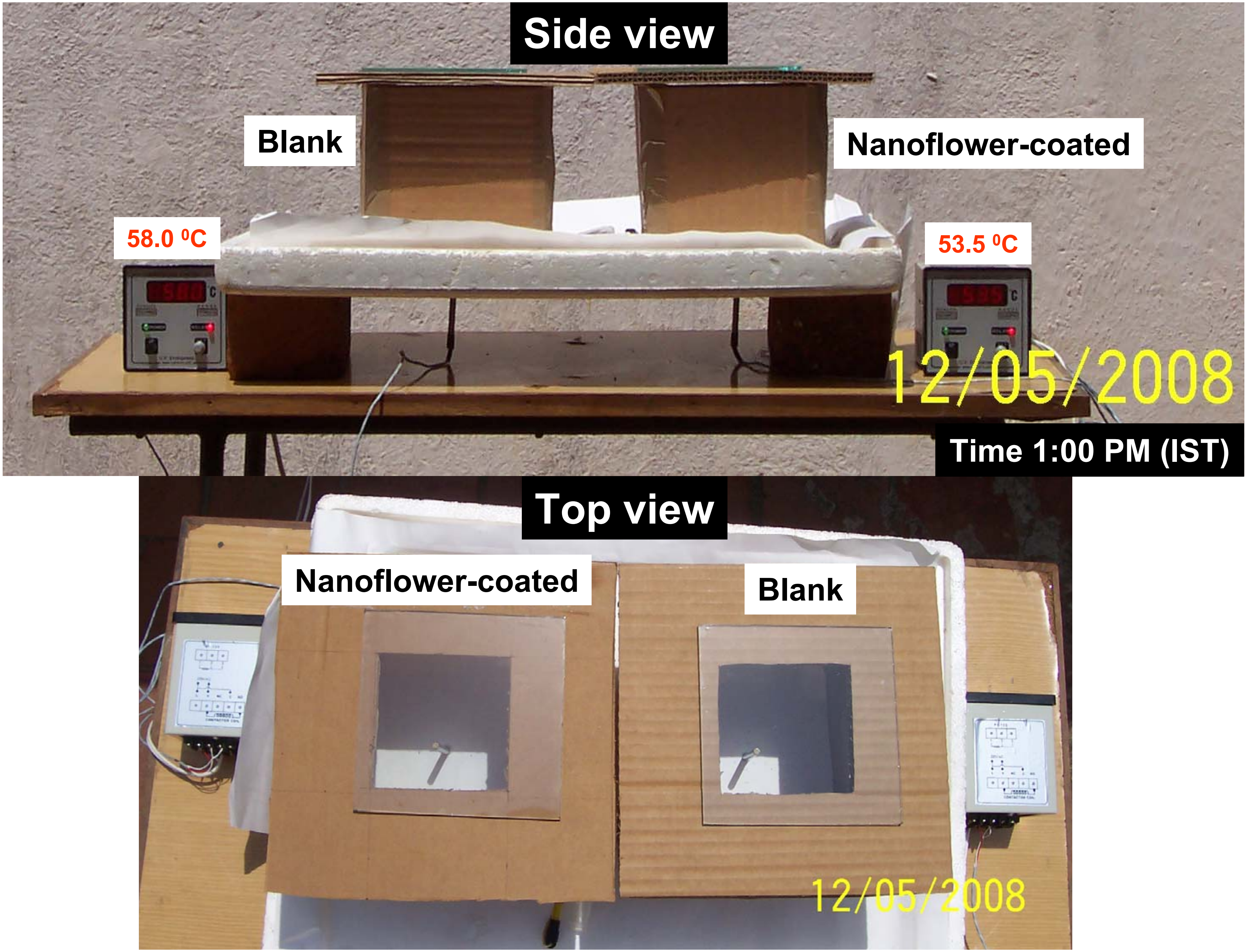

a
Au M
1 μm
b
300 nm
S4800 20.0kV 8.4mm x180k SE(M,LA1)
300nm
c
200 nm
S4800 30.0kV 8.1mm x220k SE(M,LA1)
200nm
d
~72°

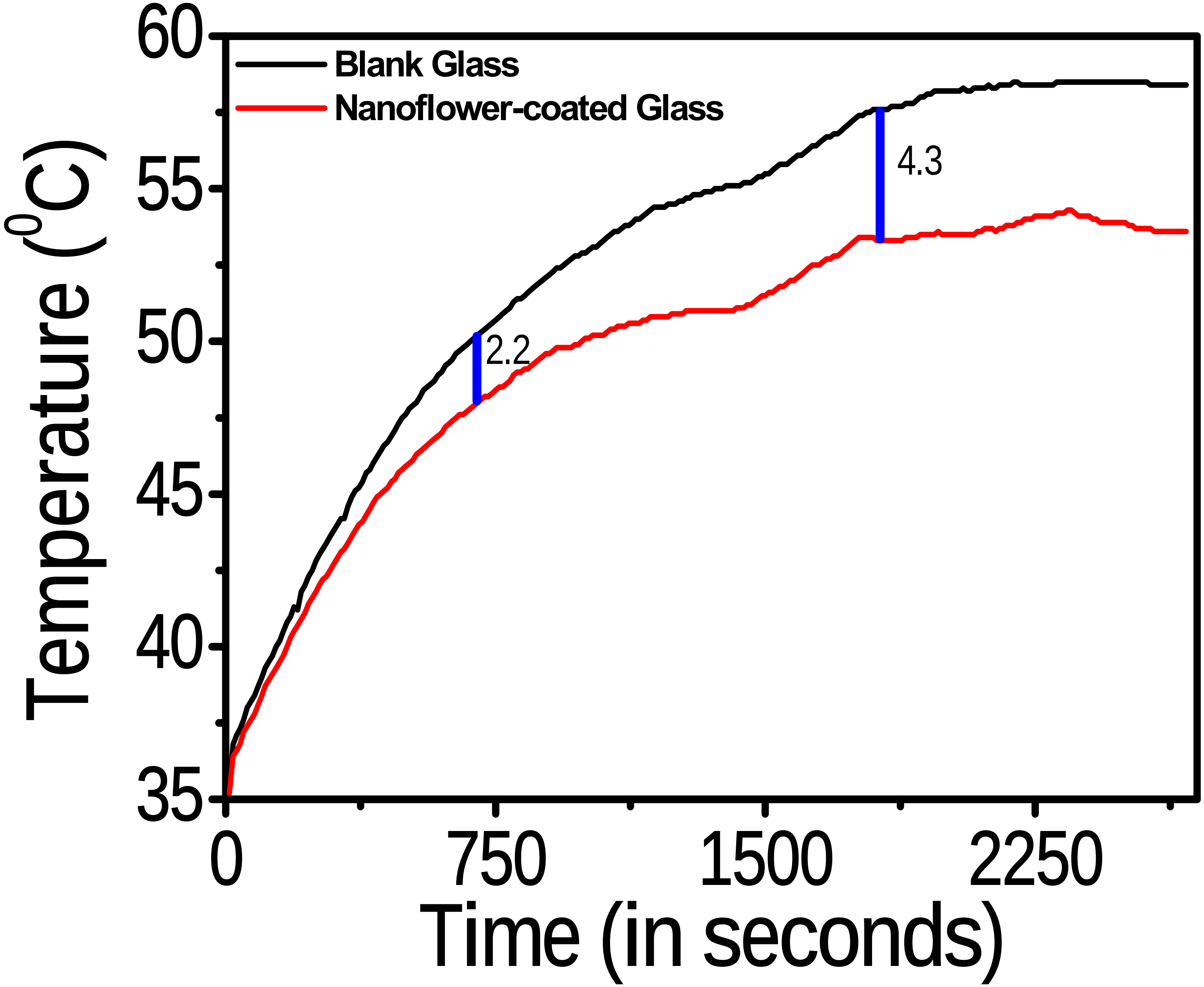


(1) Glass/Nanoflowers (1-2 μm)
(2) Glass/Nanoflowers (0.5-1 μm)
(3) Blank glass
1
2
3
0.08
0.06
0.04
0.02
0.00
Absorbance
500
1000
1500
2000
2500
Wavelength (nm)

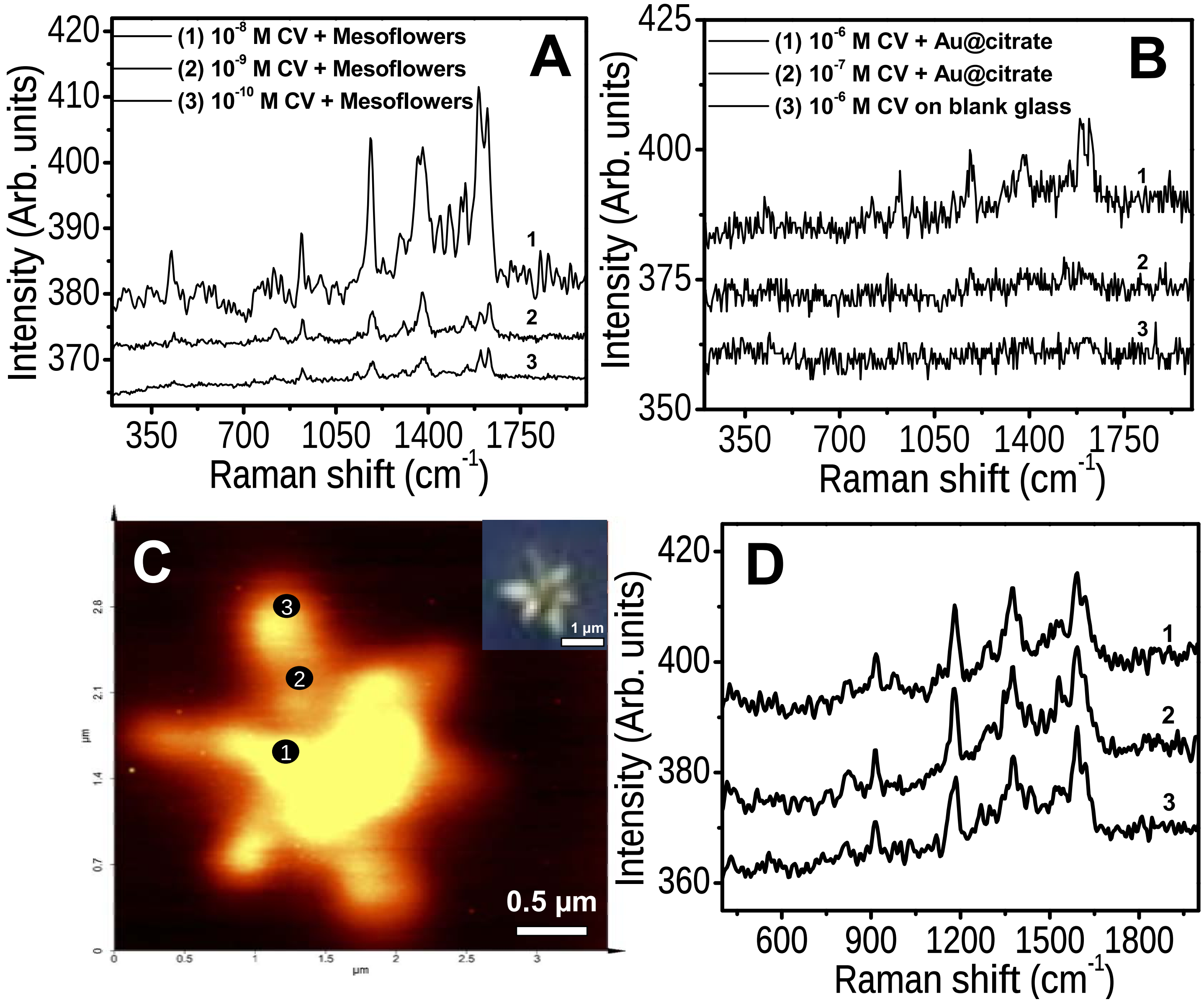


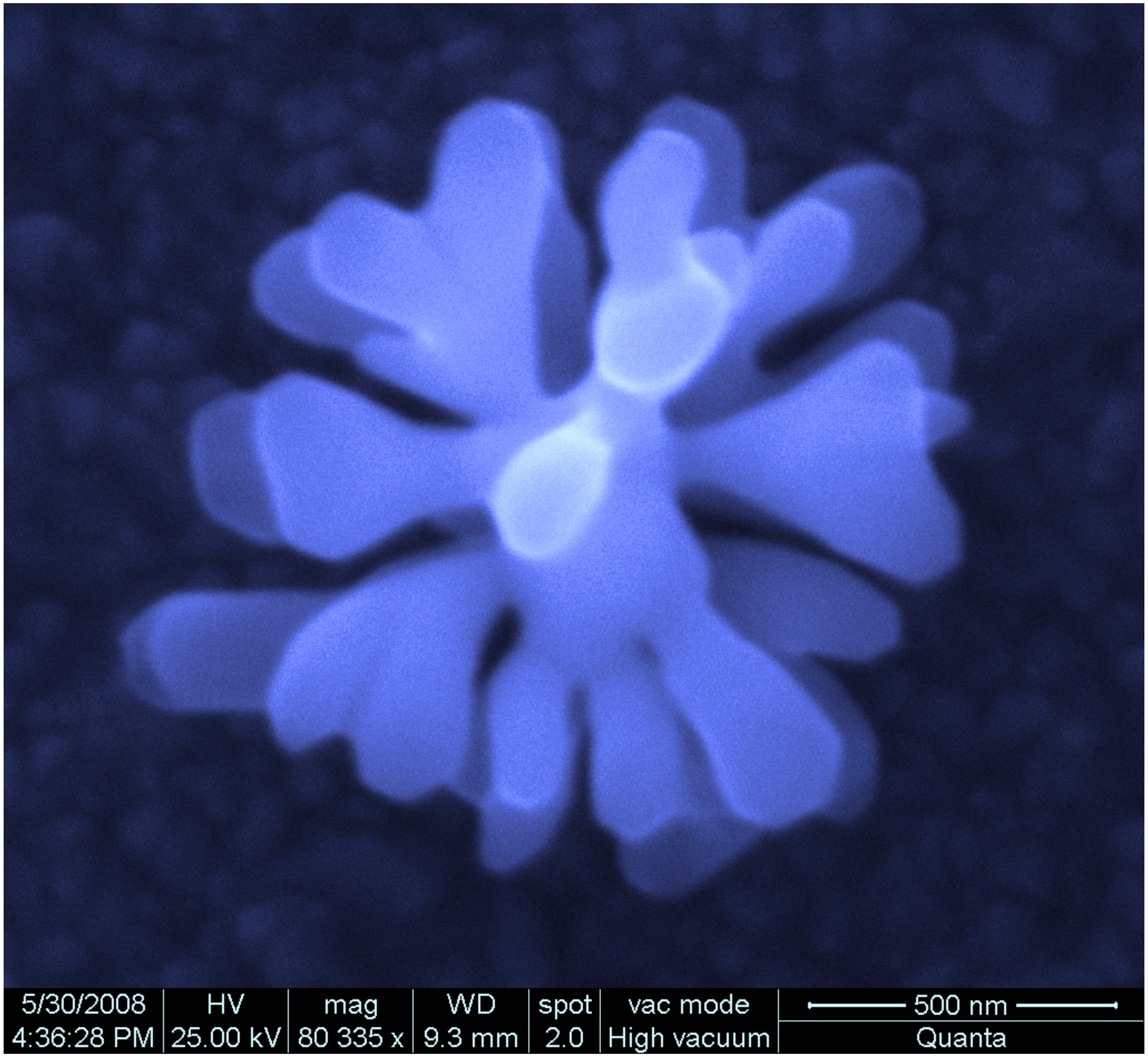
100
90
80
70
%Transmittance
400
600
800
1000
Wavelength (nm)
Blank glass
Nanoflower-coated glass

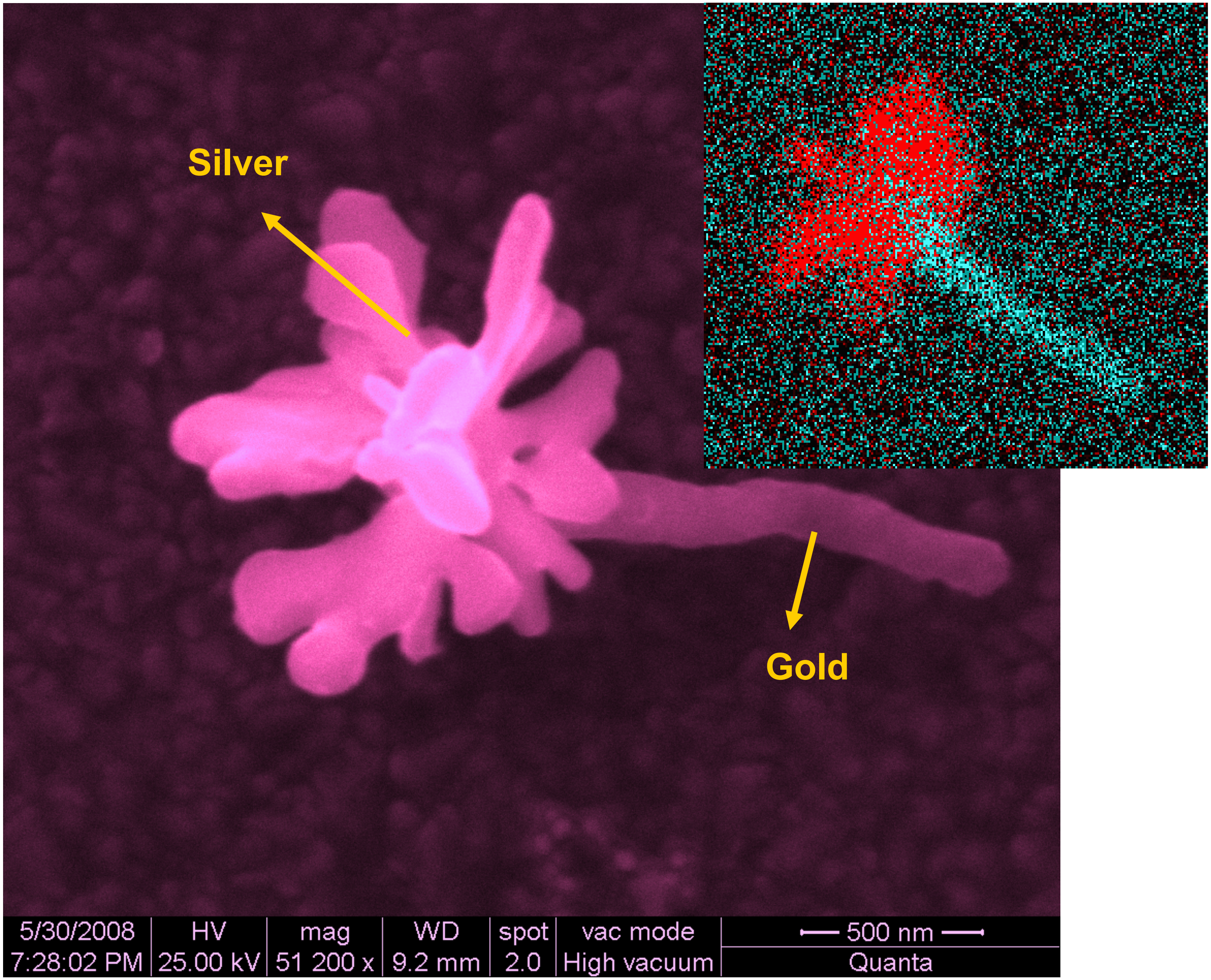

Side view
Blank
Nanoflower-coated
58.0 °C
53.5 °C
12/05/2008
Time 1:00 PM (IST)
Top view
Nanoflower-coated
Blank
12/05/2008



Blank Glass
Nanoflower-coated Glass
4.3
2.2
60
55
50
45
40
35
0
750
1500
2250
Temperature (^{0}C)
Time (in seconds)

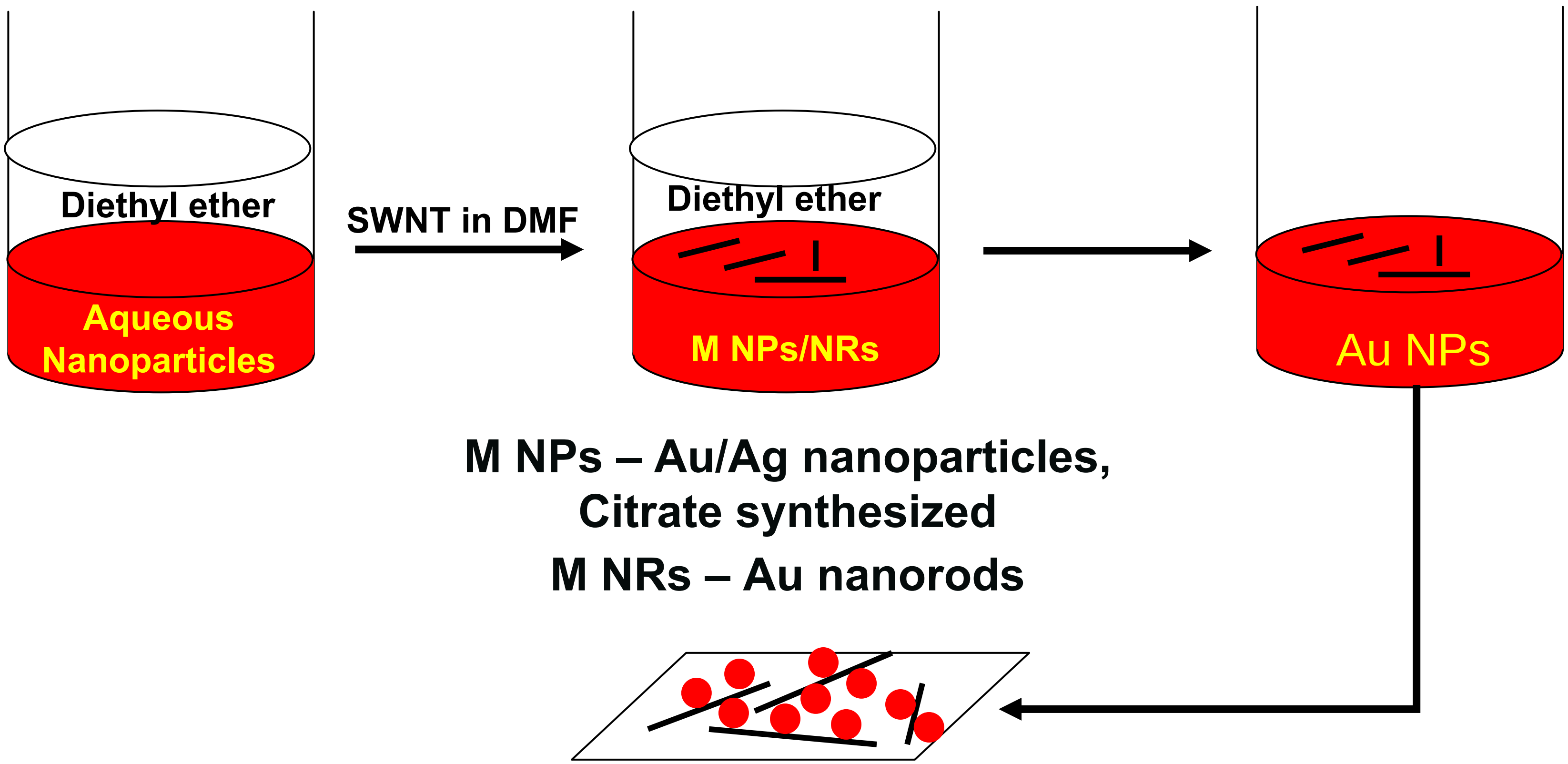

A
(1) 10-8 M CV + Mesoflowers
(2) 10-9 M CV + Mesoflowers
(3) 10-10 M CV + Mesoflowers
Intensity (Arb. units)
Raman shift (cm-1)
B
(1) 10-6 M CV + Au@citrate
(2) 10-7 M CV + Au@citrate
(3) 10-6 M CV on blank glass
Intensity (Arb. units)
Raman shift (cm-1)
C
1 µm
0.5 µm
µm
D
Intensity (Arb. units)
Raman shift (cm-1)


5/30/2008
4:36:28 PM
HV
25.00 kV
mag
80 335 x
WD
9.3 mm
spot
2.0
vac mode
High vacuum
500 nm
Quanta

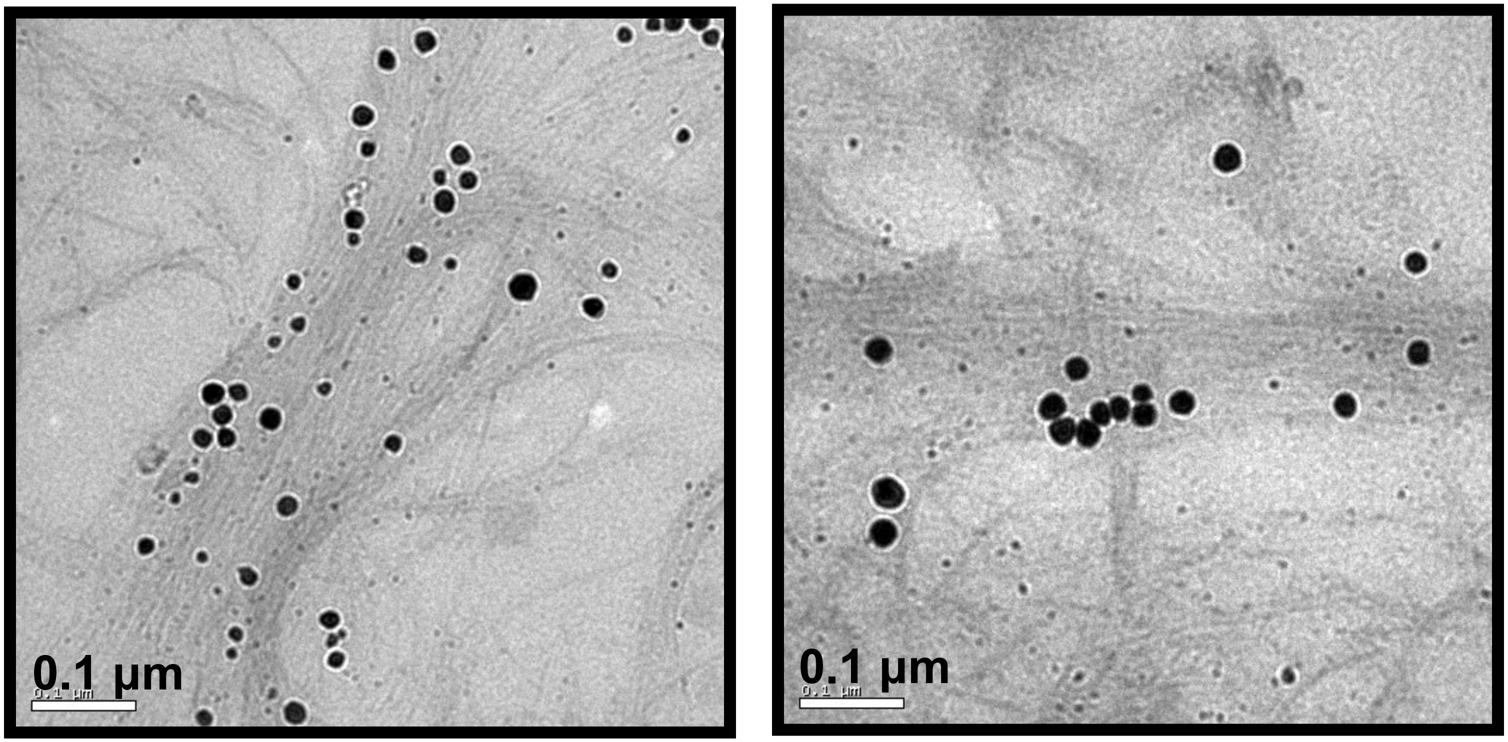

Silver
Gold
5/30/2008
7:28:02 PM
HV
25.00 kV
mag
51 200 x
WD
9.2 mm
spot
2.0
vac mode
High vacuum
500 nm
Quanta

2

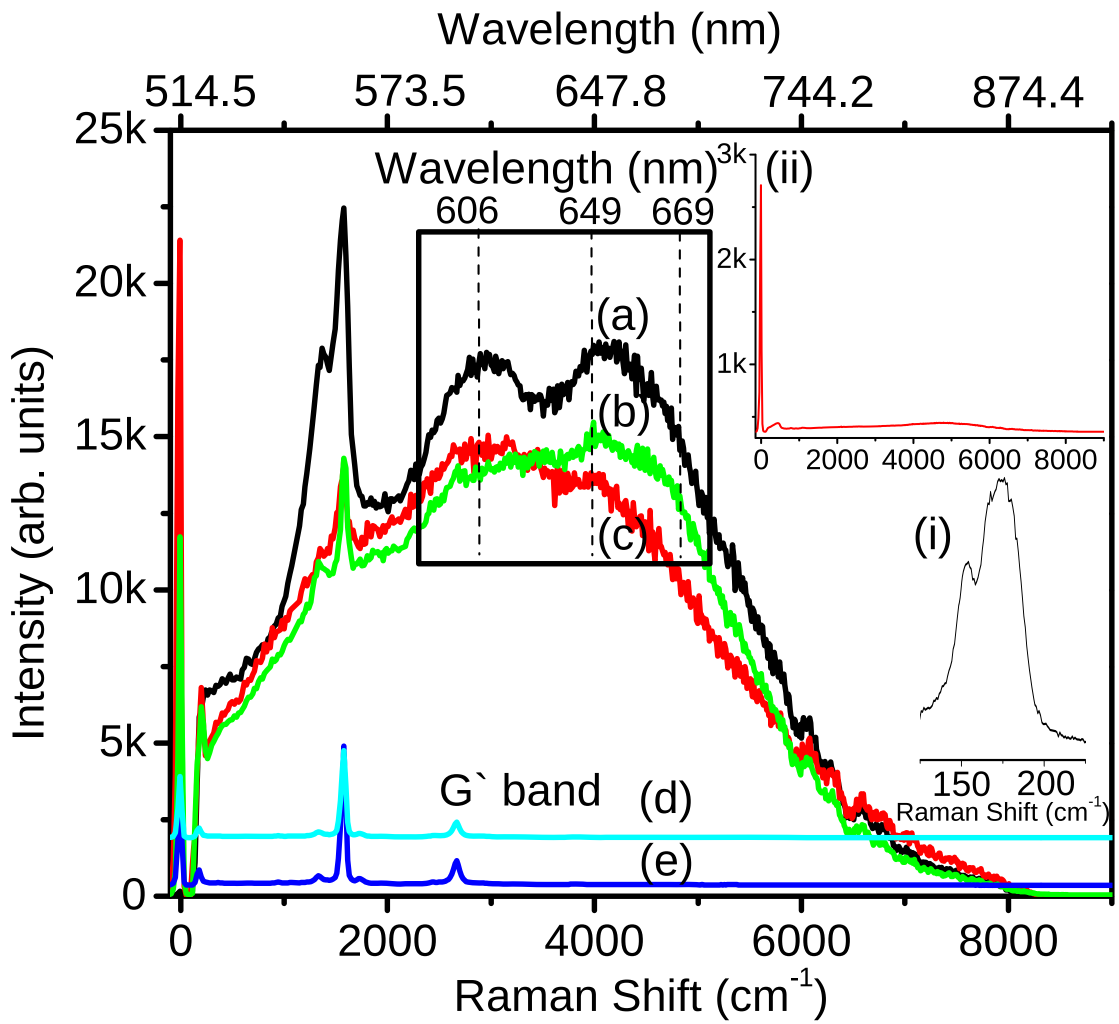
Single walled carbon nanotube-nanoparticle composite



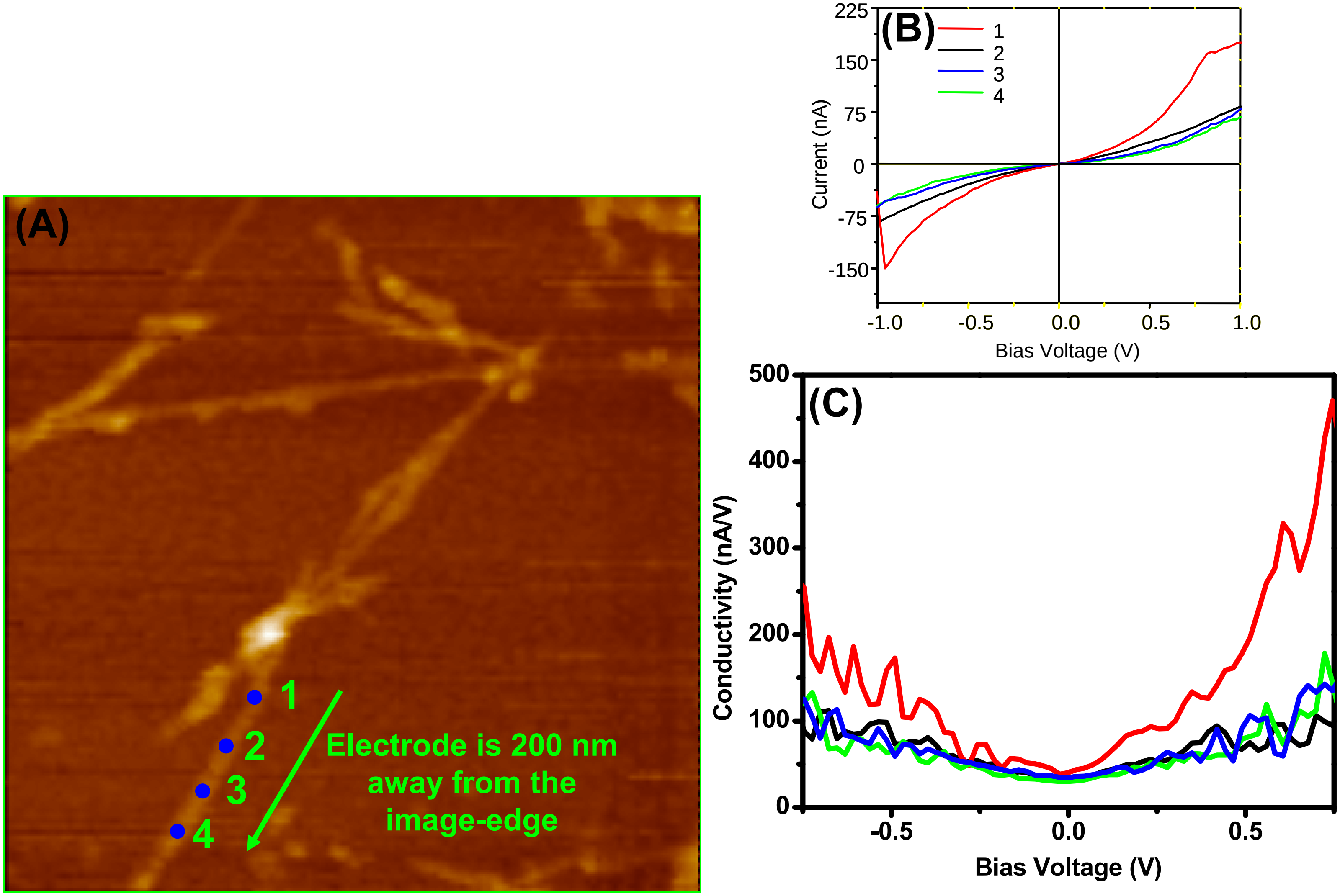
Diethyl ether
Aqueous
Nanoparticles
SWNT in DMF
Diethyl ether
M NPs/NRs
Au NPs
M NPs – Au/Ag nanoparticles,
Citrate synthesized
M NRs – Au nanorods



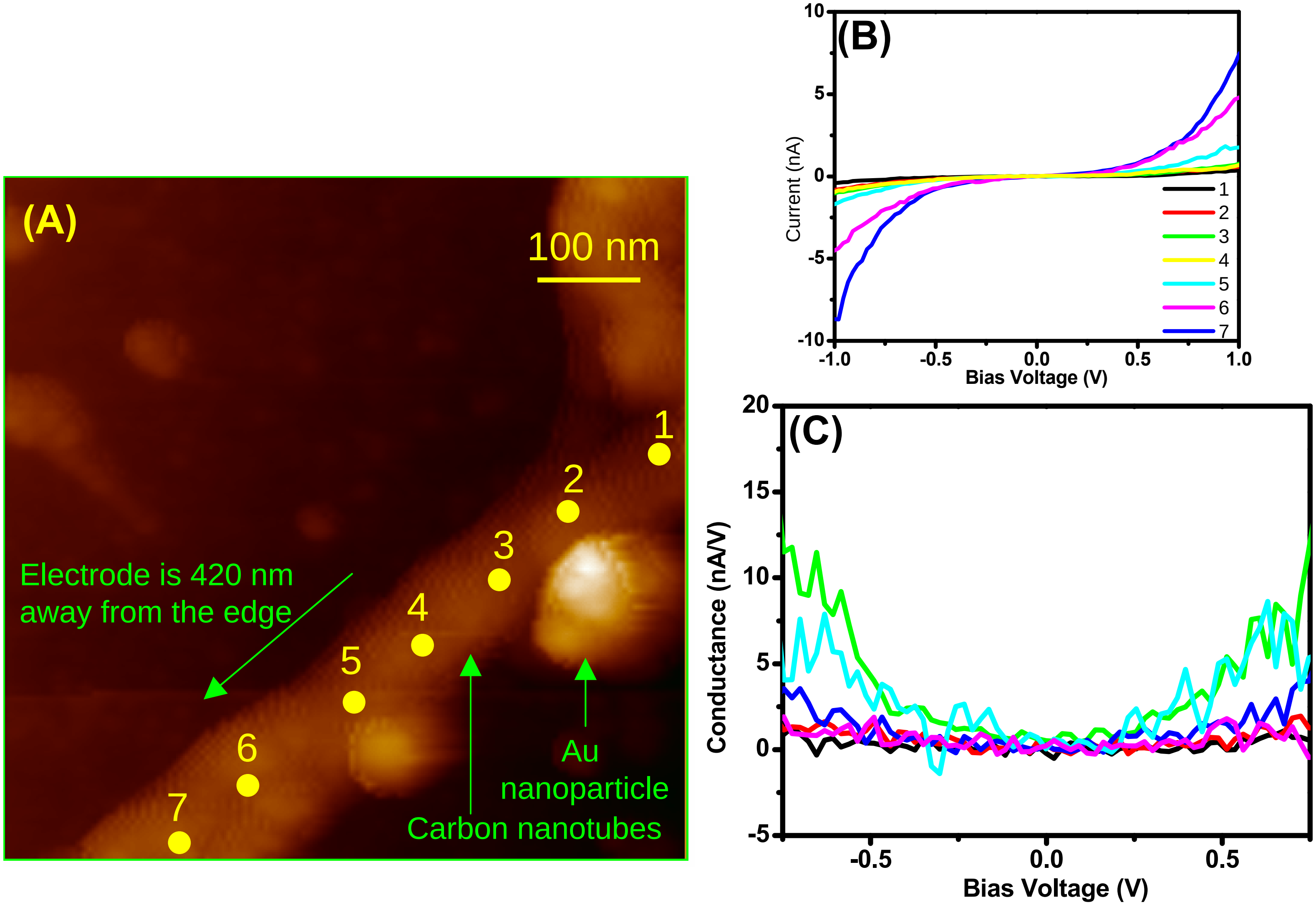
TEM images of Au-SWNTs composite acquired at 100 keV.



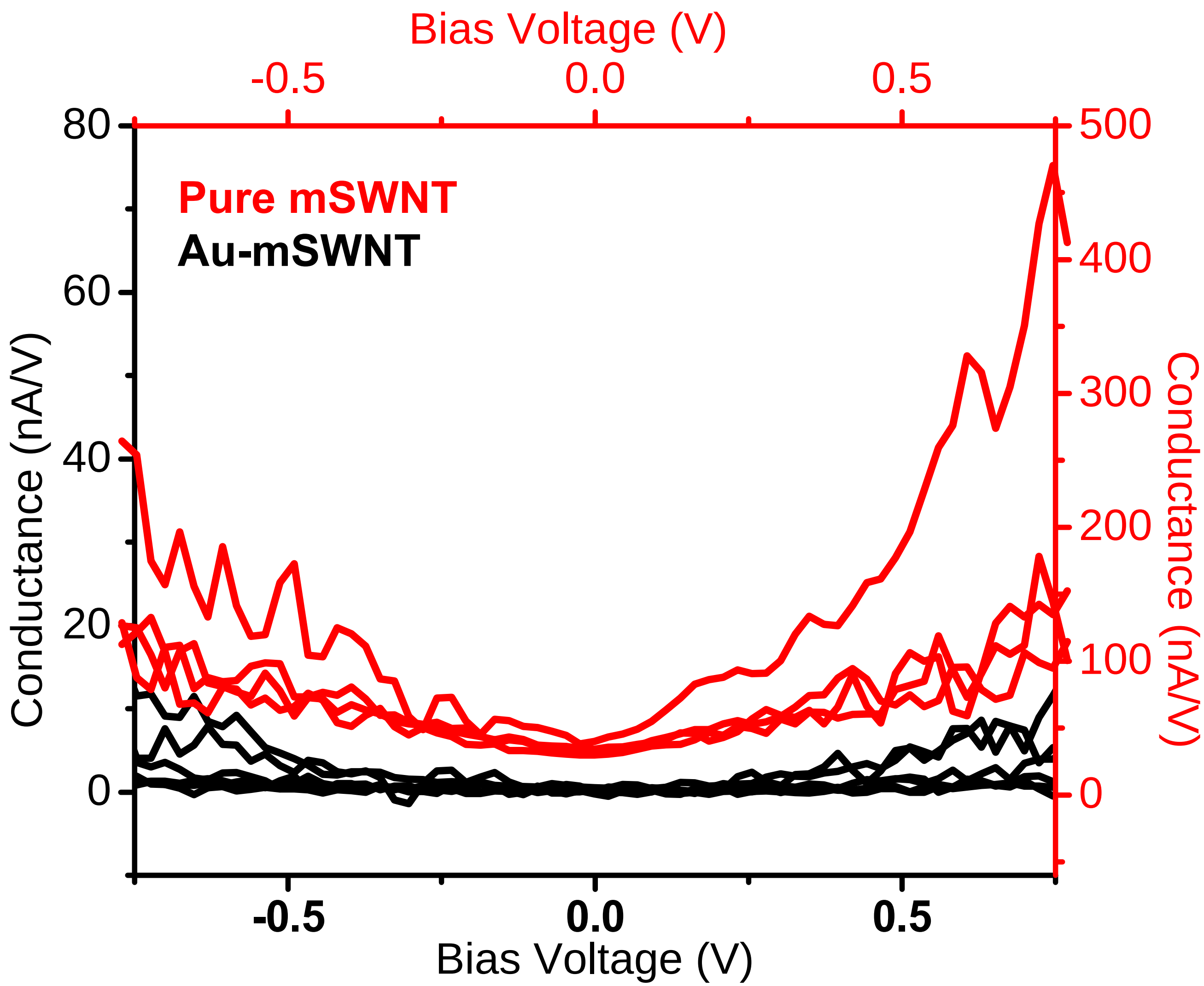
Raman Spectra of (a) Ag-SWNTs composite, (b) Au-SWNTs composite, (c) AuNR-SWNTs composite, (d) pristine SWNTs, (e) Pristine SWNTs treated with trisodium citrate and (f) Au nanorods.



(A) PCI-AFM images of pure mSWNT with (B) I-V curves and (C) plot of conductance versus bias voltage.



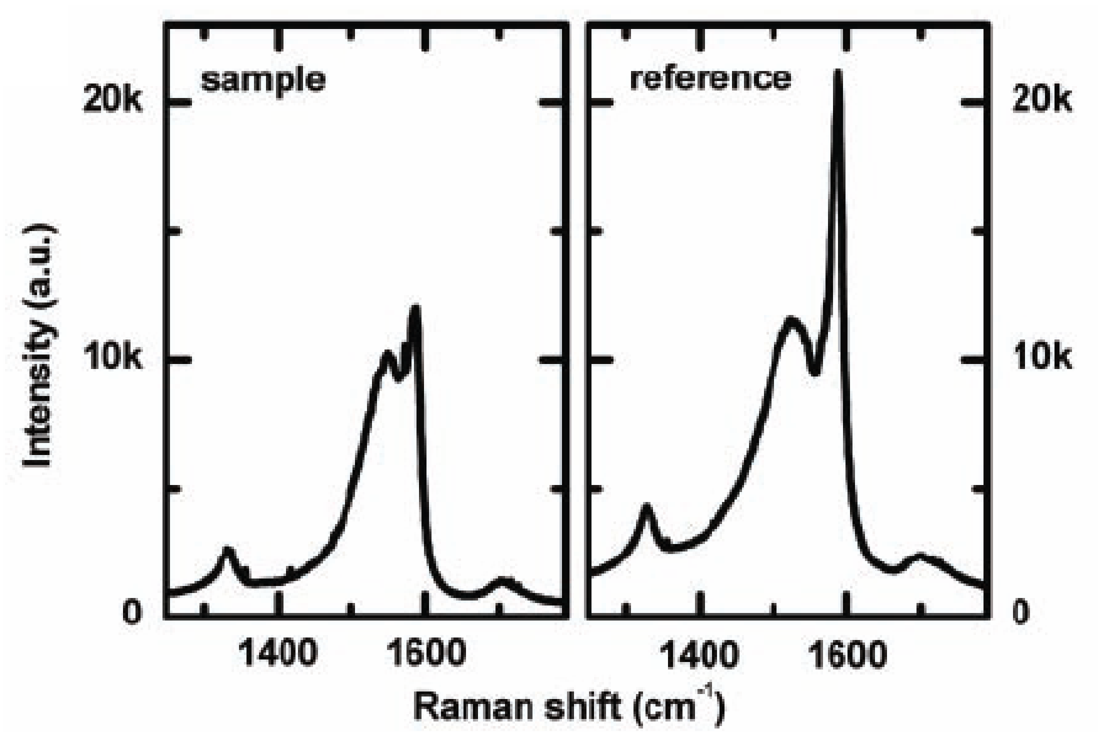
(A) PCI-AFM image of Au-mSWNT with (B) the corresponding I-V curves and (C) Plot of conductance versus bias voltage.



Comparison of conductance versus bias voltage for pure mSWNT and Au-mSWNT composite

C. Subramaniam et al Phys. Rev. Lett. 2007

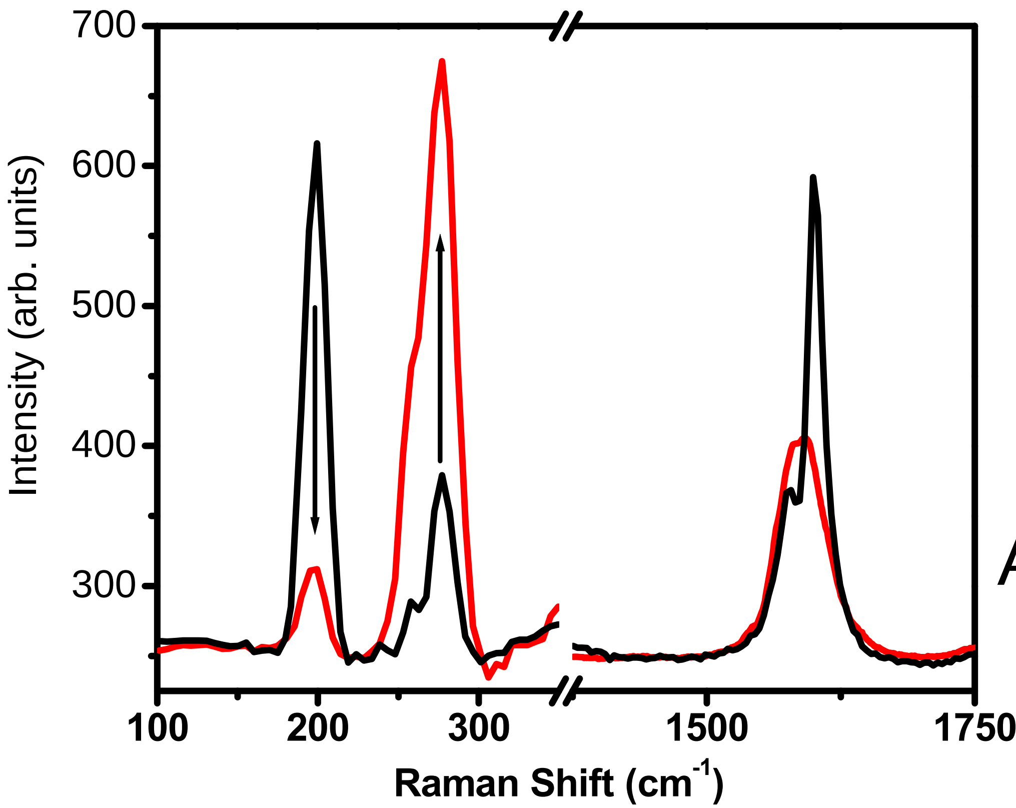
G-band line shapes of metallic and semiconducting SWNT



Changes observed in G-band for metallic (left) and pristine (right) SWNT

R. Krupe *et al.*, *Science* ***301****, 344 (2003)*.

➢ Confocal Raman investigations



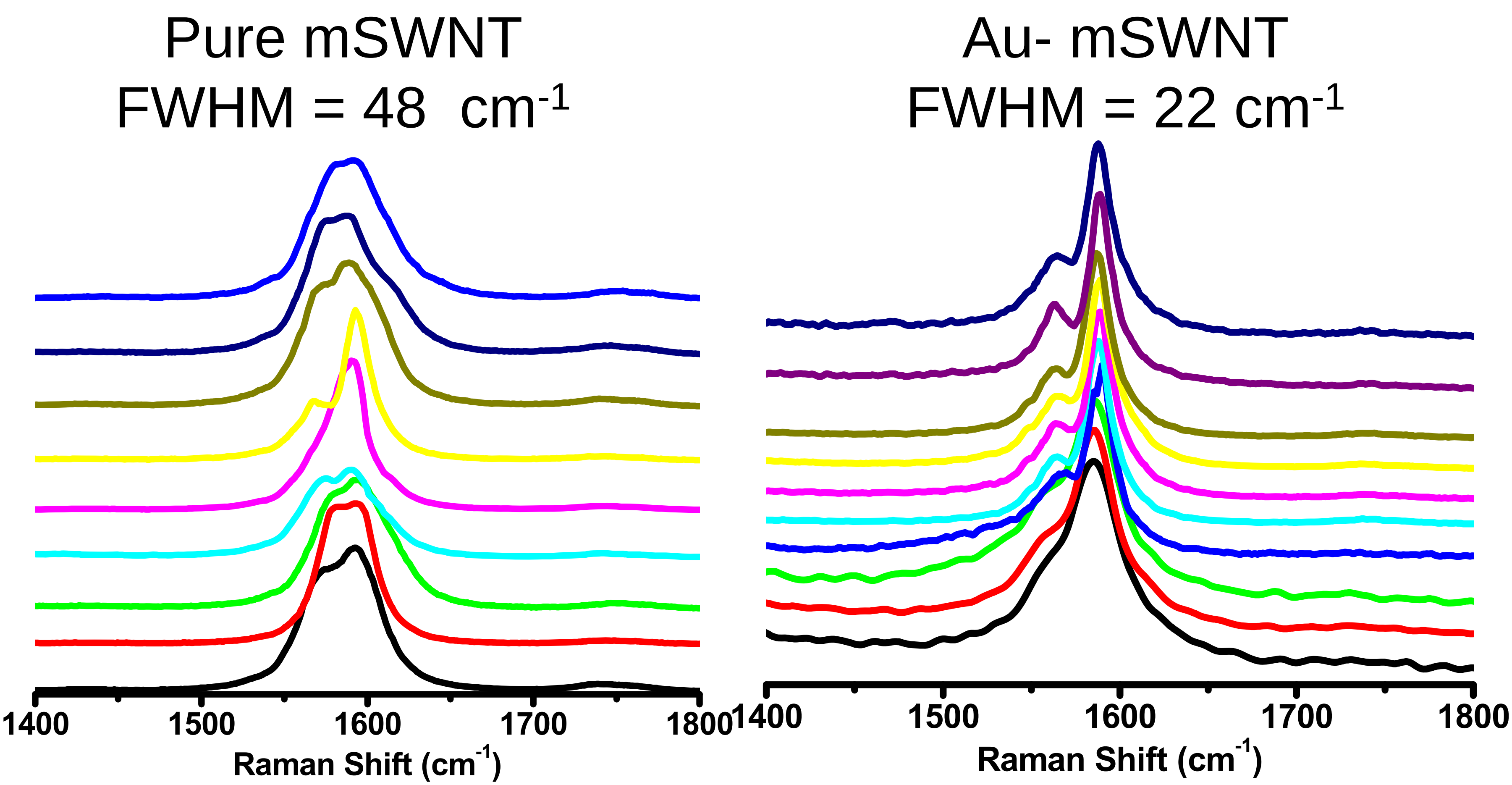
$A_s/A_m = 65.0$

$A_s/A_m = 0.14$

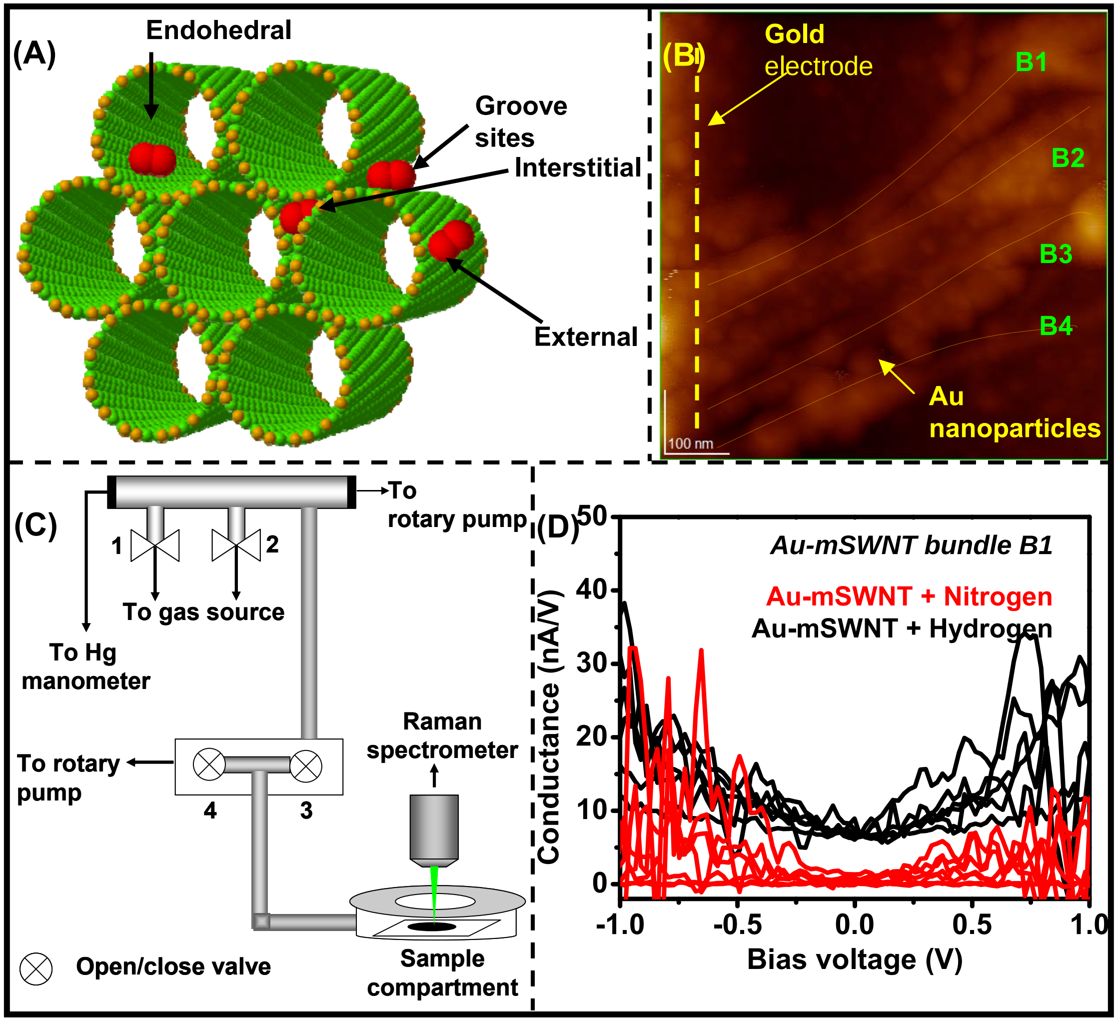
Extraction efficiency

$A_s/(A_s + A_m)* \ 100 = 88\%$

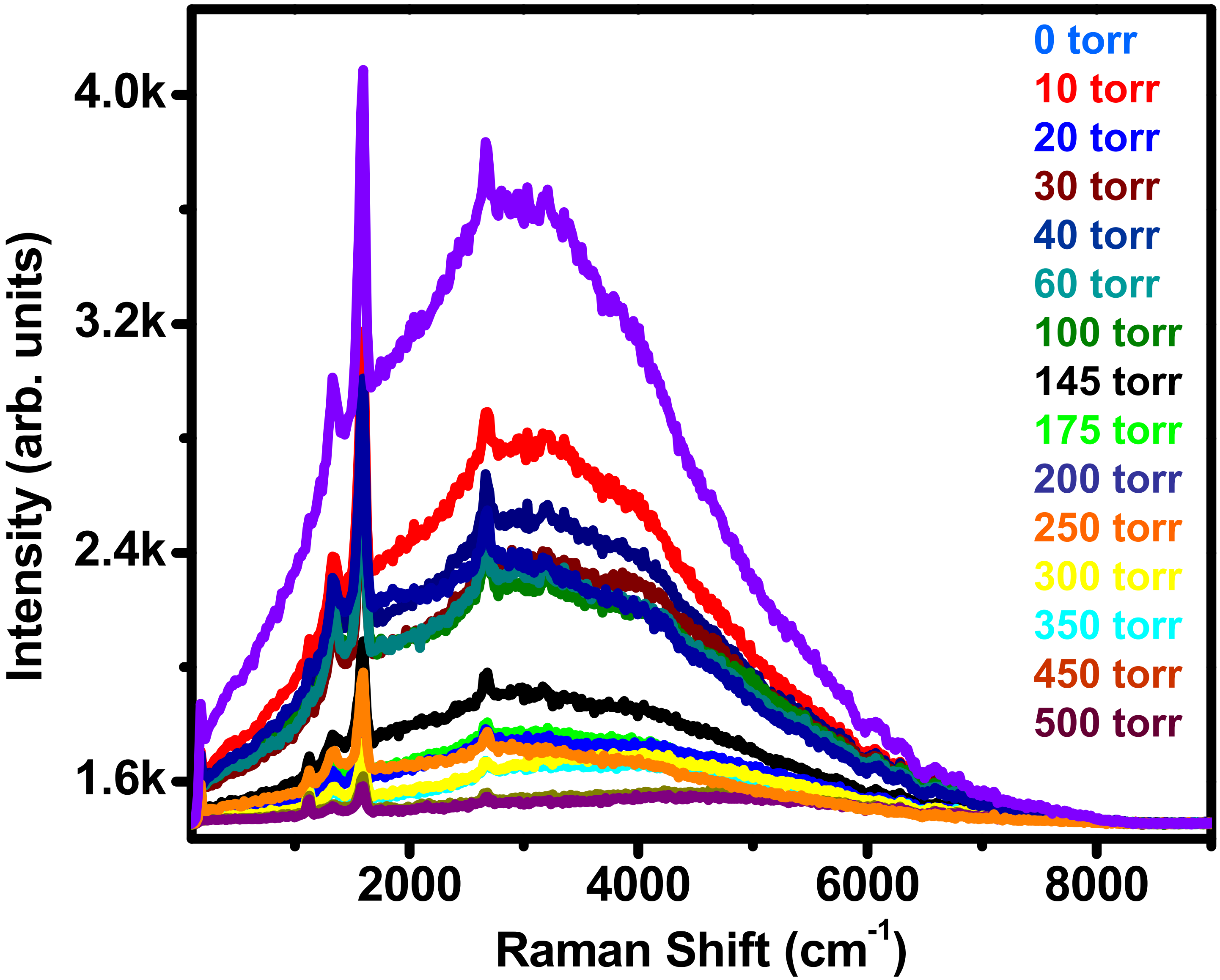
Raman spectra in RBM and G-band regions of pristine SWNT (black) and extracted mSWNT (red).



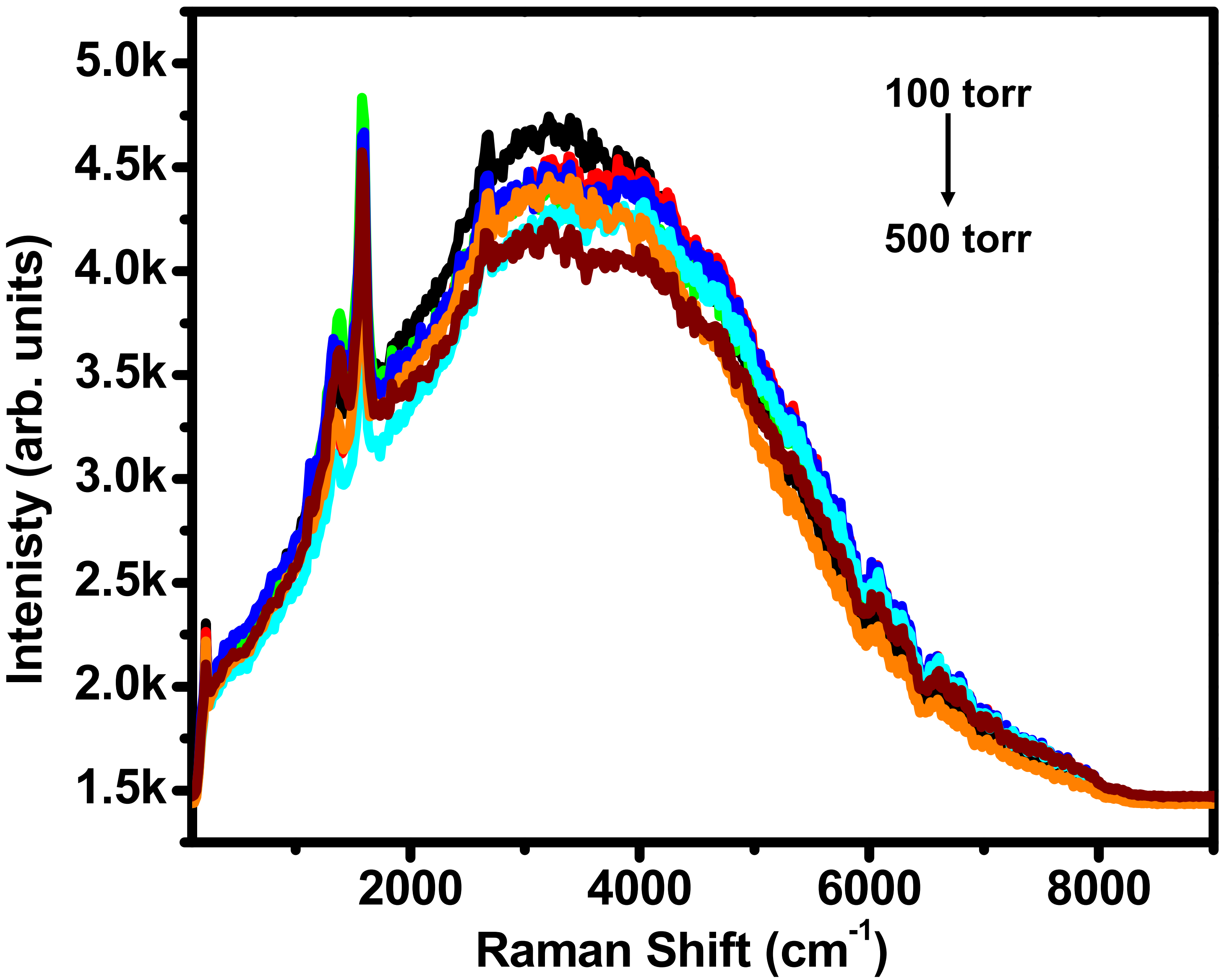
Comparison of G-band of pure mSWNT and Au-mSWNT



(A) Schematic representation of a SWNT bundle with the adsorption sites indicated. (B)Topographic image of Au-mSWNT composite. Several points on various bundles marked B1 to B4 have been analyzed though PCI-AFM. The gold electrode and the bundles have been marked with guide lines. (C) Schematic representation of the microRaman setup used for gas-exposure studies. (D) Plot of conductance versus bias voltage constructed from various points of the bundle labeled B1 in Figure 1B, under an atmosphere of nitrogen (red traces) and hydrogen (black traces).

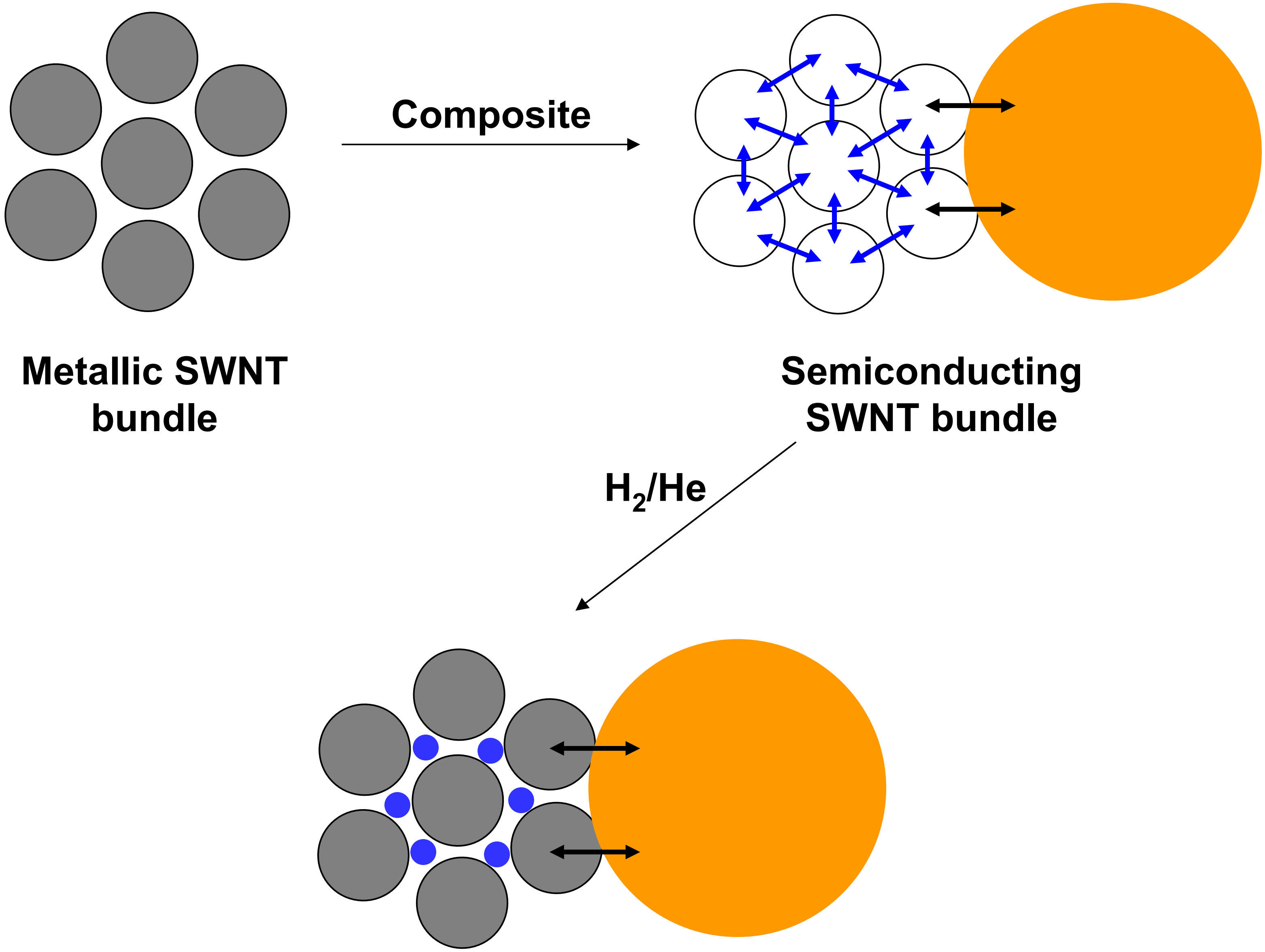


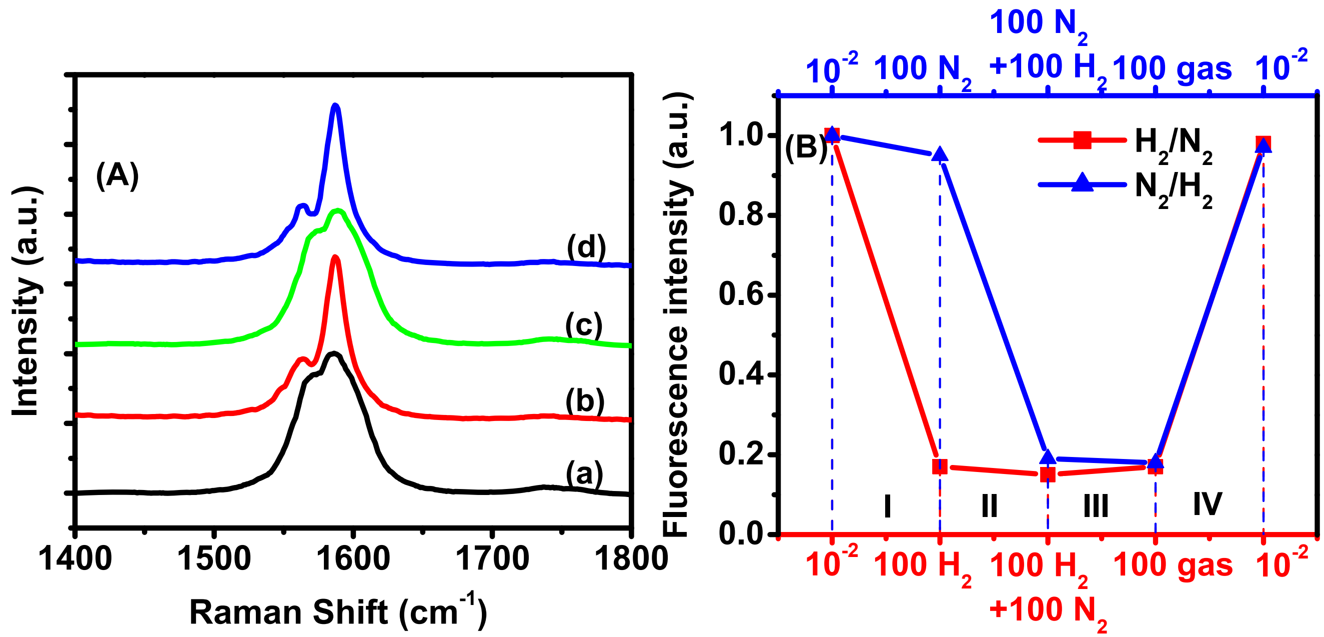
Au-SWNTs exposed to H_2 gas at various partial pressures.



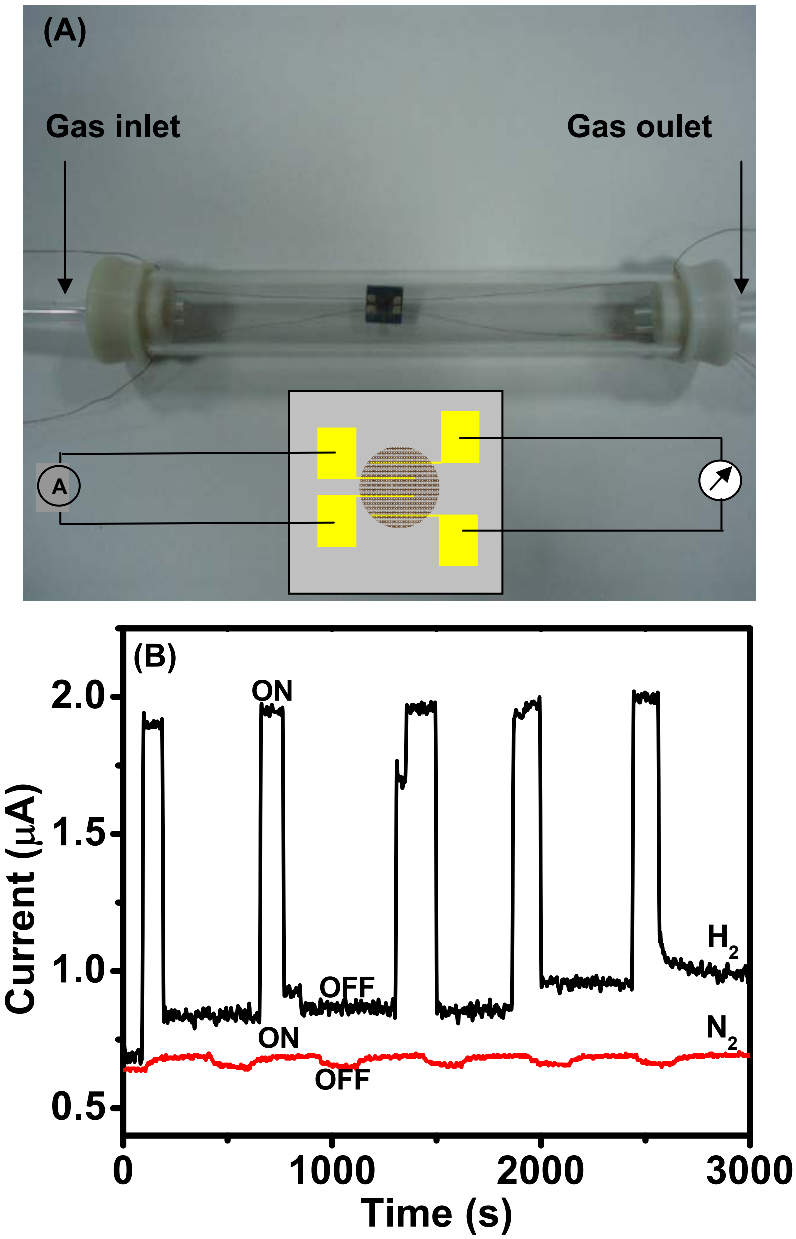
Au-SWNTs exposed to N_2 gas at various partial pressures.

Suggested mechanism





(A) Raman spectra of (a) purified mSWNTs, (b) Au-mSWNT composite, (c) Au-mSWNT upon exposure to 500 torr H2 and (d) Au-mSWNT composite after pumping out H2 exposed in (c). Spectra (a) to (d) are recorded at the same point on the composite sample. (B) Variation of fluorescence intensity upon exposing mixture of gases. Regions A to D are explained in the text. Pressures are in torr.



(A) Photograph of the device setup with a cartoon representation of the microelectrode. The shaded circle in the cartoon is used to represent the sample with the yellow regions representing the gold electrode. (B) A plot of variation of current for a bias voltage of 5 V for Au-mSWNT composite in presence of H2 (500 torr, black line) and N2 (500 torr, red line).The ON and OFF states pertain to the presence and absence of gases, respectively. While the current for the ON state is constant, that due to the OFF state increases slowly with increase in cycles as hydrogen exposed during the previous cycle is not removed completely, consistent with the fluorescence data (Fig. 3A inset). Current measurements appear to be sensitive to tiny quantities of adsorbed gases.

PCT Applied 2008

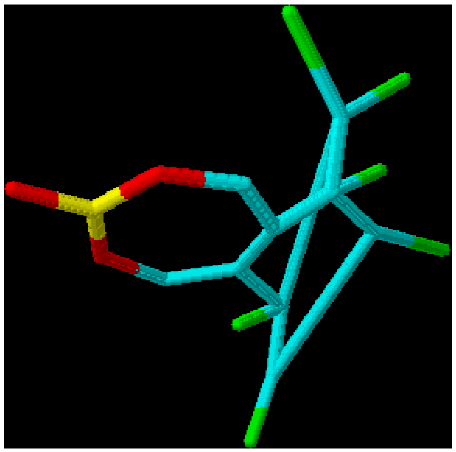
3

Nanoparticle superlattices

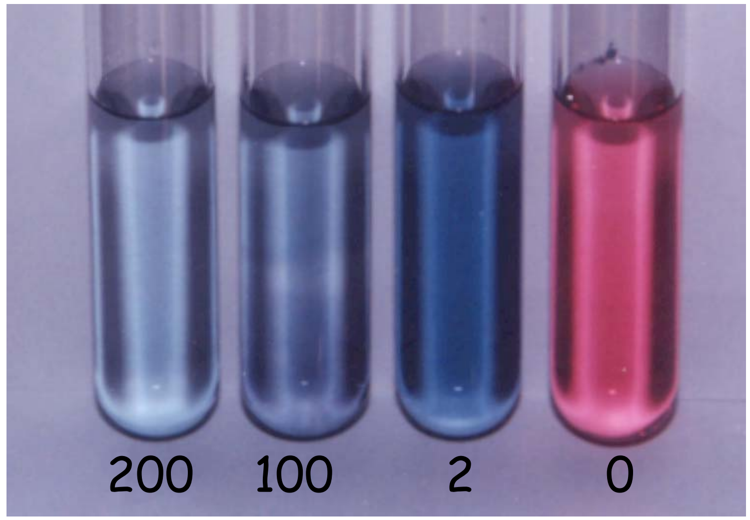
New chemistry

Color of gold nanoparticles with endosulfan

Example



Endosulfan



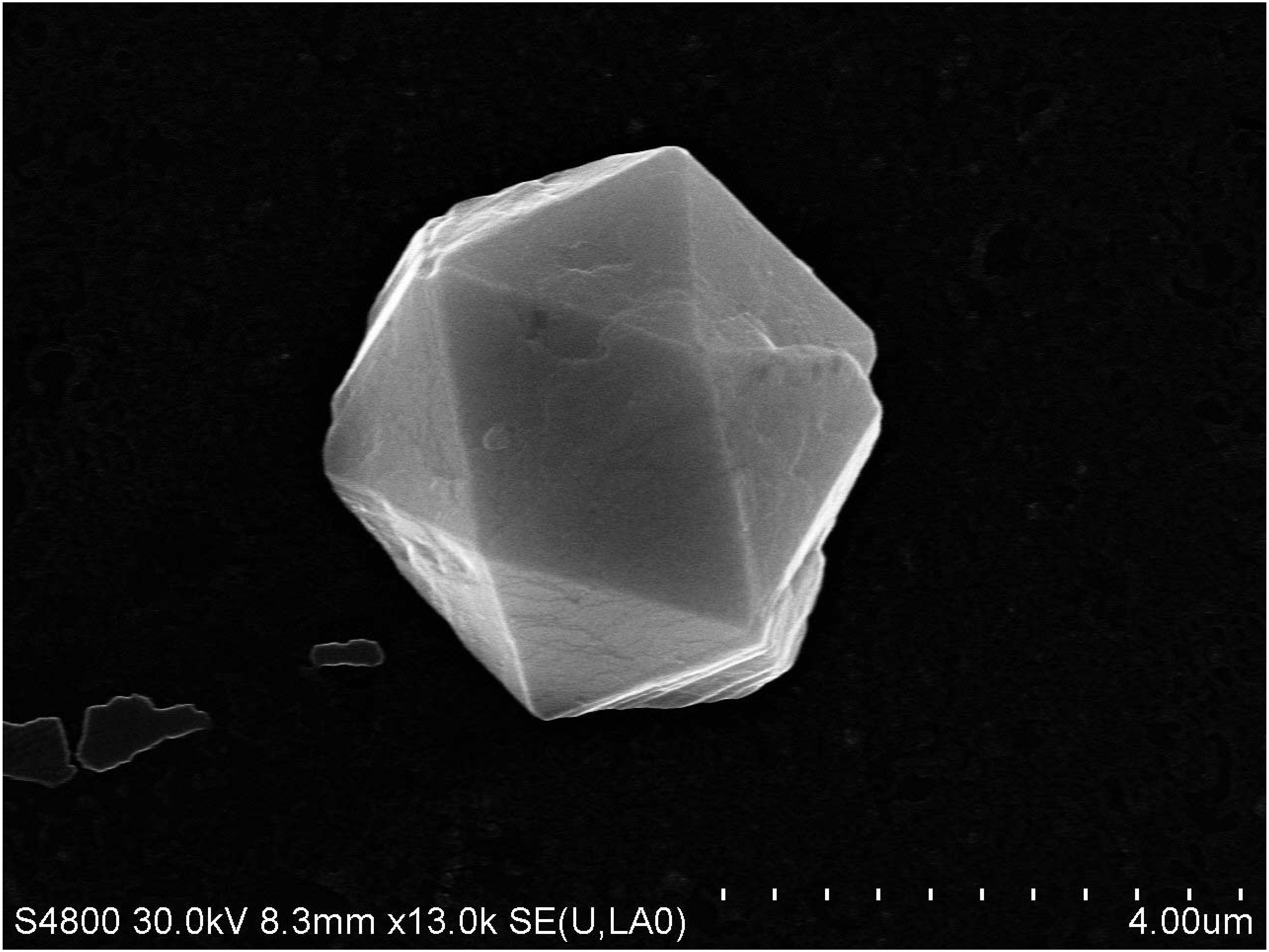
Endosulfan concentration in ppm

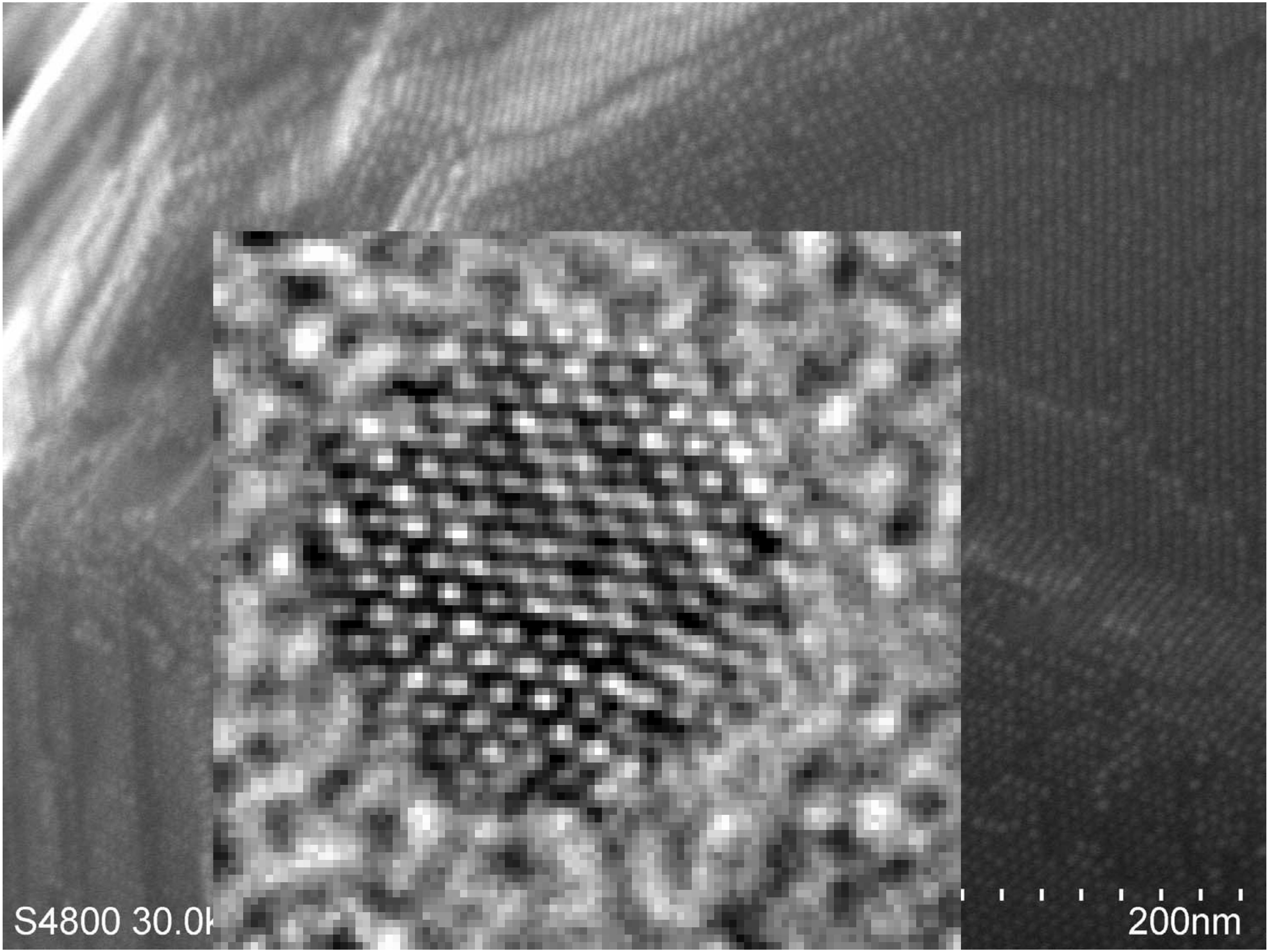
Chemistry world 2007

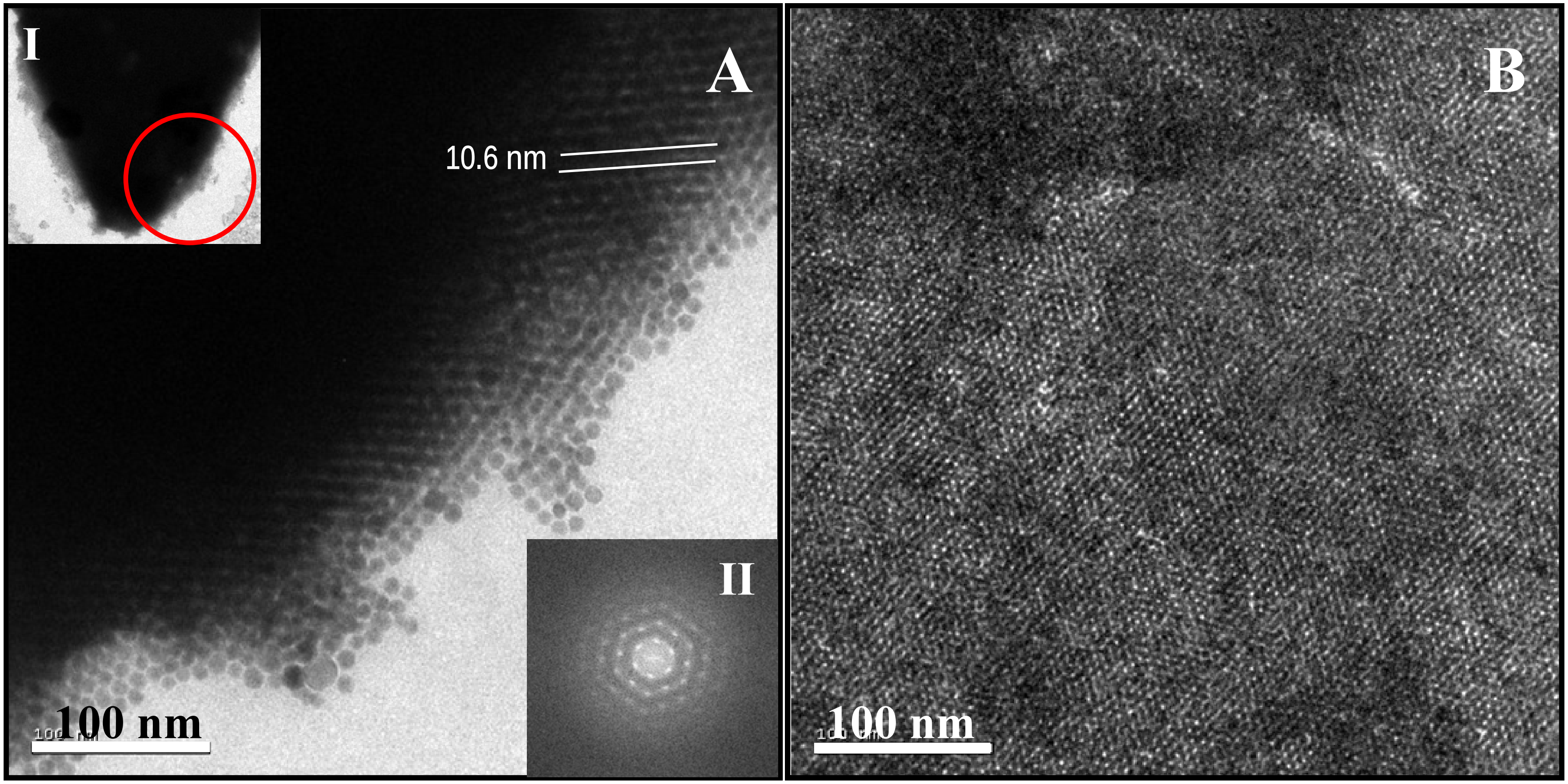
Color changes with pesticide concentration
Good response at lower concentrations
Down to 0.1 ppm
Adsorbed pesticides can be removed from solution

Pesticide removal
Indian Patent granted
International patent filed
Technology commercialized, factory put up

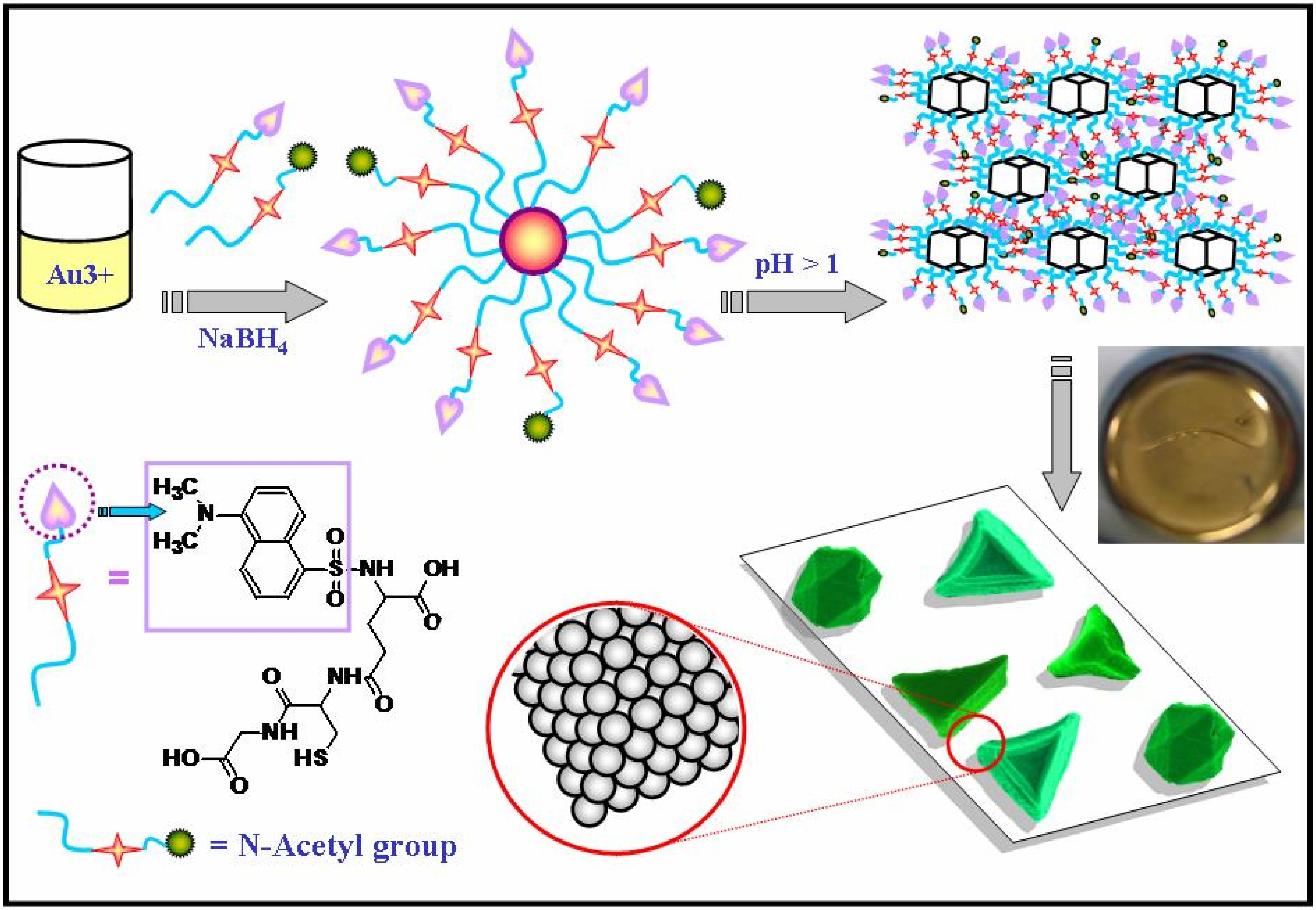
J. Environ. Monitoring. 2003


S4800 30.0kV 8.3mm x13.0k SE(U,LA0)
4.00um

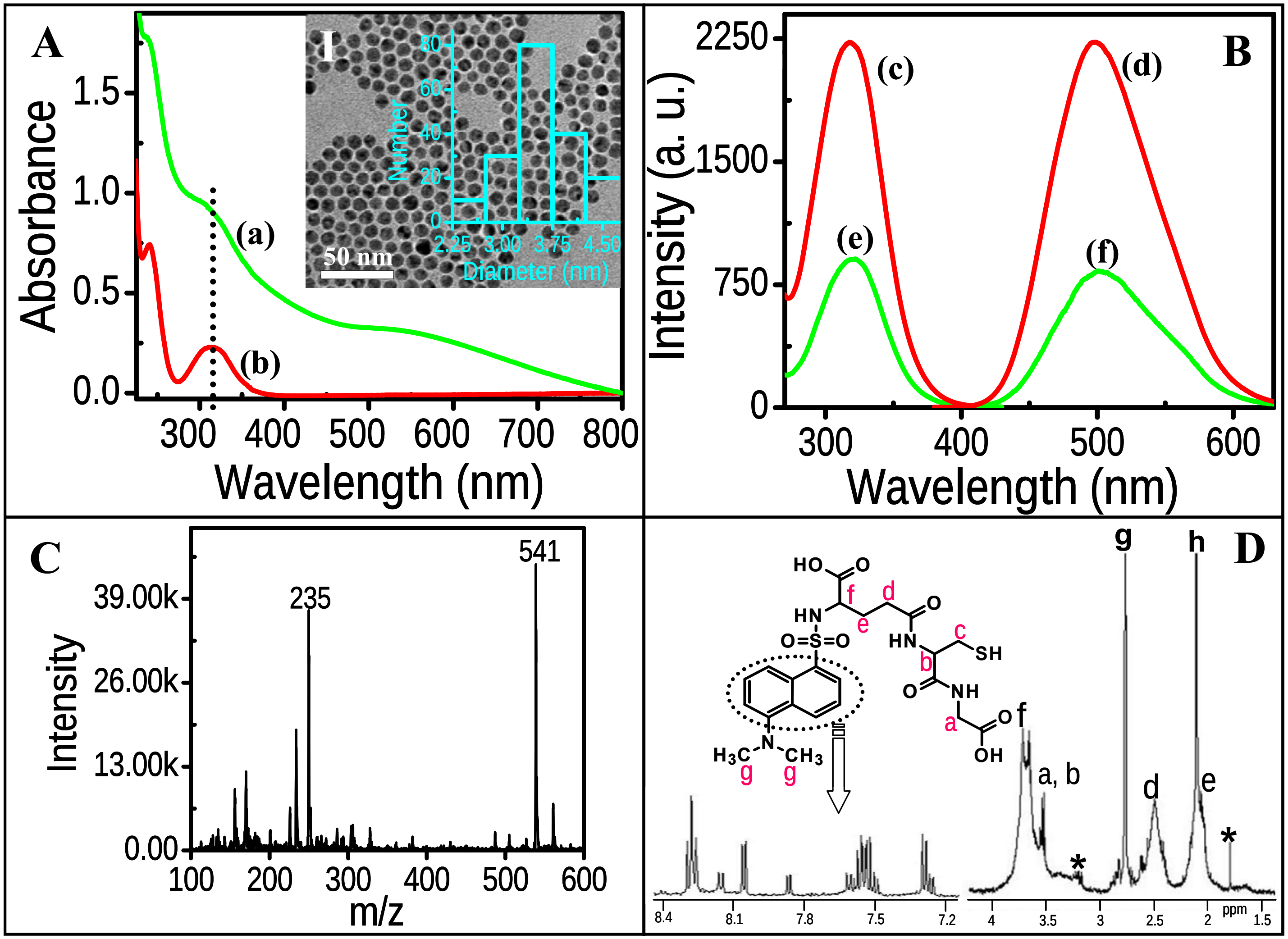

S4800 30.0k
200nm



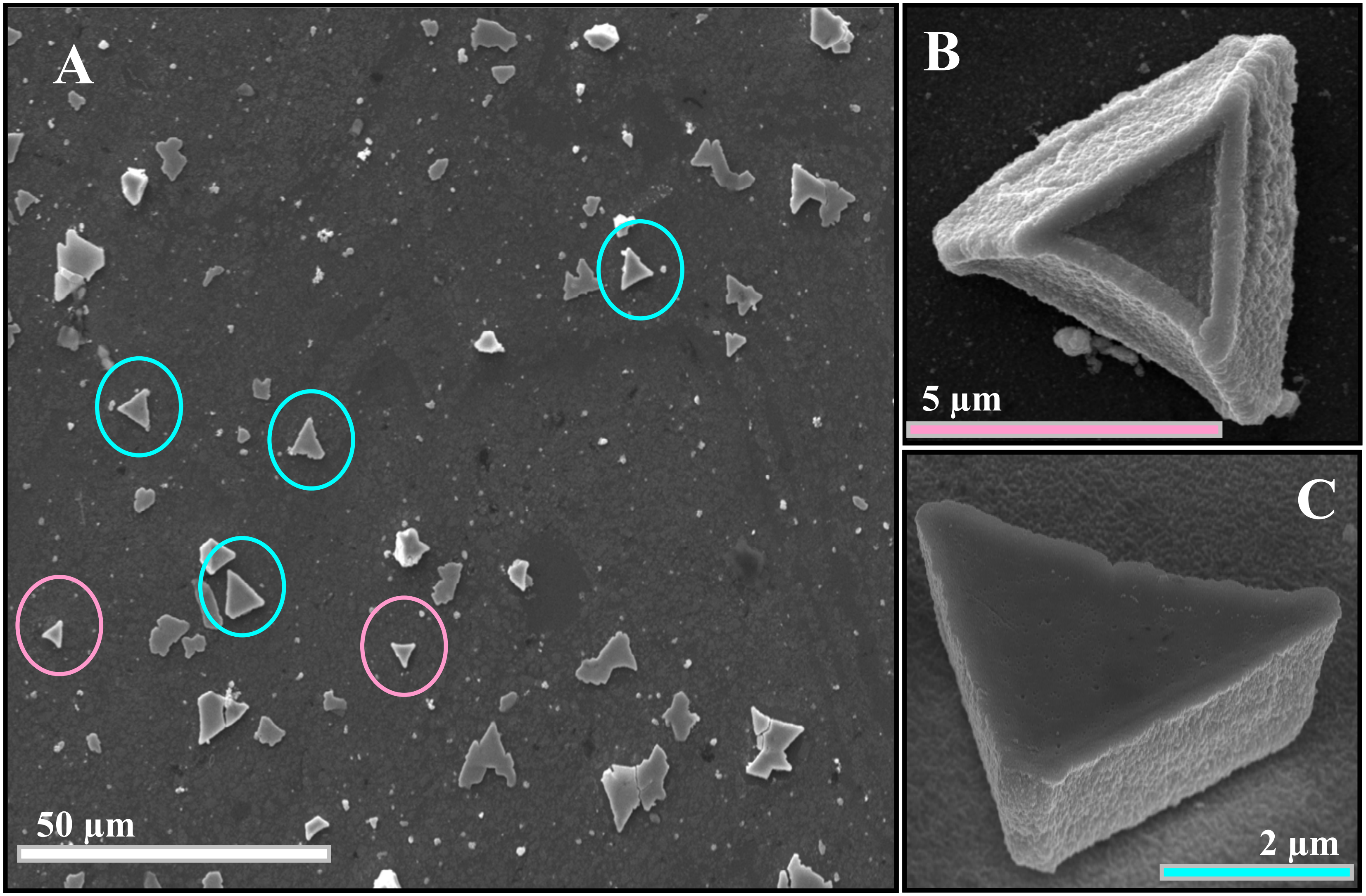
Shibu et al. Adv. Mat. 2008b



Au3+
NaBH4
pH > 1
H3C
N
H3C
O
S
O
NH
OH
O
NH
O
O
NH
HS
HO
O
= N-Acetyl group

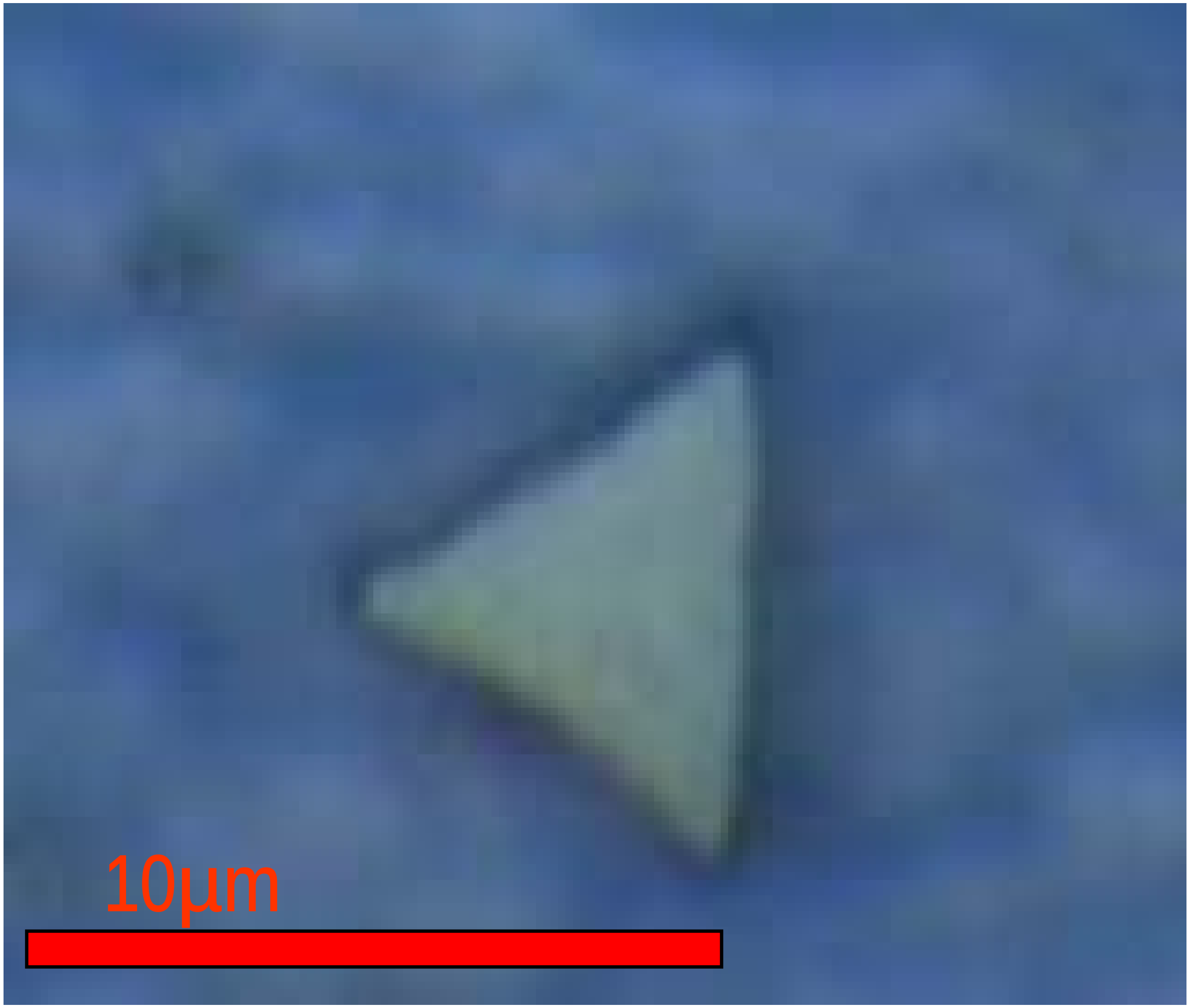


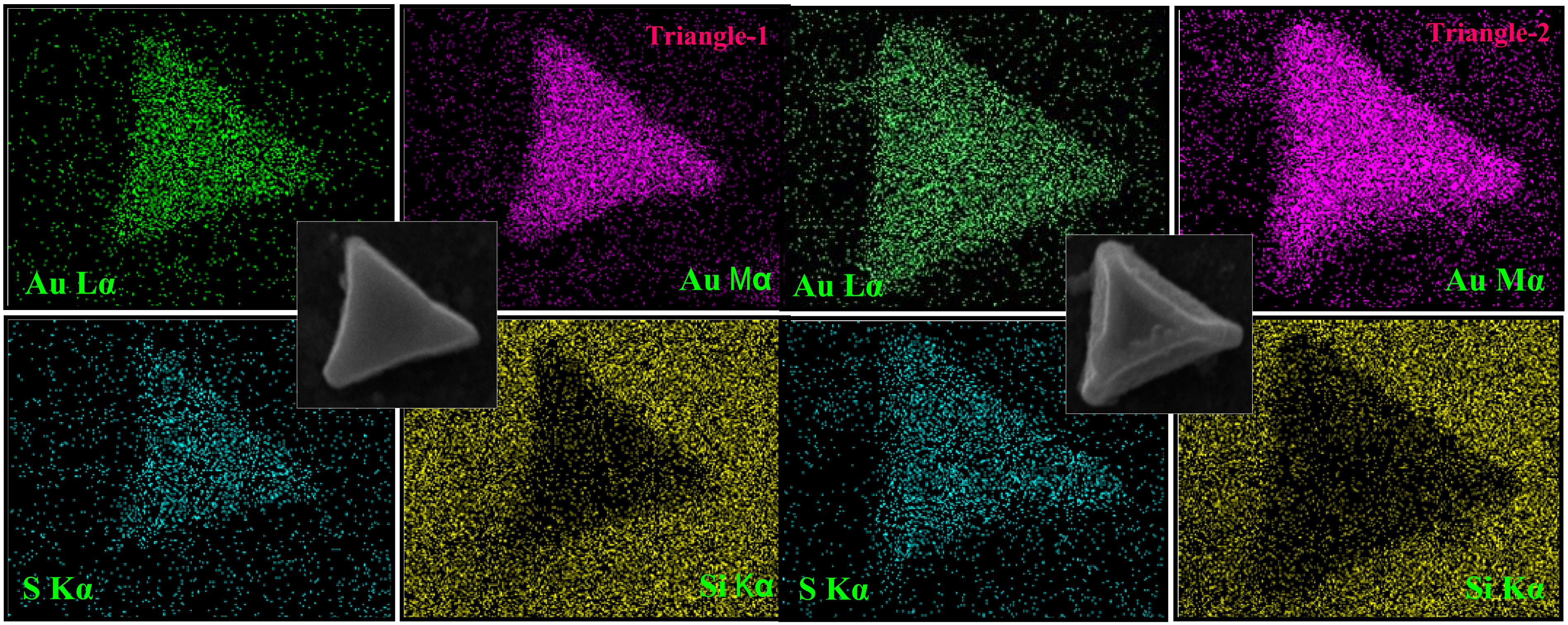
E. S. Shibu et al Nano Res. 2009



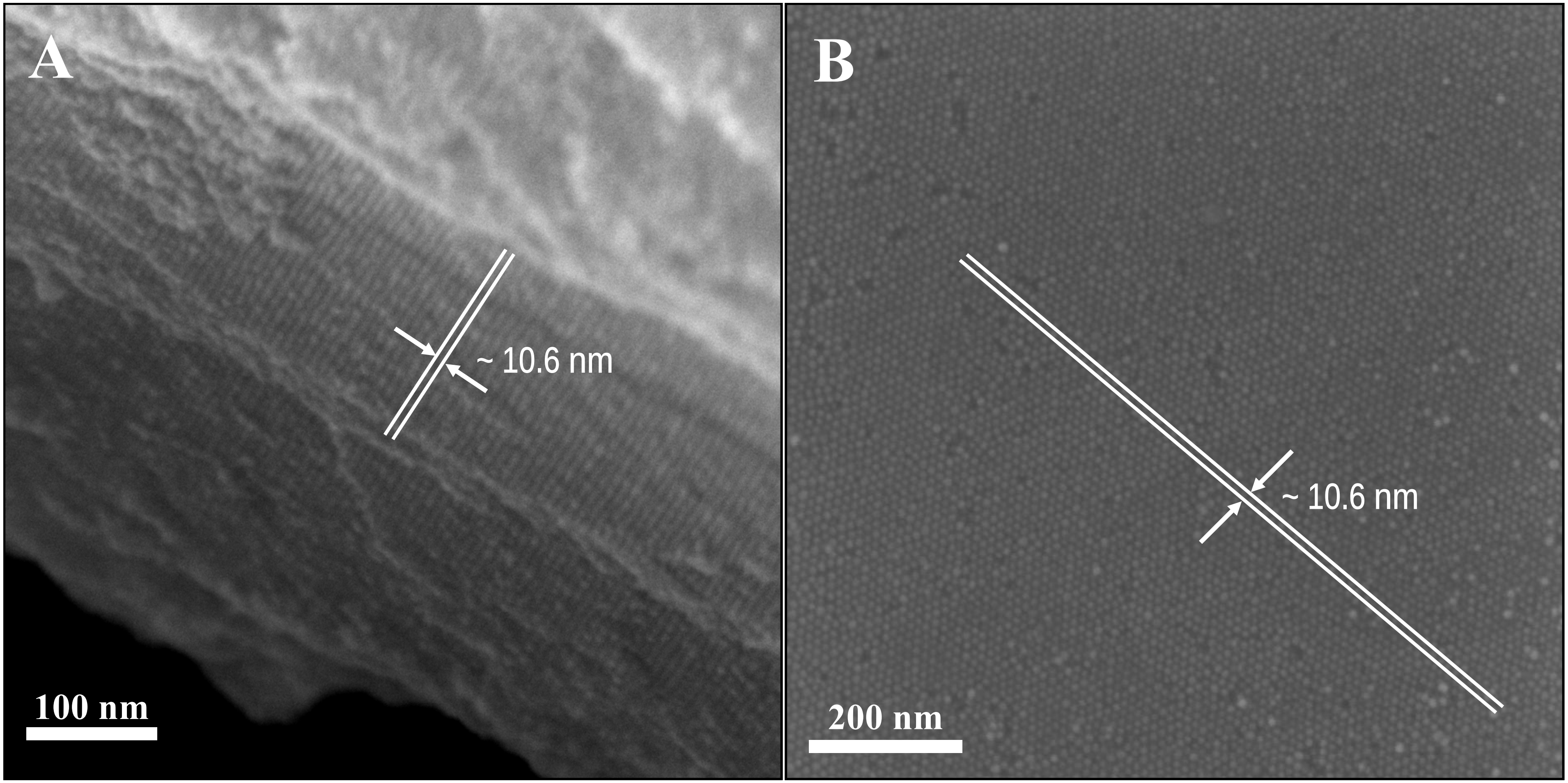
Two different morphologies

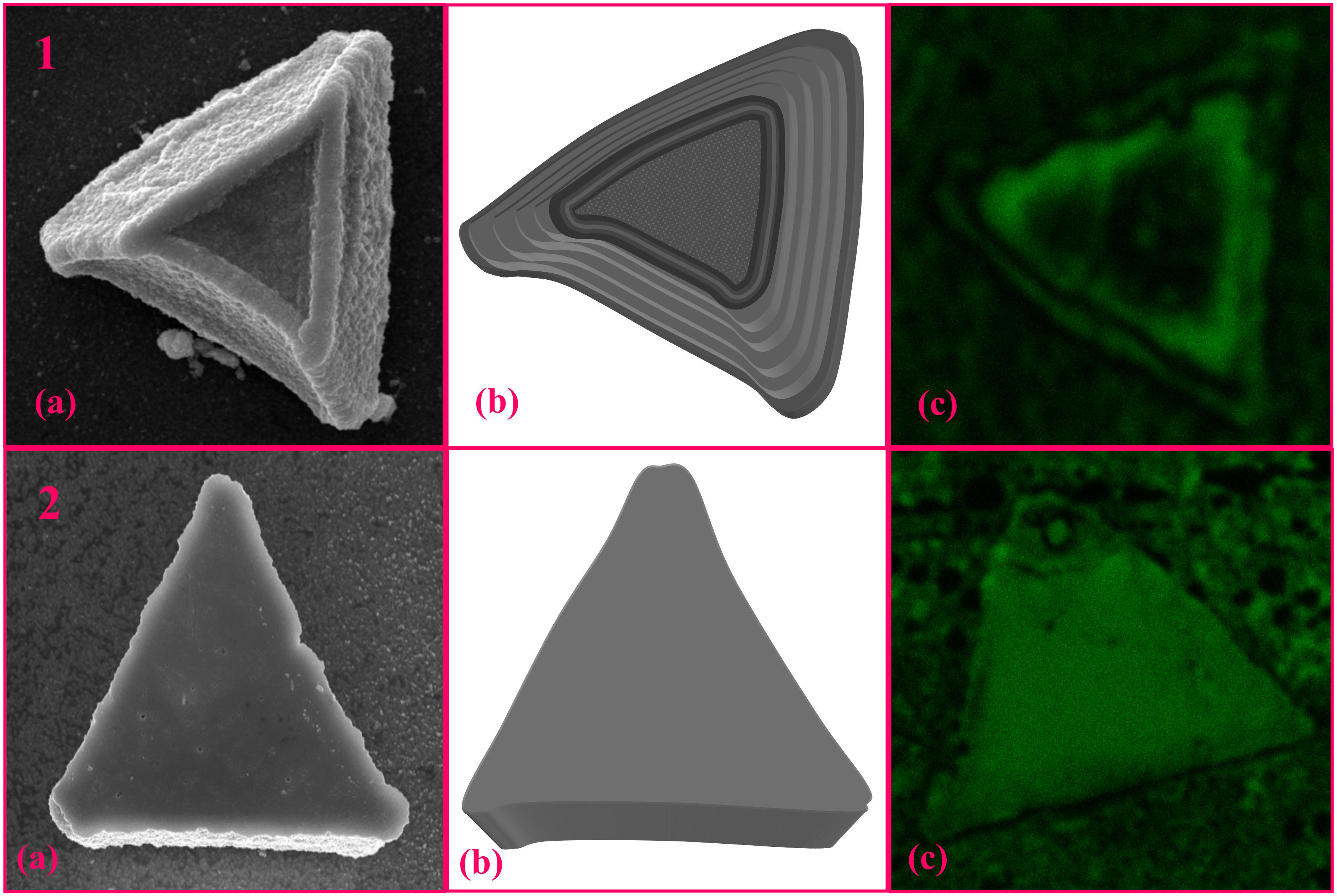
FESEM images – G.U. Kulkarni, K. Kimura

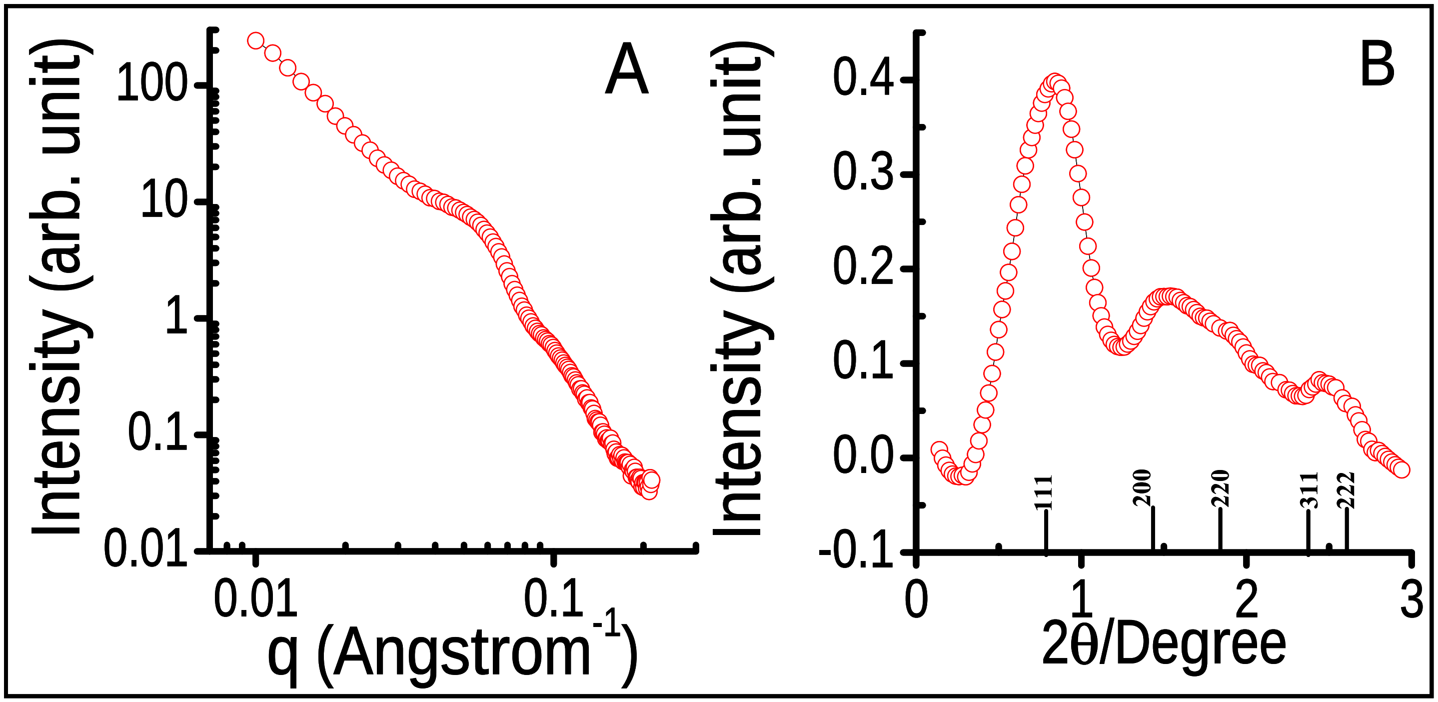

10μm



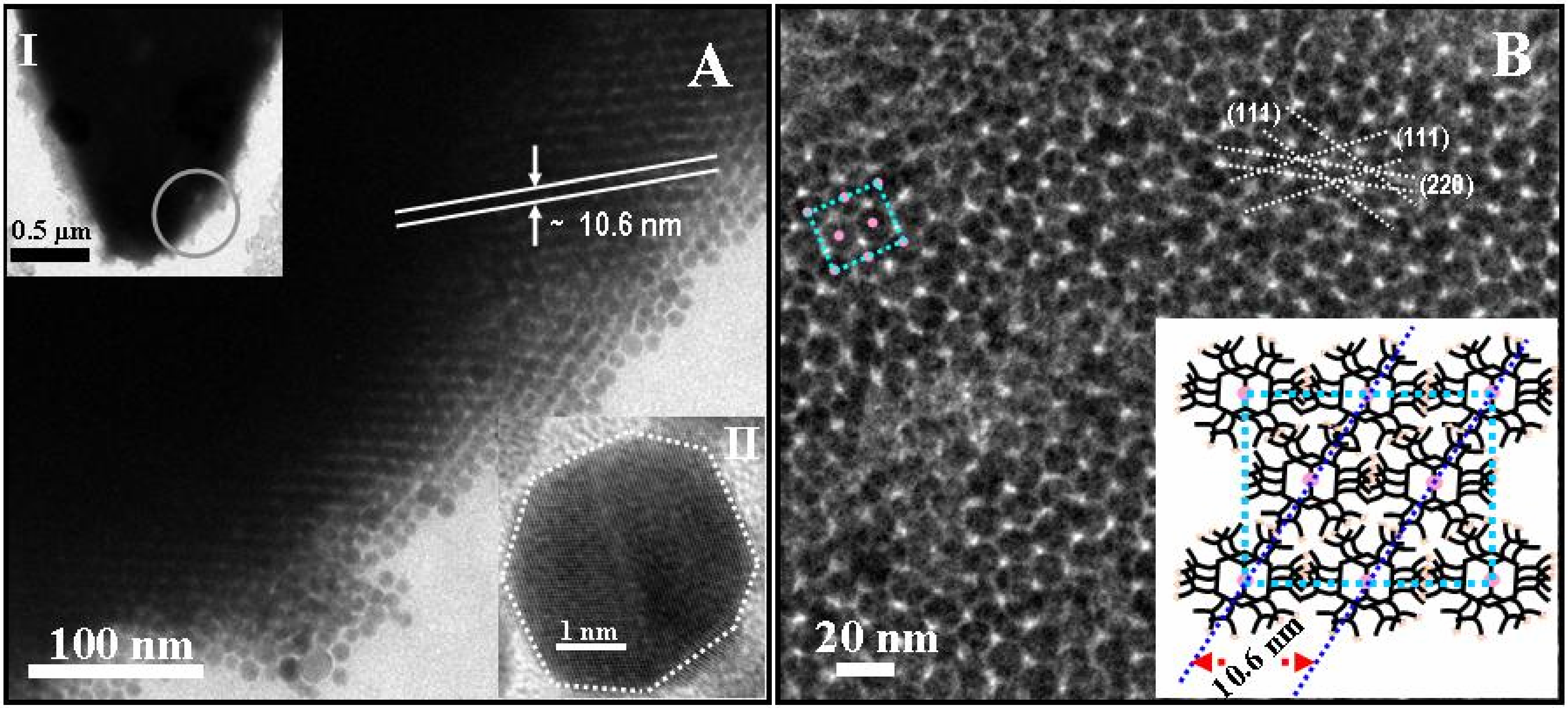
Au Lα
Triangle-1
Au Mα
Au Lα
Triangle-2
Au Mα
S Kα
Si Kα
S Kα
Si Kα


A
~ 10.6 nm
100 nm
B
~ 10.6 nm
200 nm

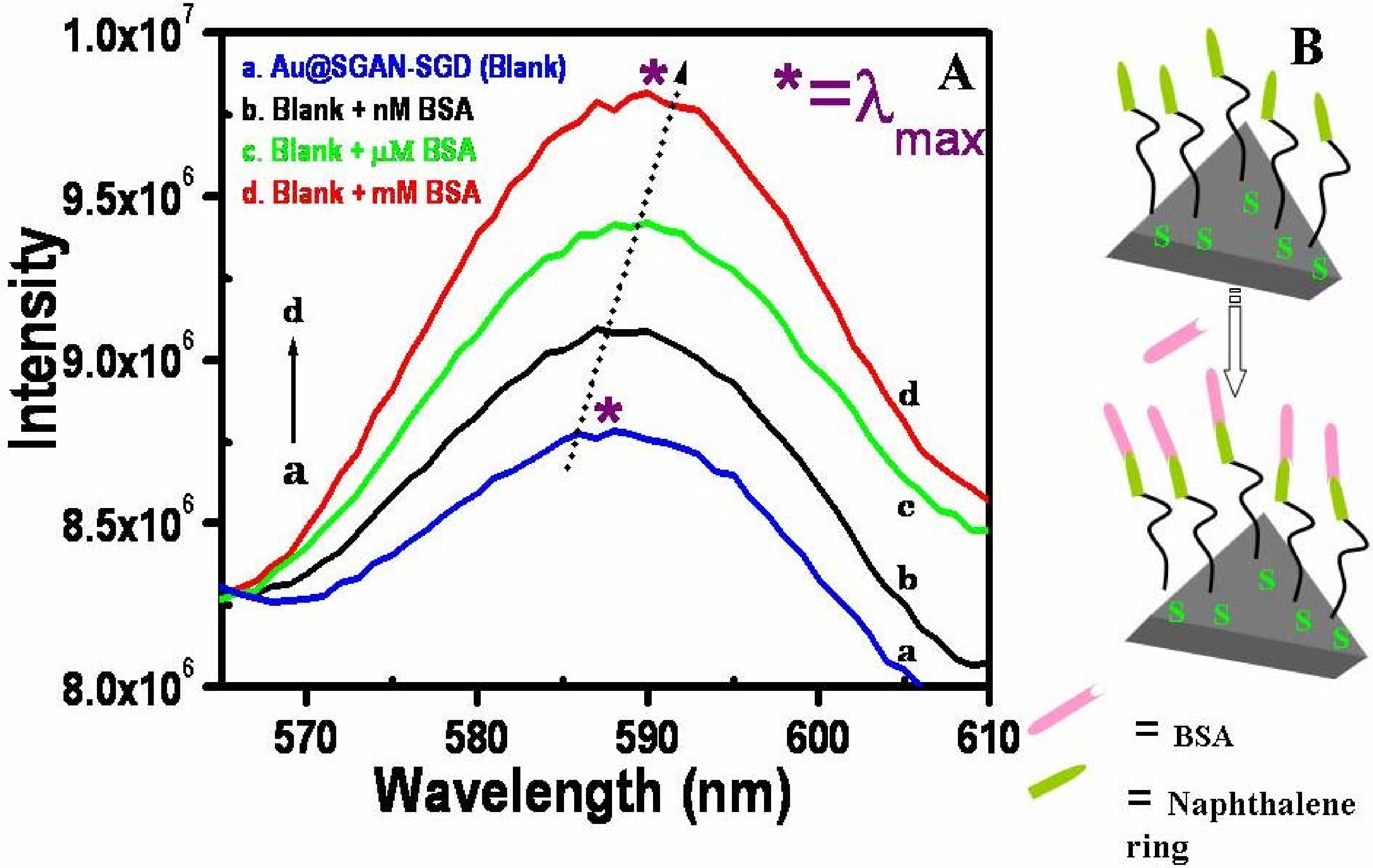

1
(a)
(b)
(c)
2
(a)
(b)
(c)



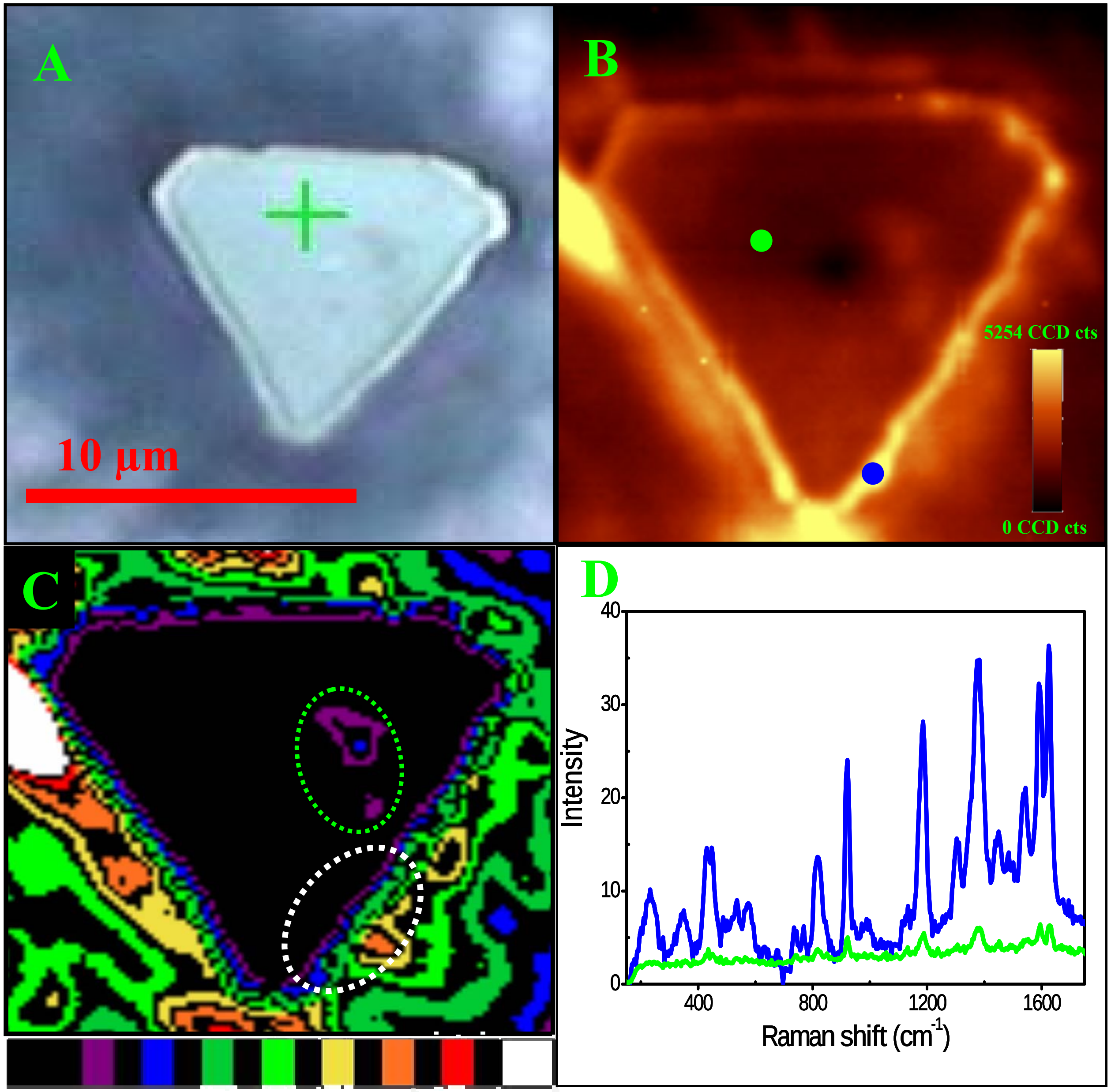
Measured in CNR Rao's lab



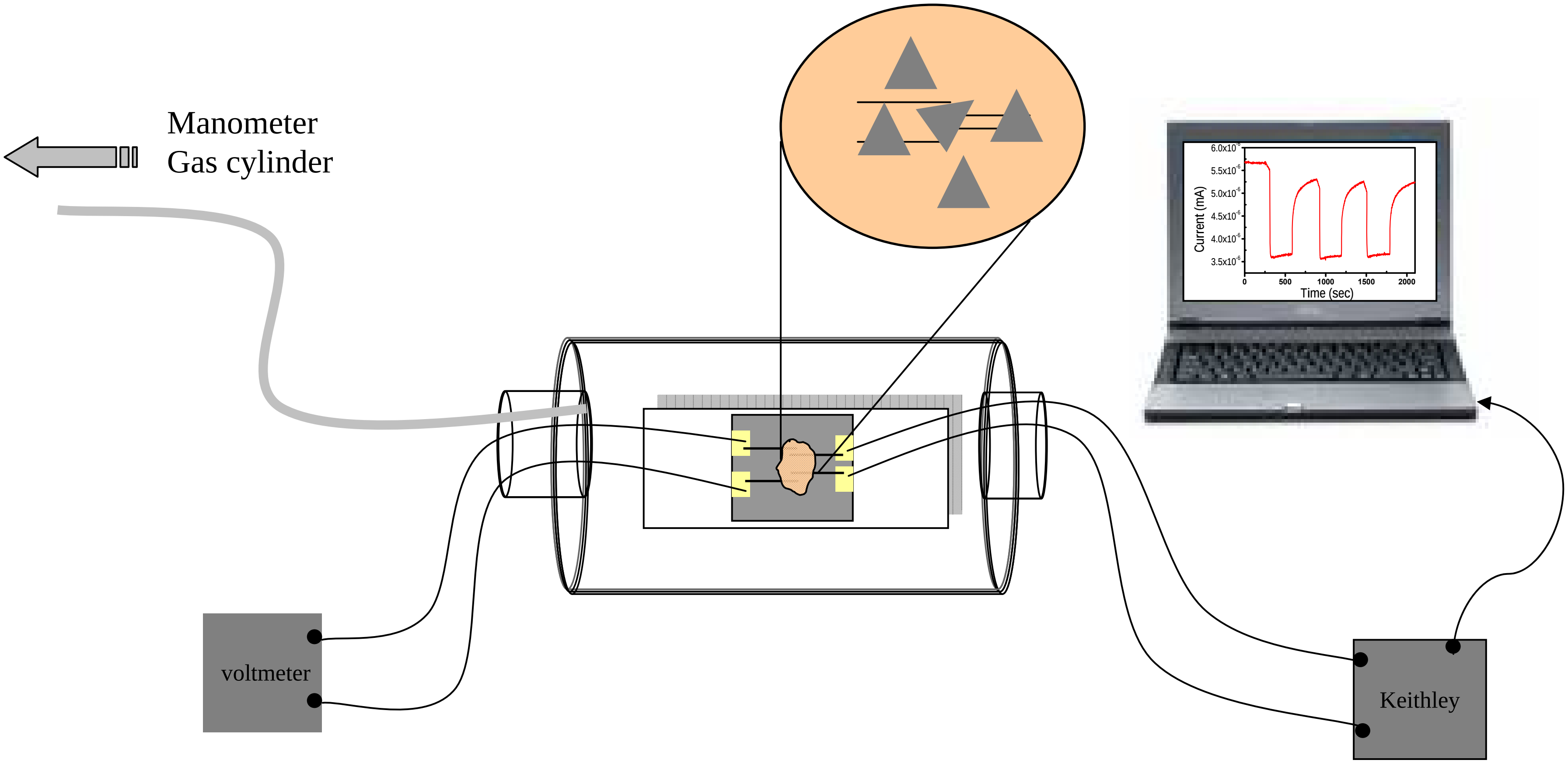
I
A
0.5 μm
~ 10.6 nm
100 nm
II
1 nm
B
(111)
(111)
(220)
20 nm
10.6 nm



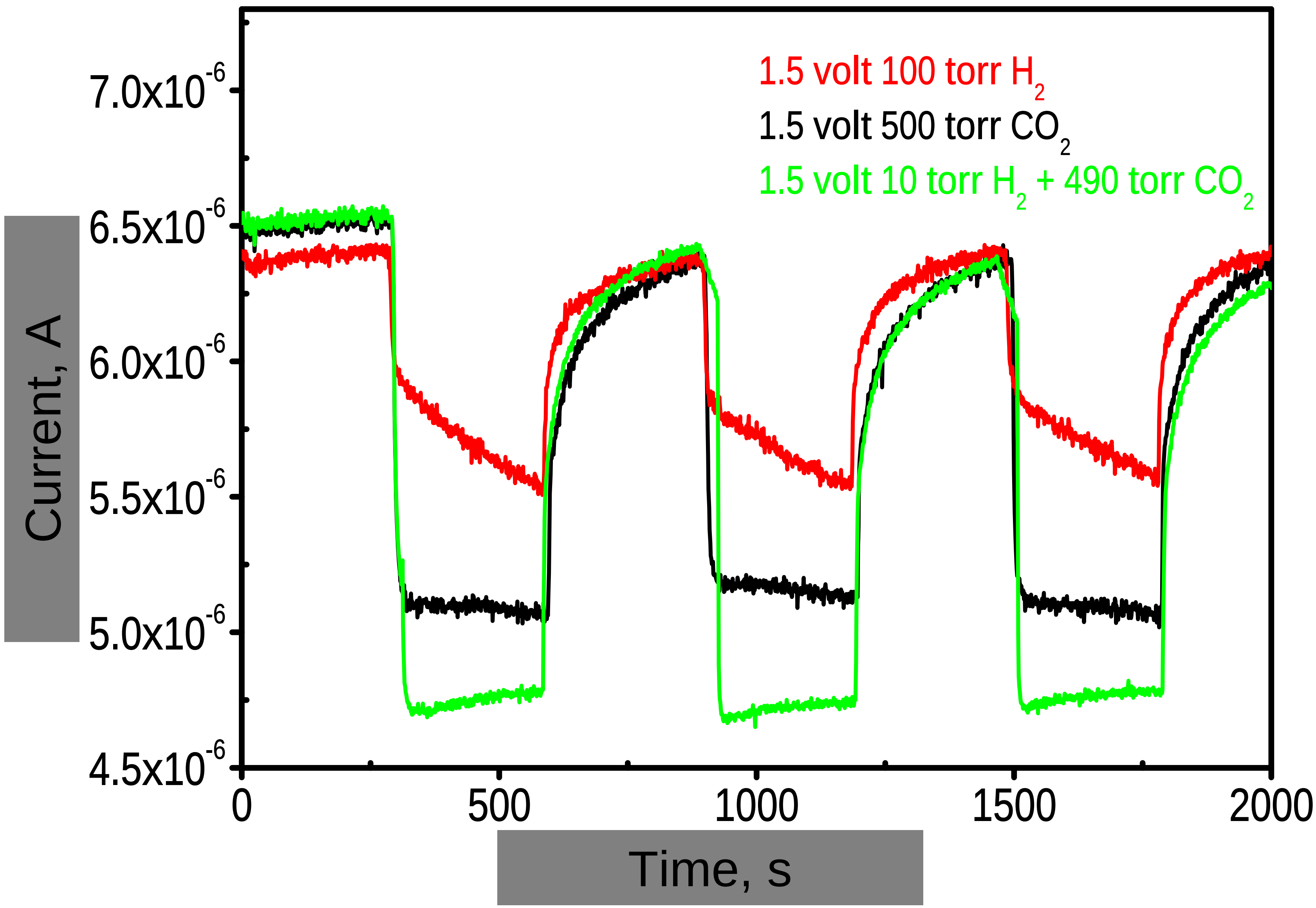
a. Au@SGAN-SGD (Blank)
b. Blank + nM BSA
c. Blank + μM BSA
d. Blank + mM BSA
A
*=λmax
Intensity
Wavelength (nm)
1.0x10^7
9.5x10^6
9.0x10^6
8.5x10^6
8.0x10^6
570
580
590
600
610
d
a
b
c
B
S
= BSA
= Naphthalene ring



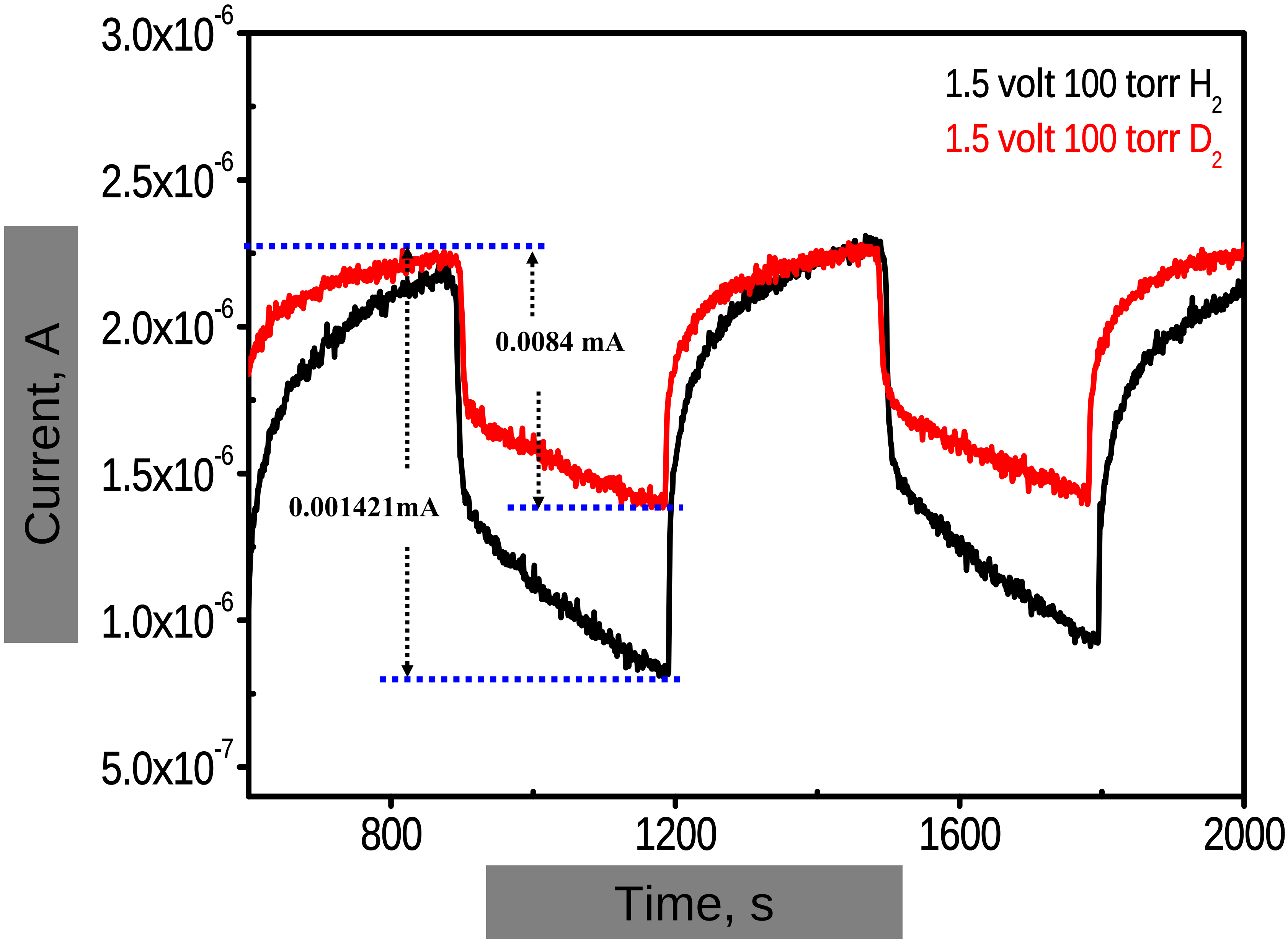
A
10 µm
B
5254 CCD cts
0 CCD cts
C
D
40
30
20
10
0
Intensity
400
800
1200
1600
Raman shift (cm-1)



Manometer
Gas cylinder
6.0x10^-6
5.5x10^-6
5.0x10^-6
4.5x10^-6
4.0x10^-6
3.5x10^-6
Current (mA)
0
500
1000
1500
2000
Time (sec)
voltmeter
Keithley



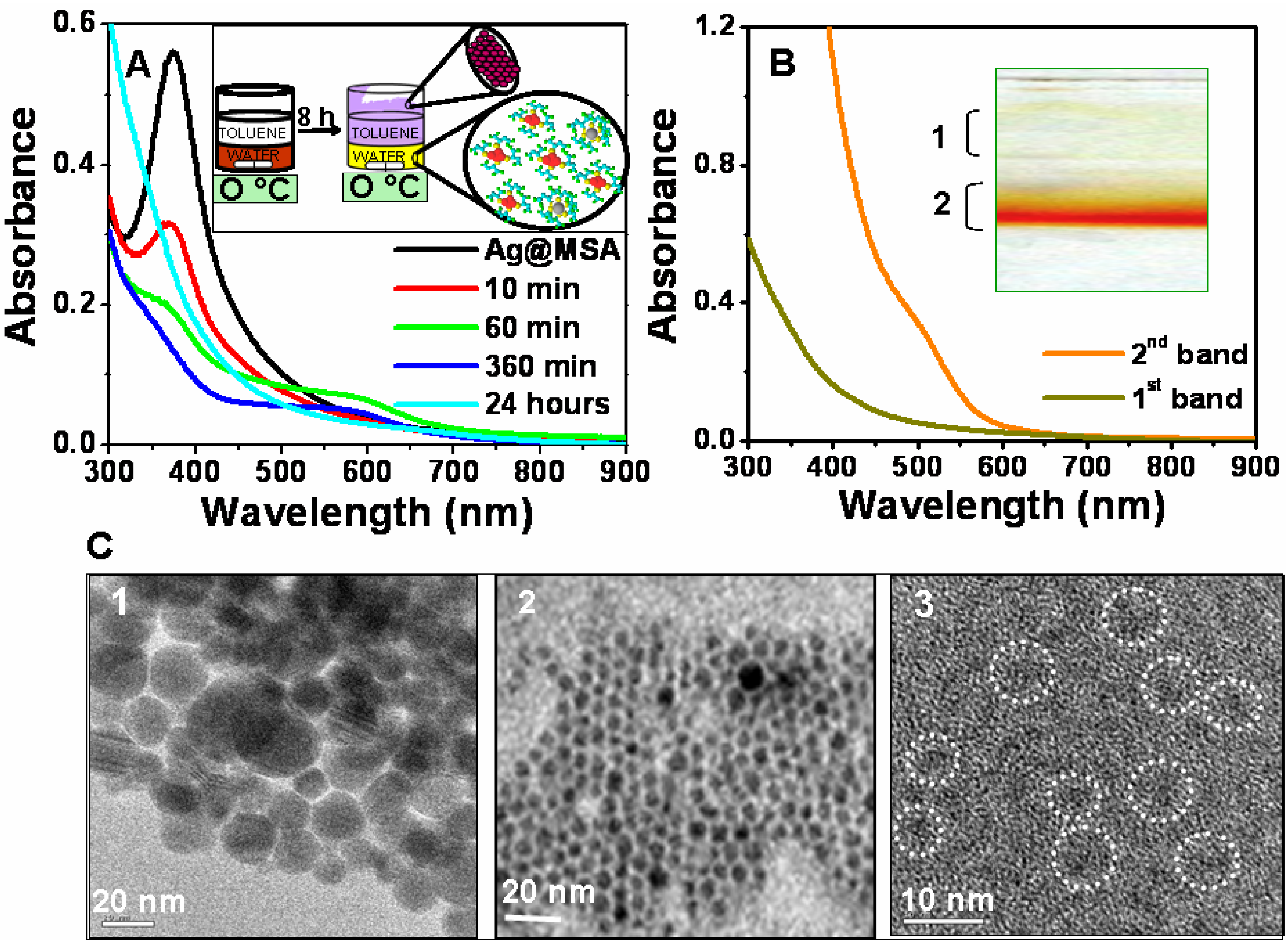
1.5 volt 100 torr H2
1.5 volt 500 torr CO2
1.5 volt 10 torr H2 + 490 torr CO2
7.0x10-6
6.5x10-6
6.0x10-6
5.5x10-6
5.0x10-6
4.5x10-6
Current, A
0
500
1000
1500
2000
Time, s



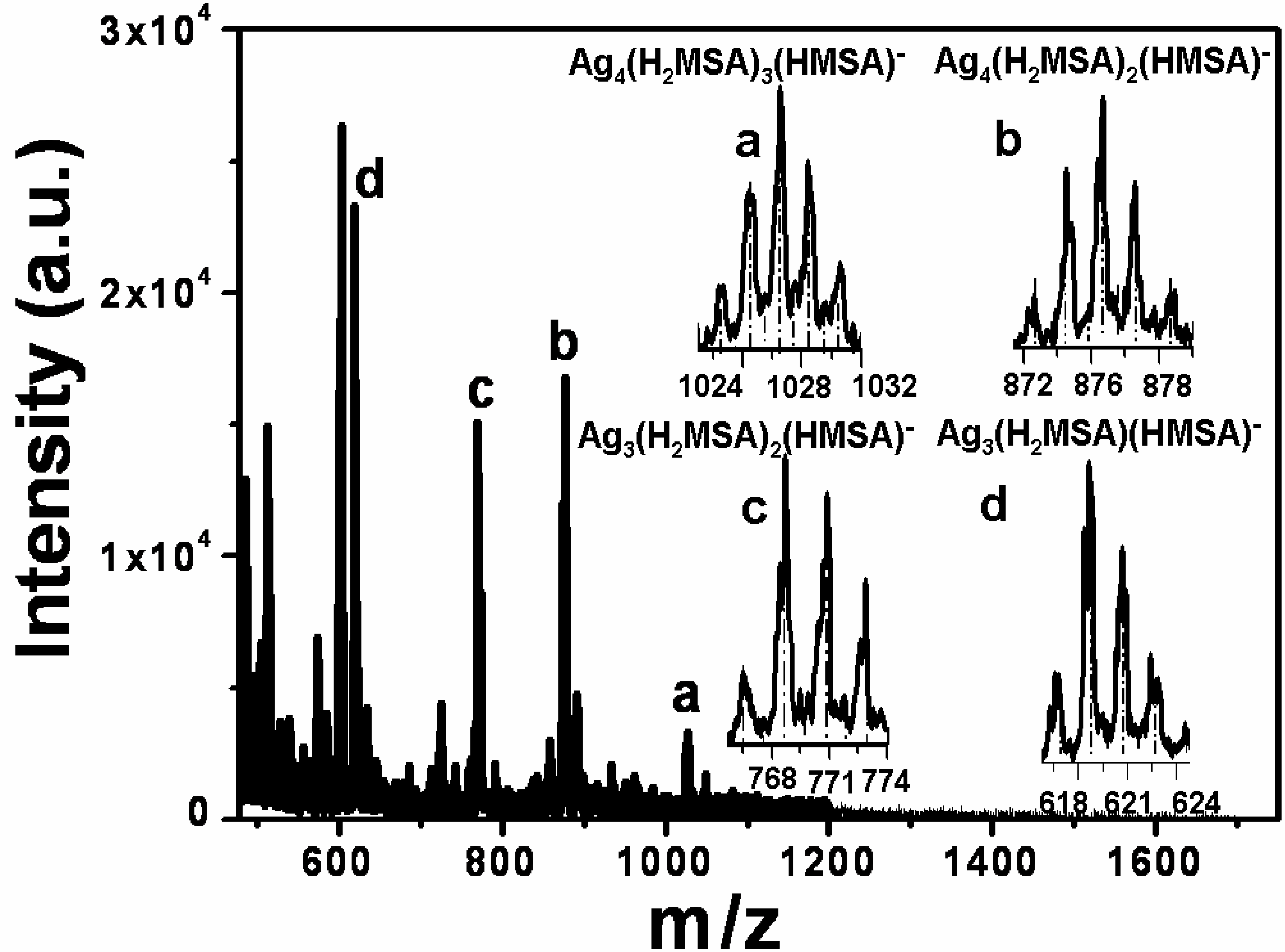
3.0x10-6
2.5x10-6
2.0x10-6
1.5x10-6
1.0x10-6
5.0x10-7
Current, A
800
1200
1600
2000
Time, s
1.5 volt 100 torr H2
1.5 volt 100 torr D2
0.0084 mA
0.001421mA

4

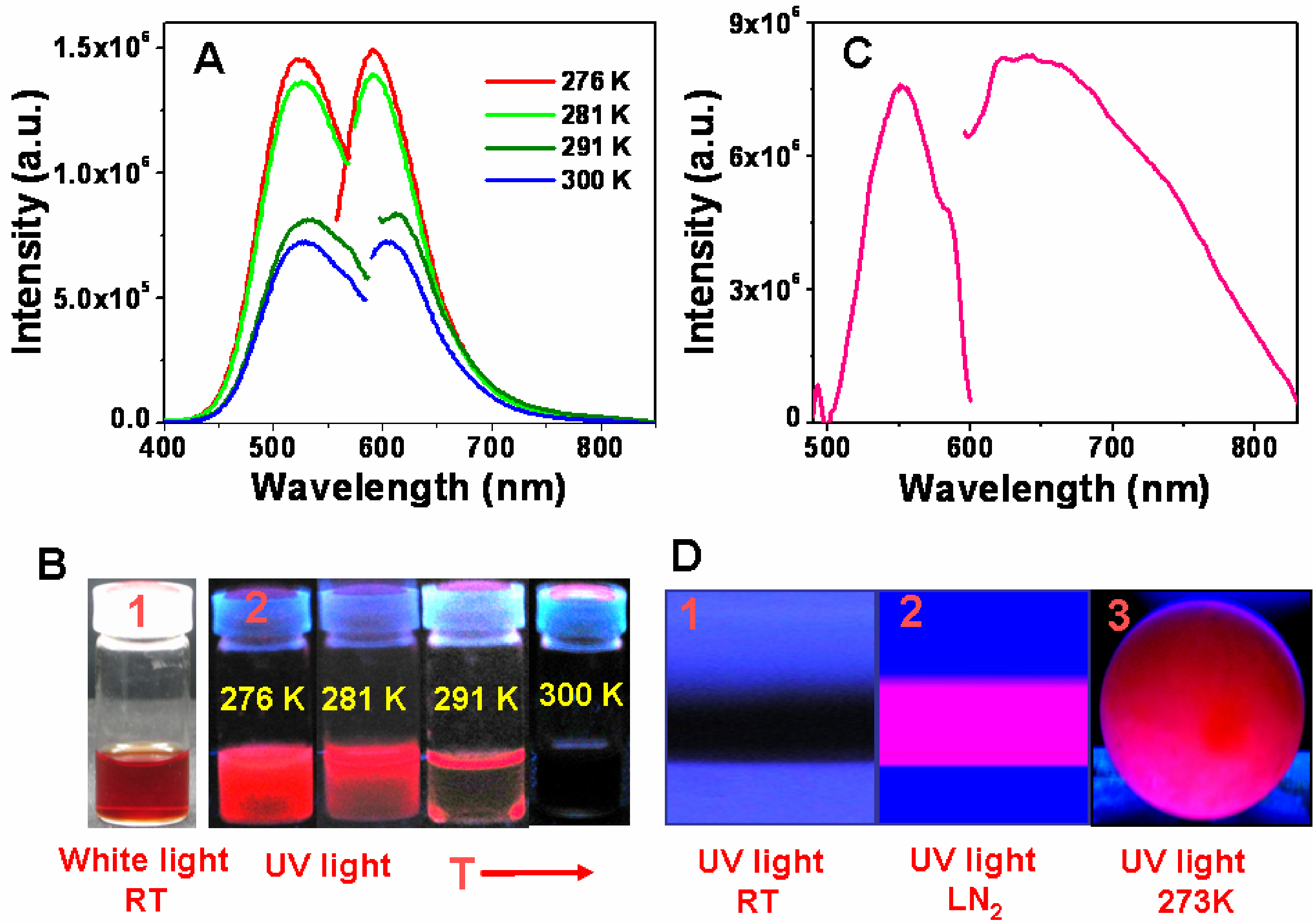
Clusters



A
TOLUENE
WATER
8 h
O °C
Ag@MSA
10 min
60 min
360 min
24 hours
Absorbance
Wavelength (nm)
B
1
2
2nd band
1st band
C
1
2
3
20 nm
20 nm
10 nm



Intensity (a.u.)
m/z
Ag4(H2MSA)3(HMSA)-
Ag4(H2MSA)2(HMSA)-
Ag3(H2MSA)2(HMSA)-
Ag3(H2MSA)(HMSA)-
a
b
c
d
1024 1028 1032
872 876 878
768 771 774
618 621 624
0
1x10^4
2x10^4
3x10^4
600 800 1000 1200 1400 1600



Udaya Bhaskara Rao and Pradeep, Submitted

Summary

New sensors using mesoflowers, nanoparticle-carbon nanotube composites, metal nanoparticle superlattices and molecular clusters have been developed.

They offer new possibilities for collaborative exploration.

IIT Madras

Thank you all