New phenomena and novel nanomaterials for gas sensing and infrared absorption

T. Pradeep

Department of Chemistry and Sophisticated Analytical Instrument Facility
Indian Institute of Technology Madras
Chennai 600 036

http://www.chem.iitm.ac.in/professordetails/profpradeep/index.php

Indo-US JNCASR, August 19-21, 2008

New materials, Novel phenomena, Molecular solids

Novel materials for IR absorption
Novel phenomena for gas sensing

Confocal Raman Microscope

MALDI TOF MS

QTrap MS

Transmission Electron Microscope

Ultramicrotome

Nanoscience and Nanotechnology Initiative of the DST

Acknowledgements

DST – Nanomission

Dr. C. Subramaniam

Dr. Jaydeb Chakrabarti

Prof. Chandrabhas Narayana

Prof. Takuji Ogawa

Mr. E. S. Shibu

Mr. P. R. Sajanlal

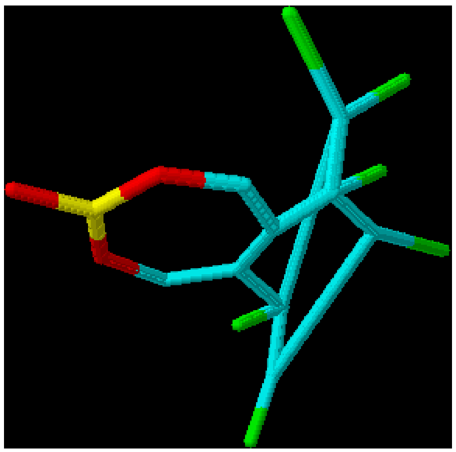
1

Novel chemical reactions at the nanoscale

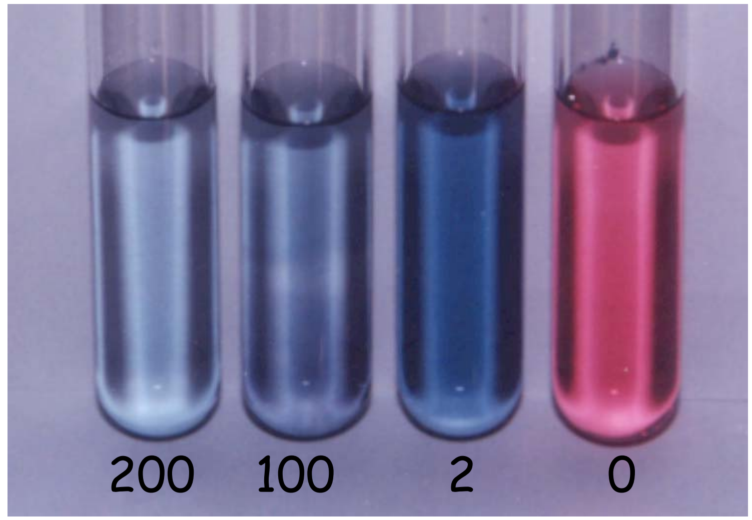
New chemistry

Color of gold nanoparticles with endosulfan

Example



Endosulfan



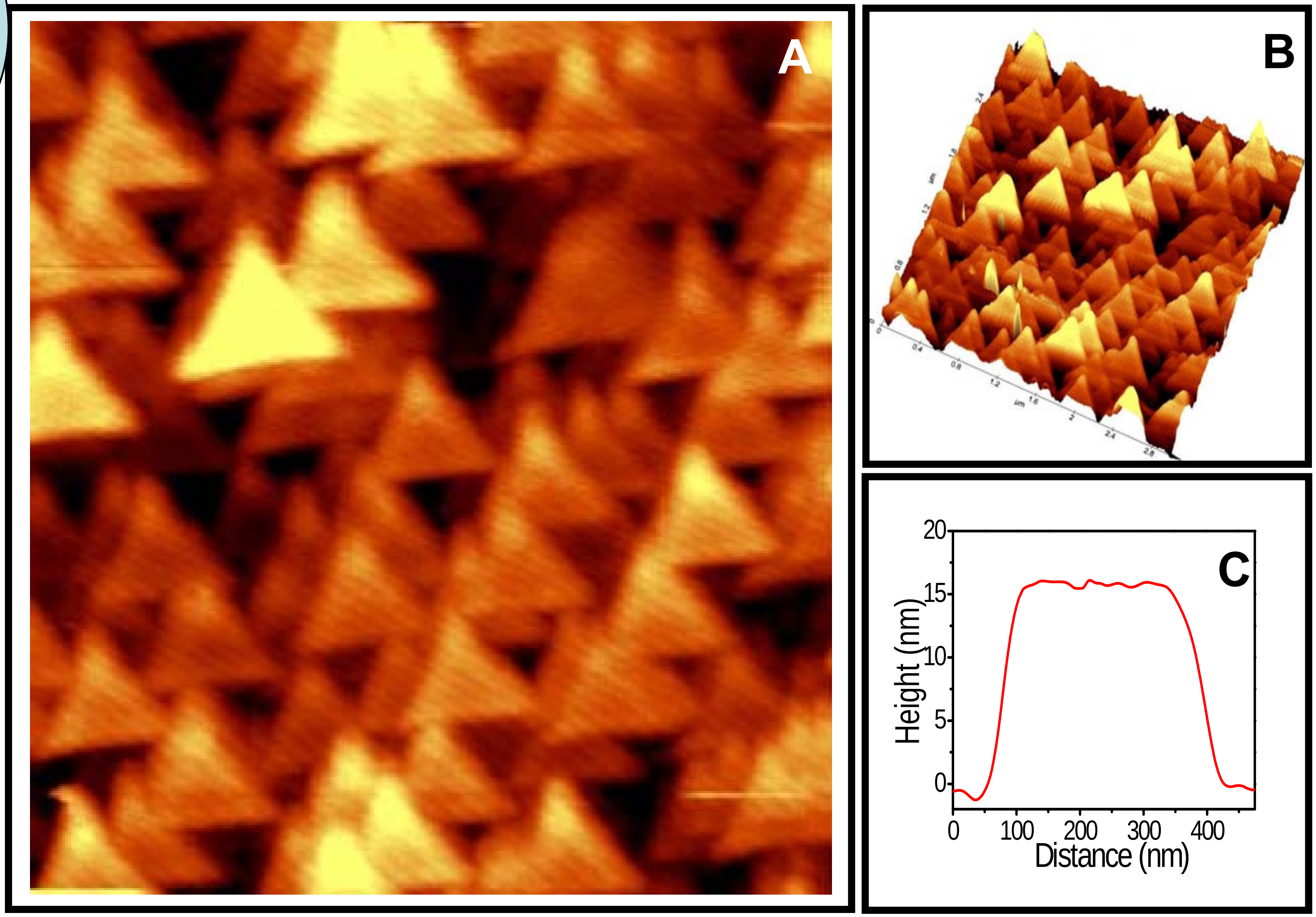
Endosulfan concentration in ppm

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

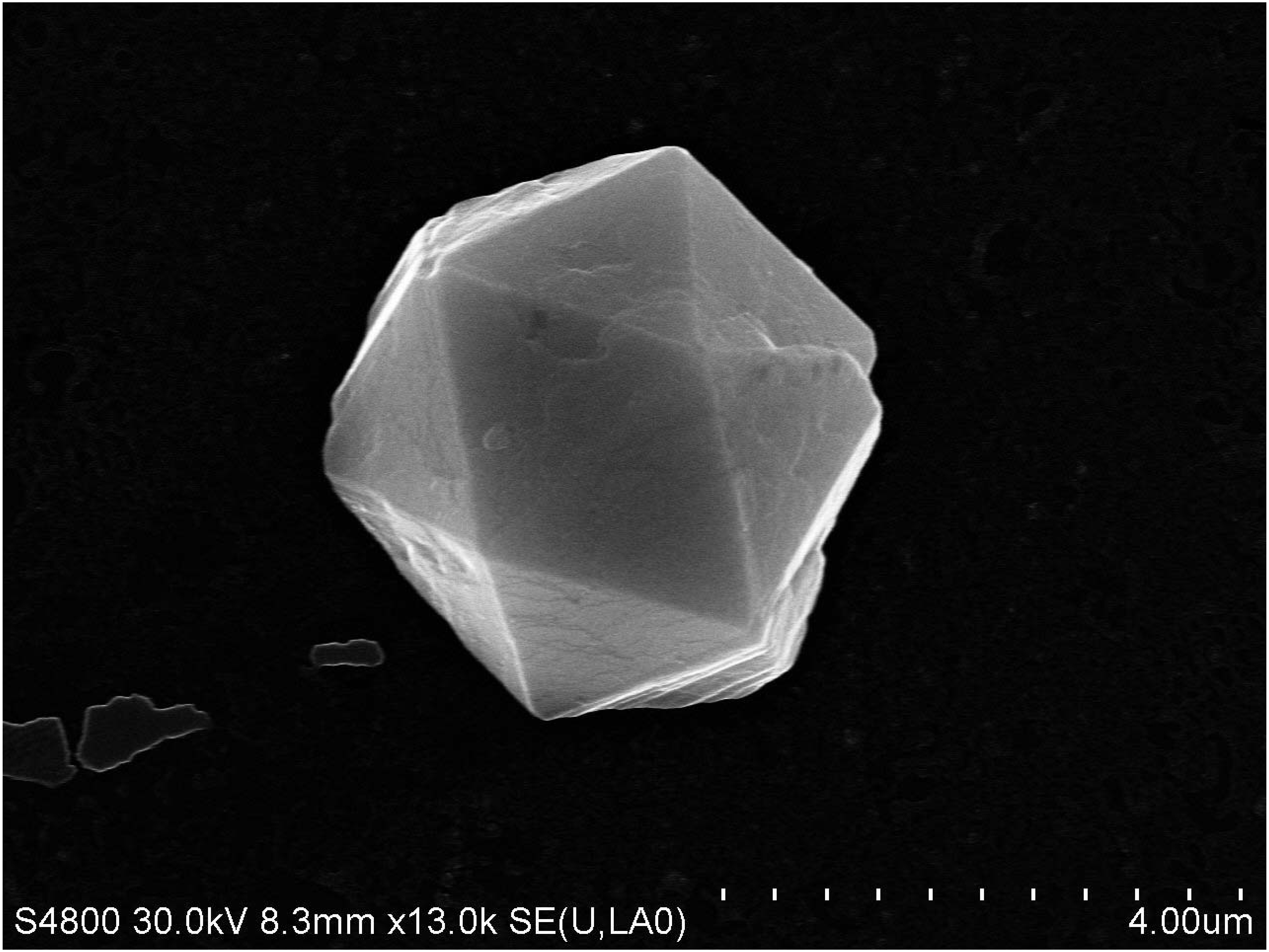
Color changes with pesticide concentration
Good response at lower concentrations
Down to 0.1 ppm
Adsorbed pesticides can be removed from solution

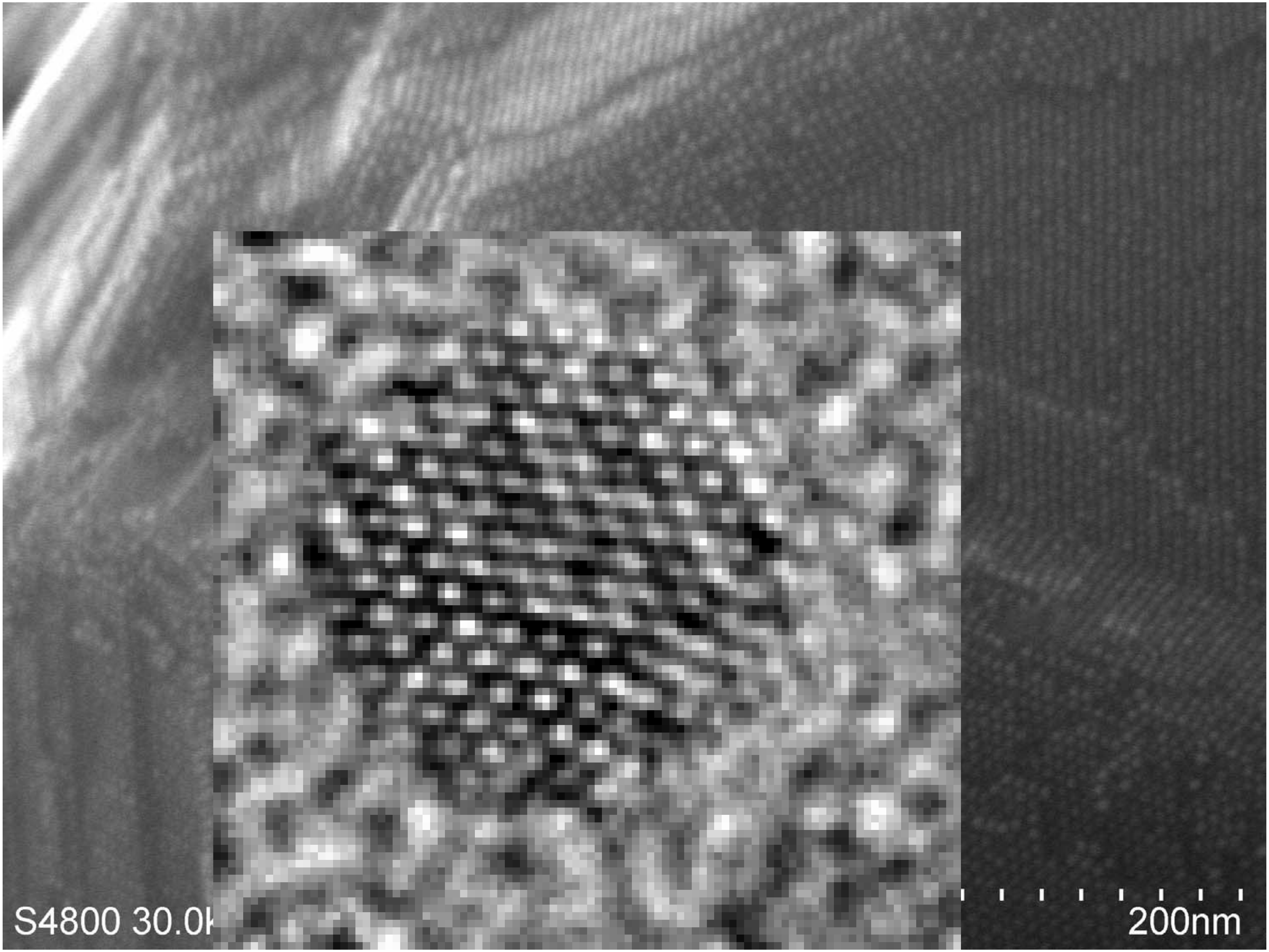
J. Environ. Monitoring. 2003

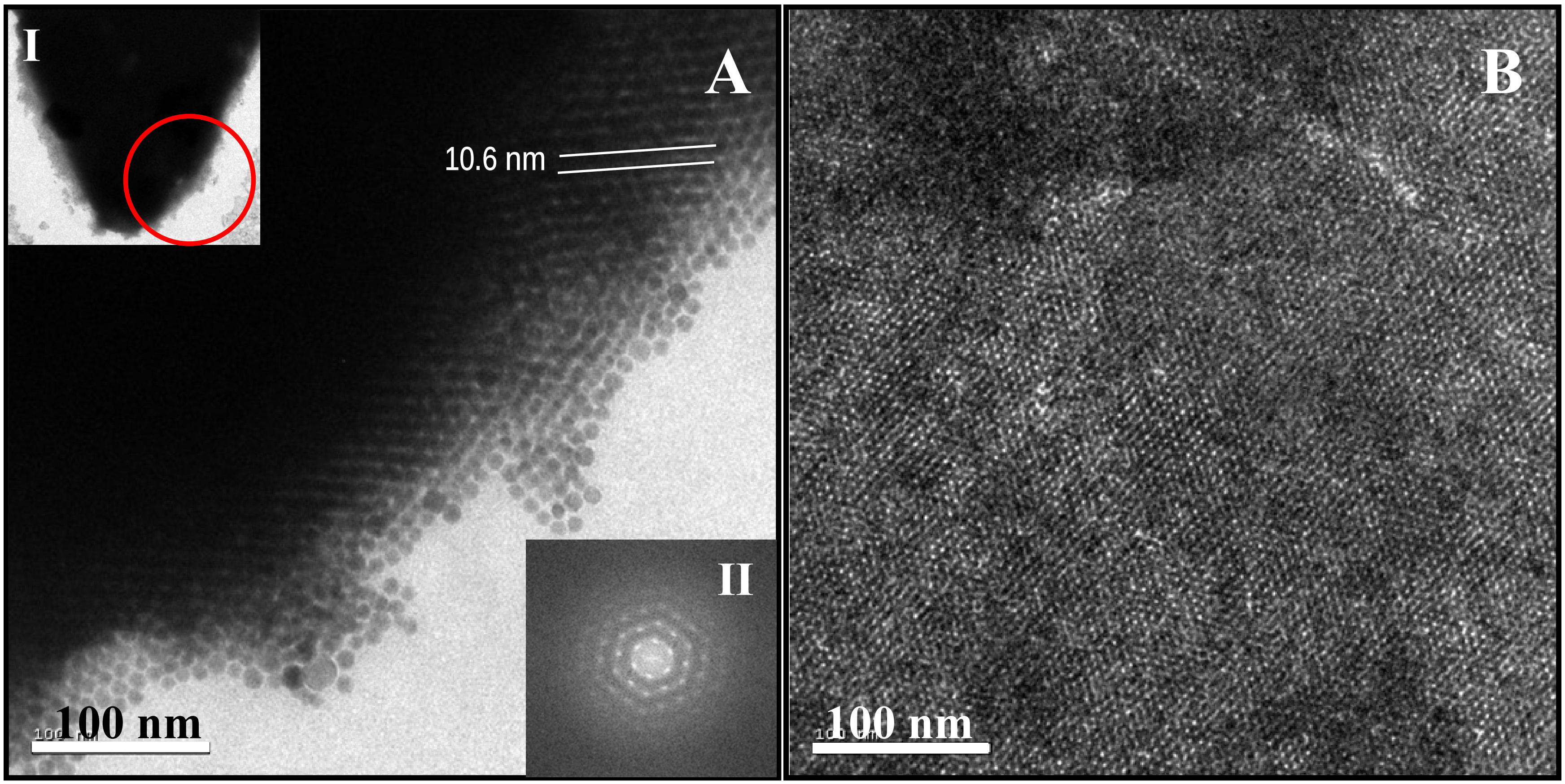
2



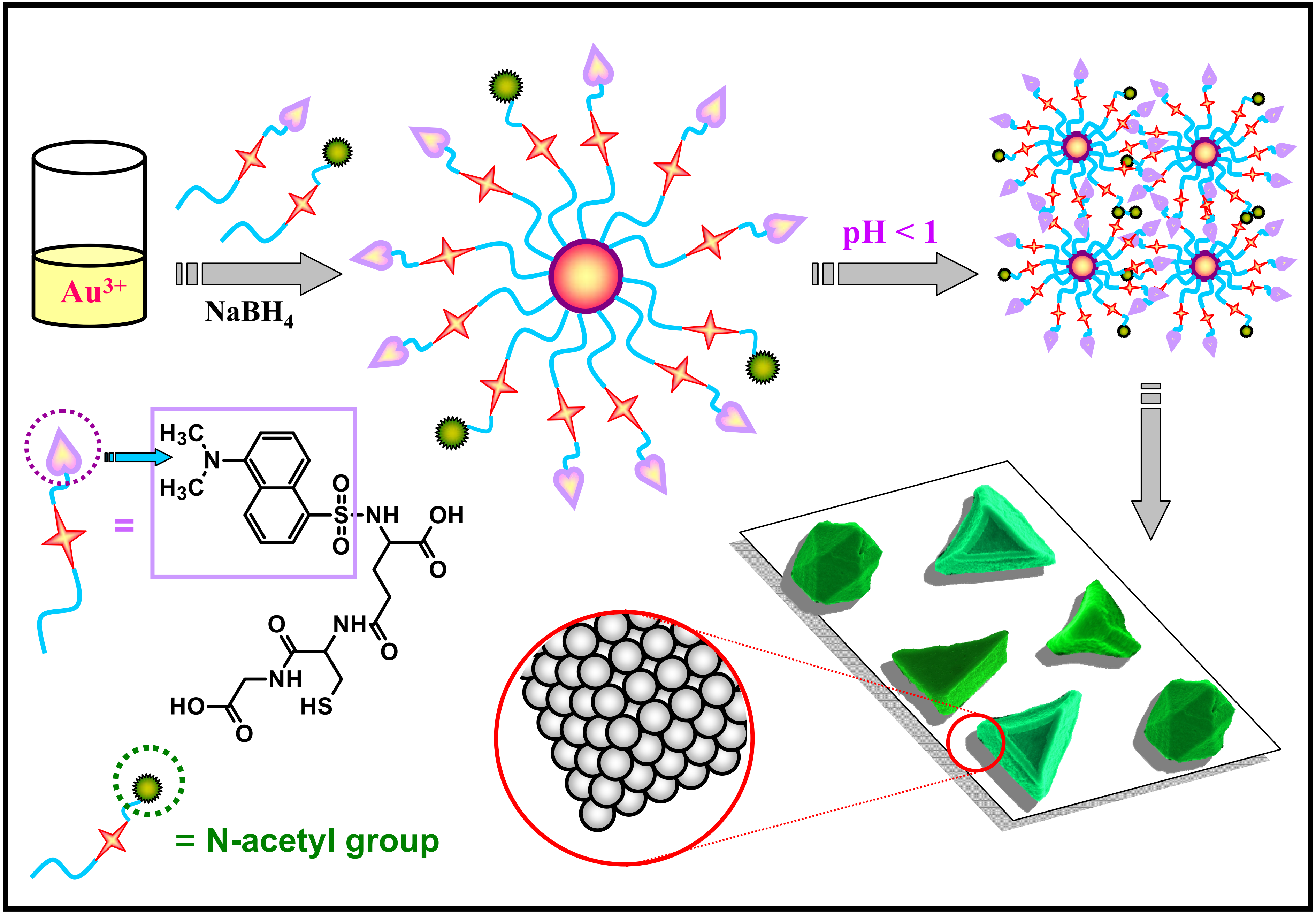
Sajanlal and Pradeep, Adv. Mater., 20 (2008) 980


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

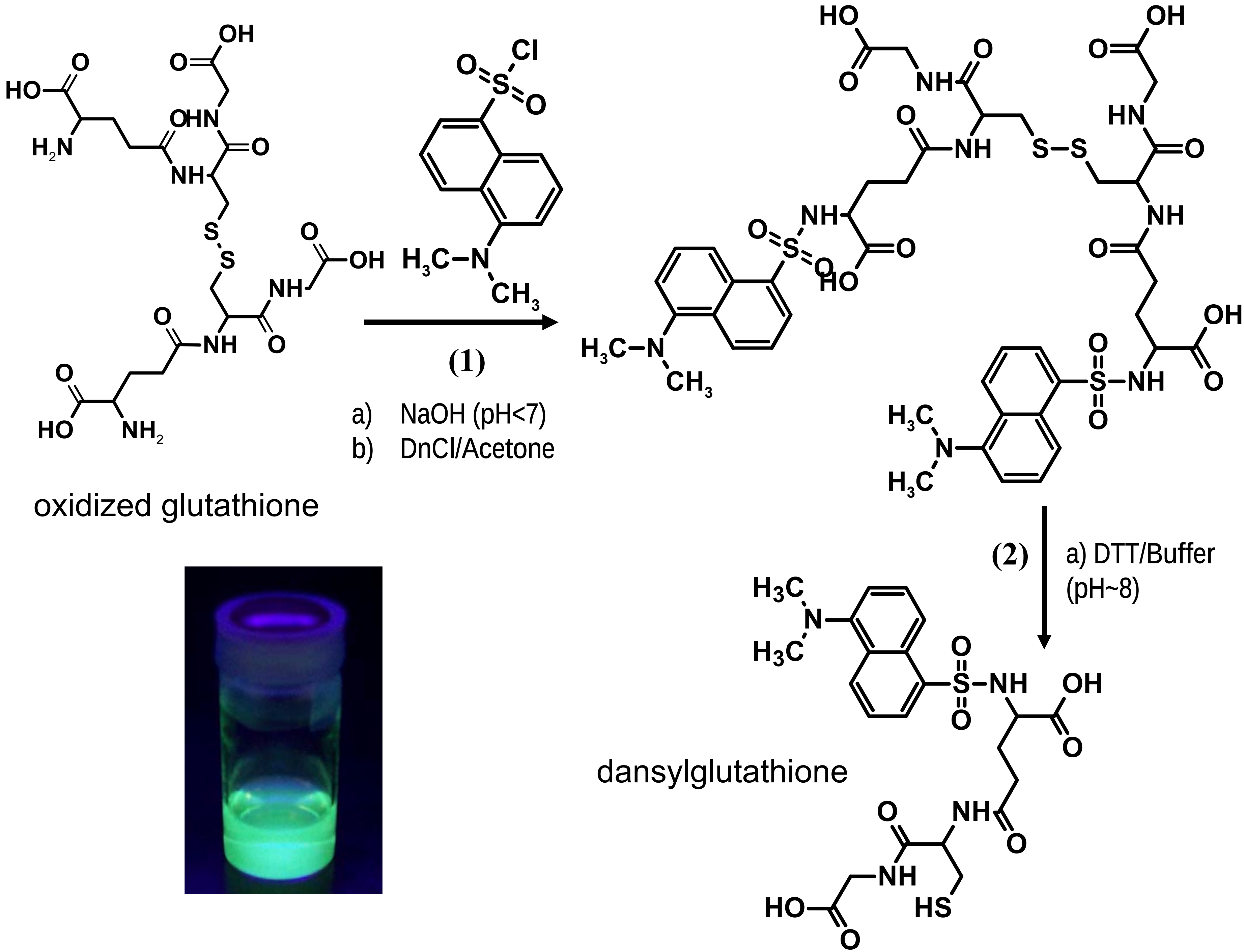

S4800 30.0k
200nm



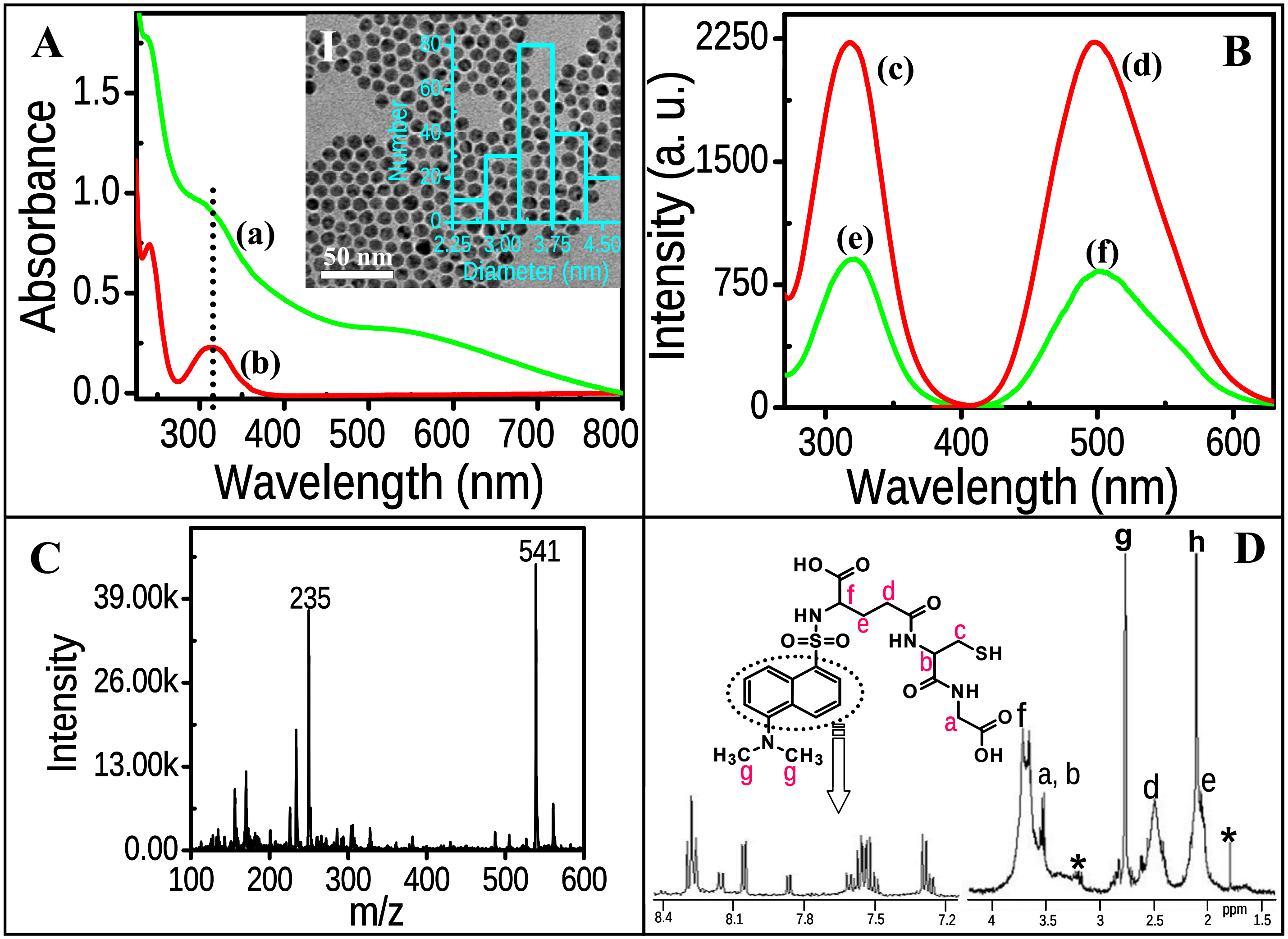
Shibu et al. Adv. Mat. 2008b

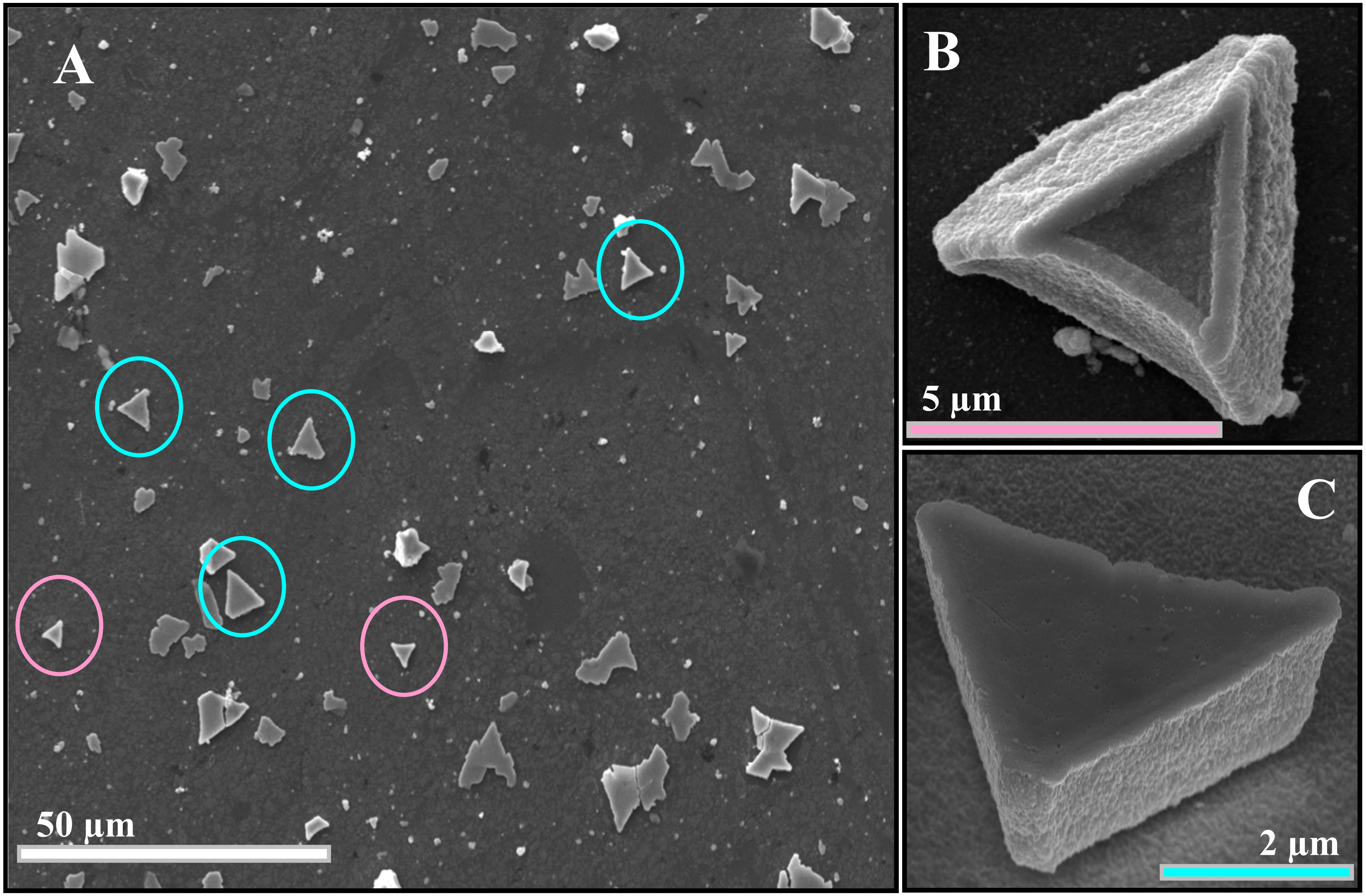


Au3+
NaBH4
pH < 1
H3C
N
H3C
O
S
O
NH
OH
O
NH
O
O
NH
HO
O
HS
=
= N-acetyl group



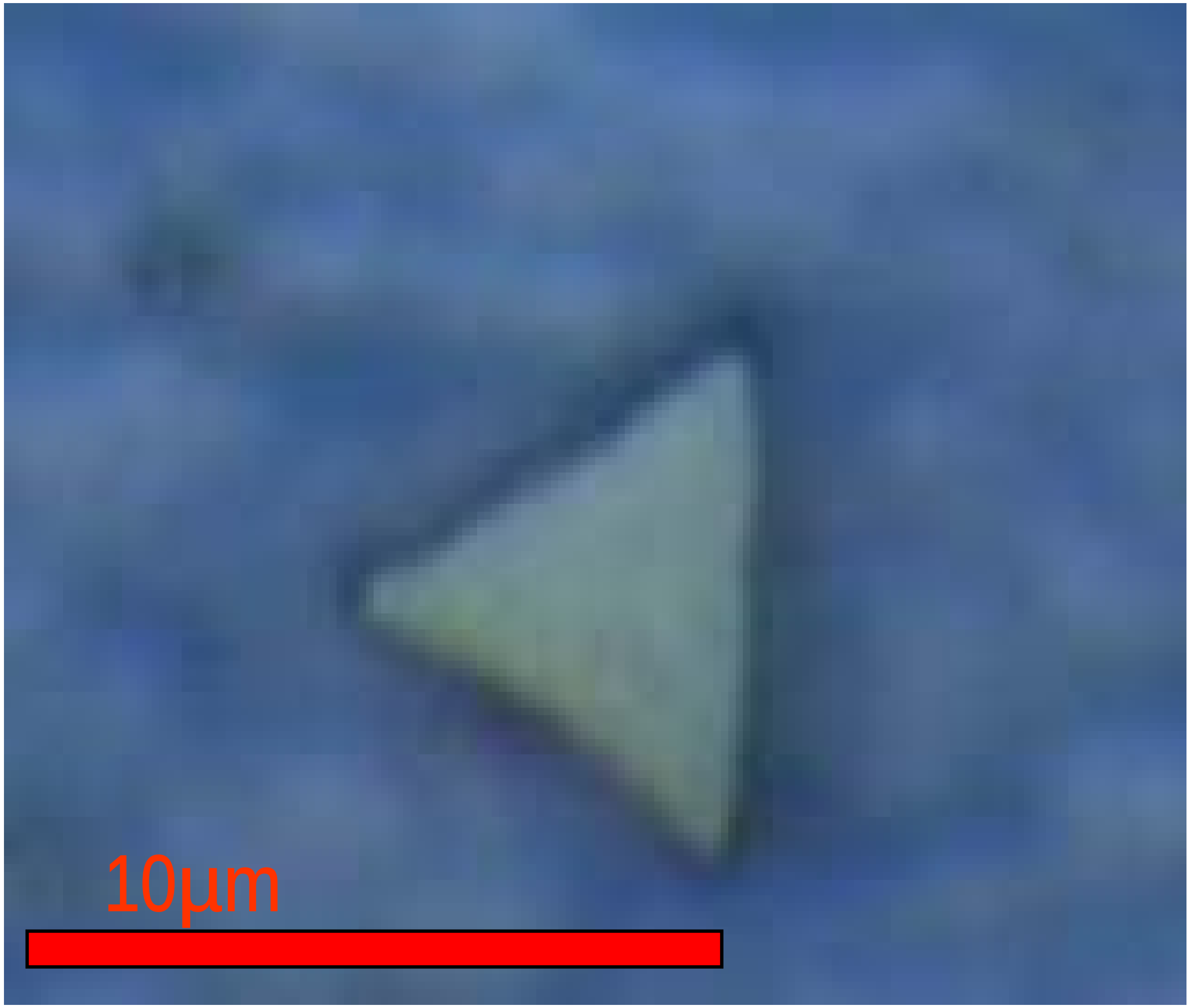
(1)
a) NaOH (pH<7)
b) DnCl/Acetone
oxidized glutathione
(2)
a) DTT/Buffer
(pH~8)
dansylglutathione

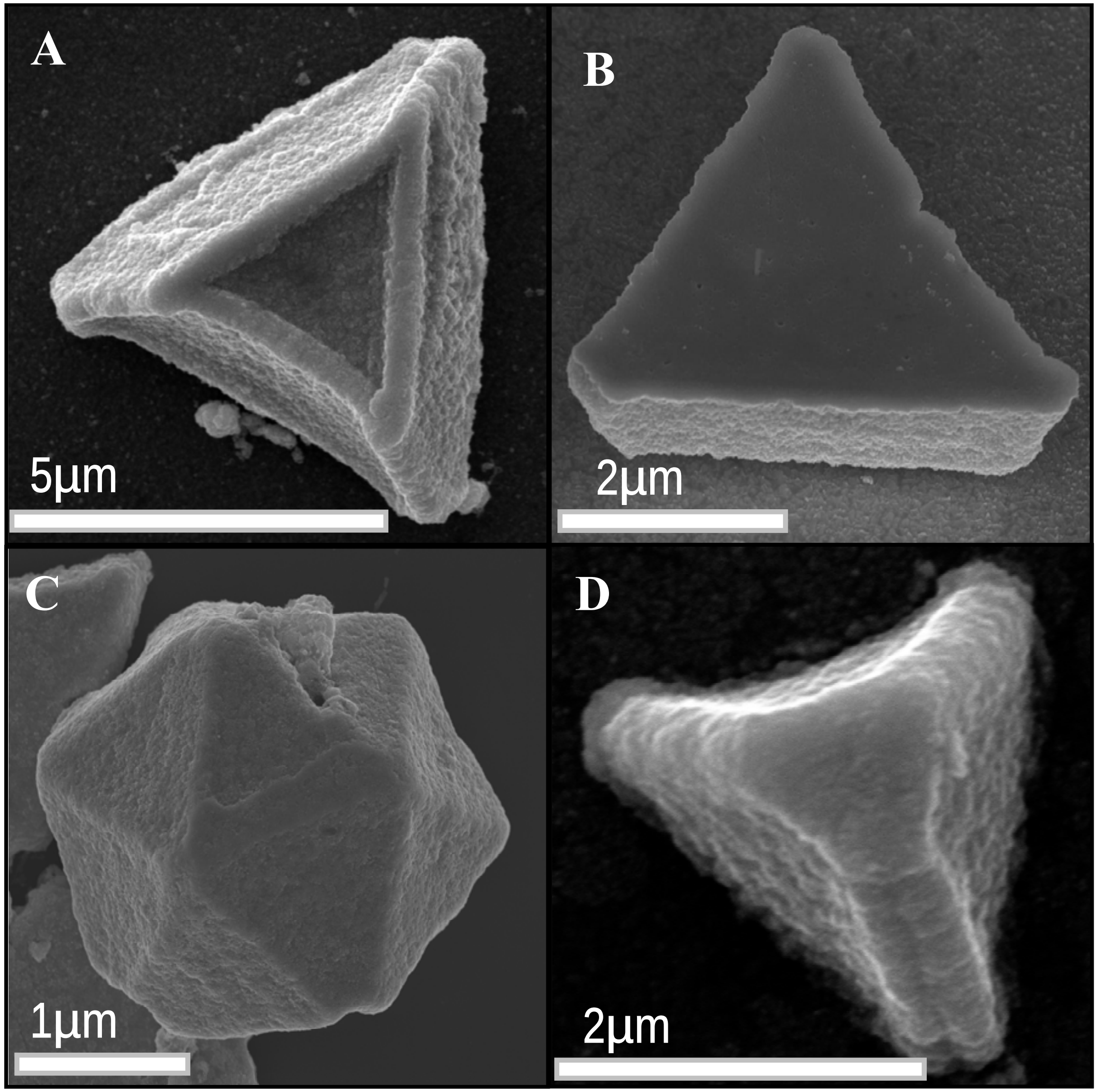

A
Absorbance
Wavelength (nm)
(a)
(b)
I
50 nm
Number
Diameter (nm)
B
Intensity (a. u.)
Wavelength (nm)
(c)
(d)
(e)
(f)
C
Intensity
m/z
235
541
D
HO
HN
O=S=O
H3C
CH3
SH
NH
OH
a, b
ppm

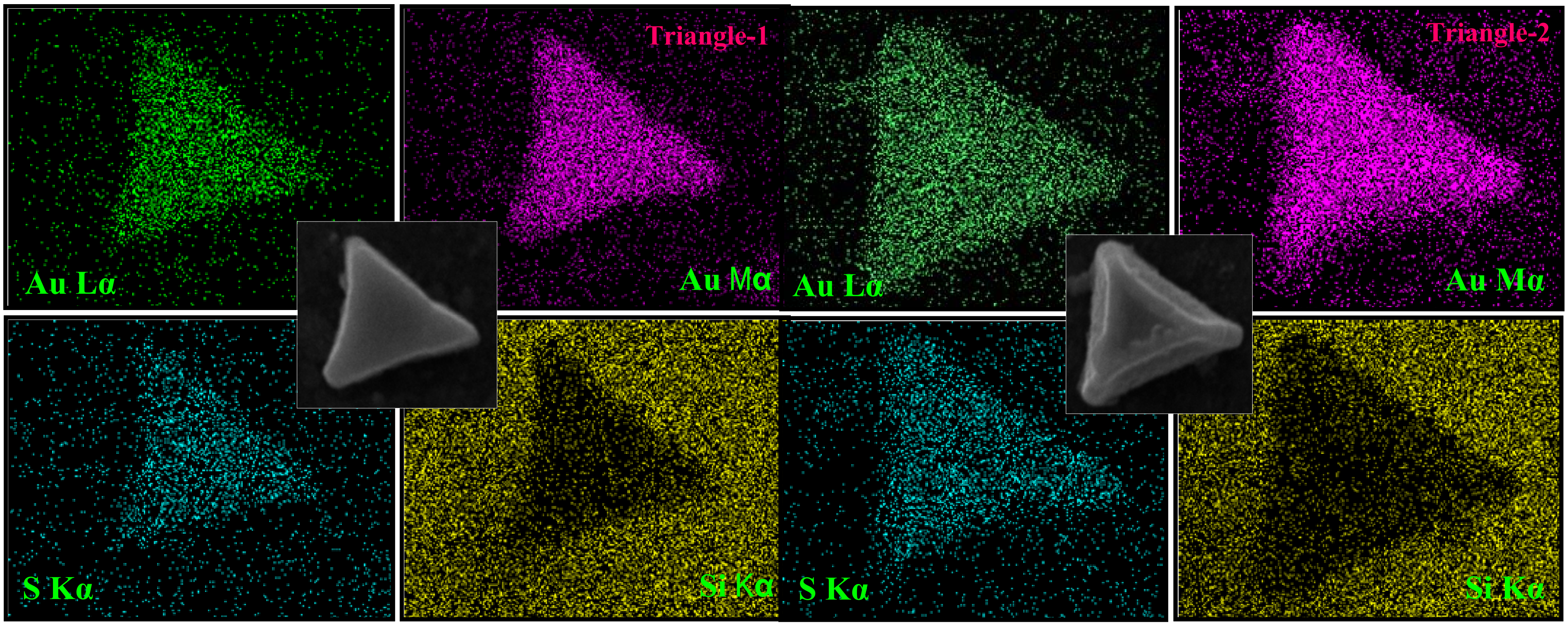


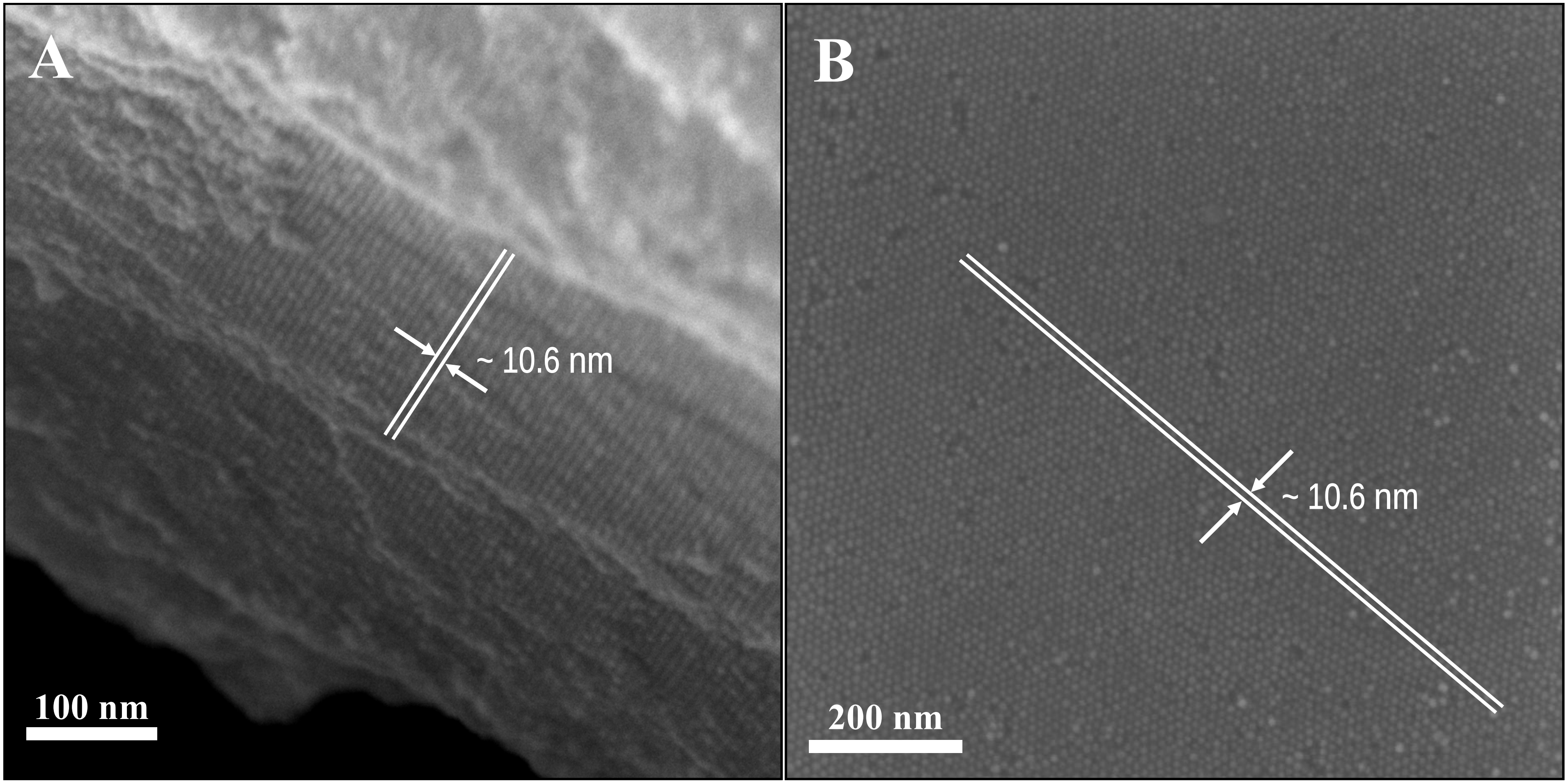
Two different morphologies

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

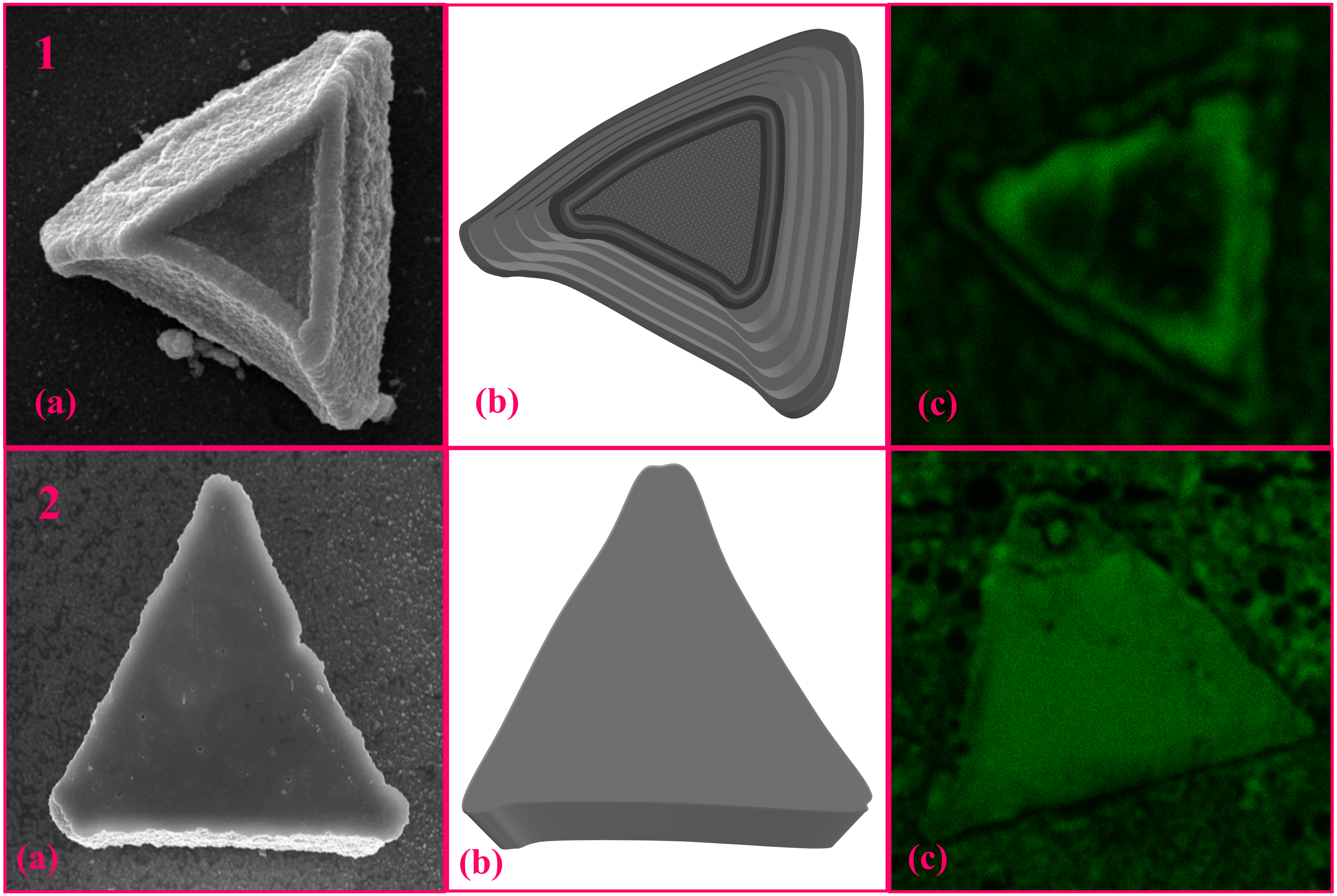

10µm

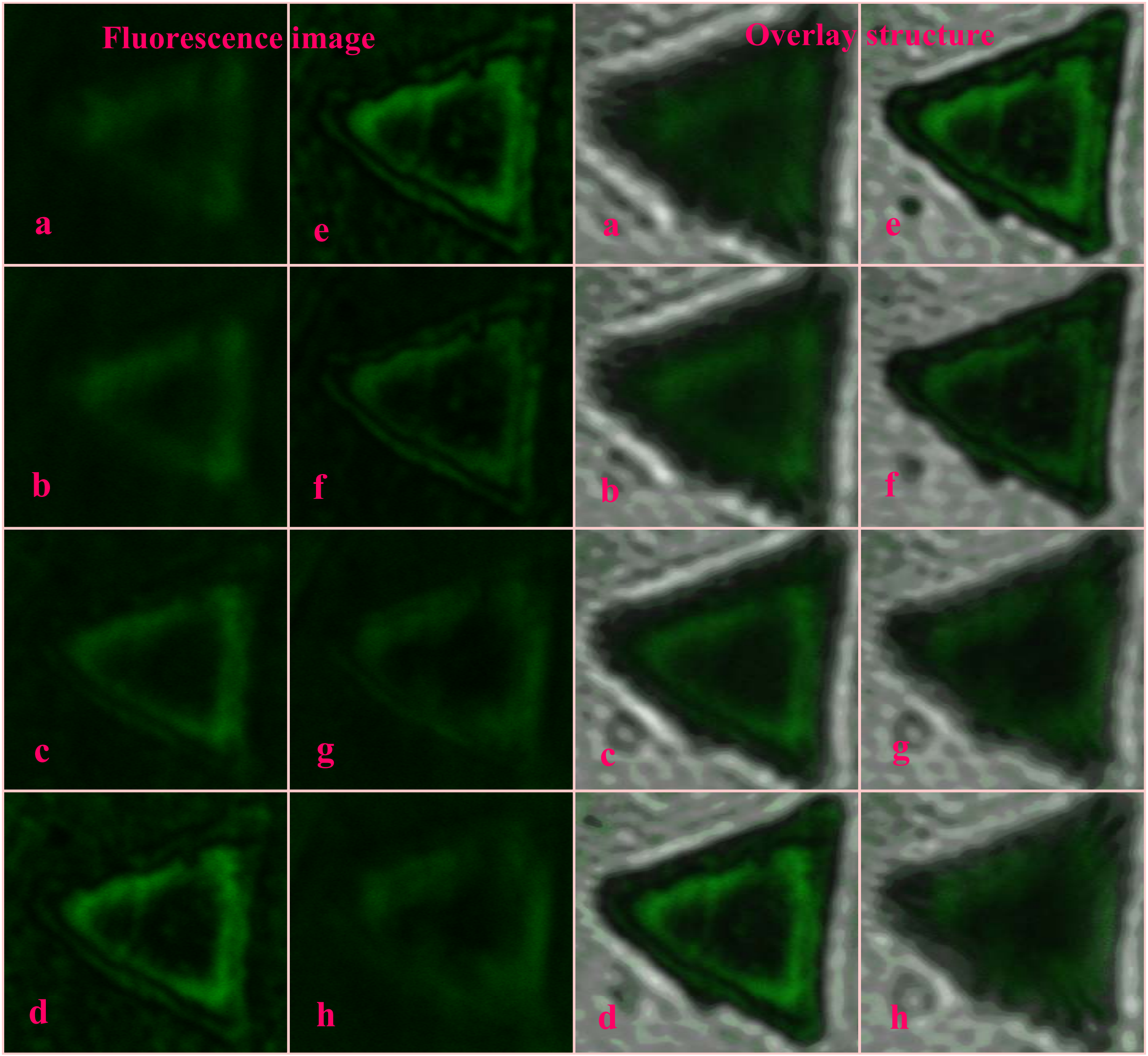

A
5μm
B
2μm
C
1μm
D
2μm


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

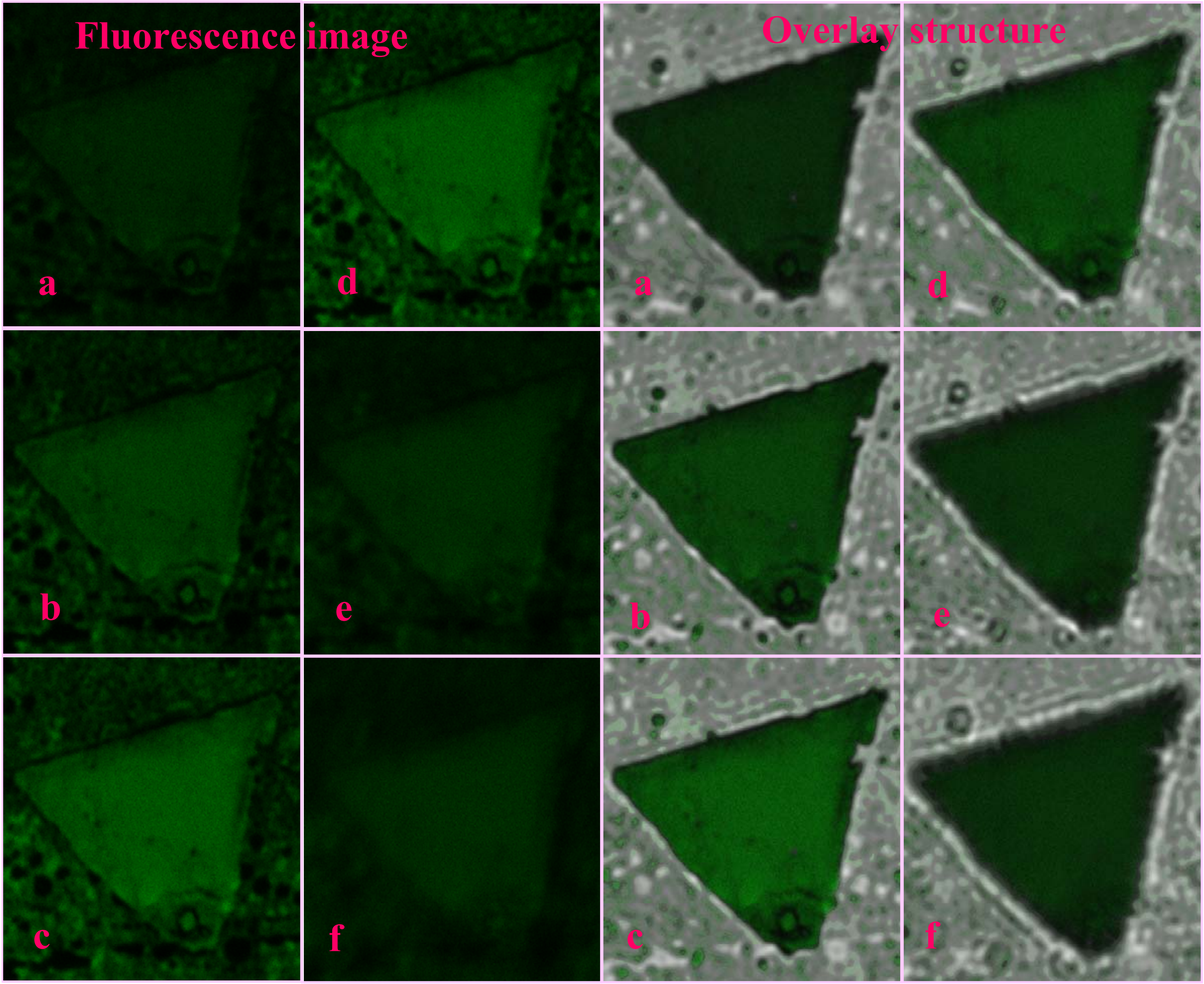


A
~ 10.6 nm
100 nm
B
~ 10.6 nm
200 nm

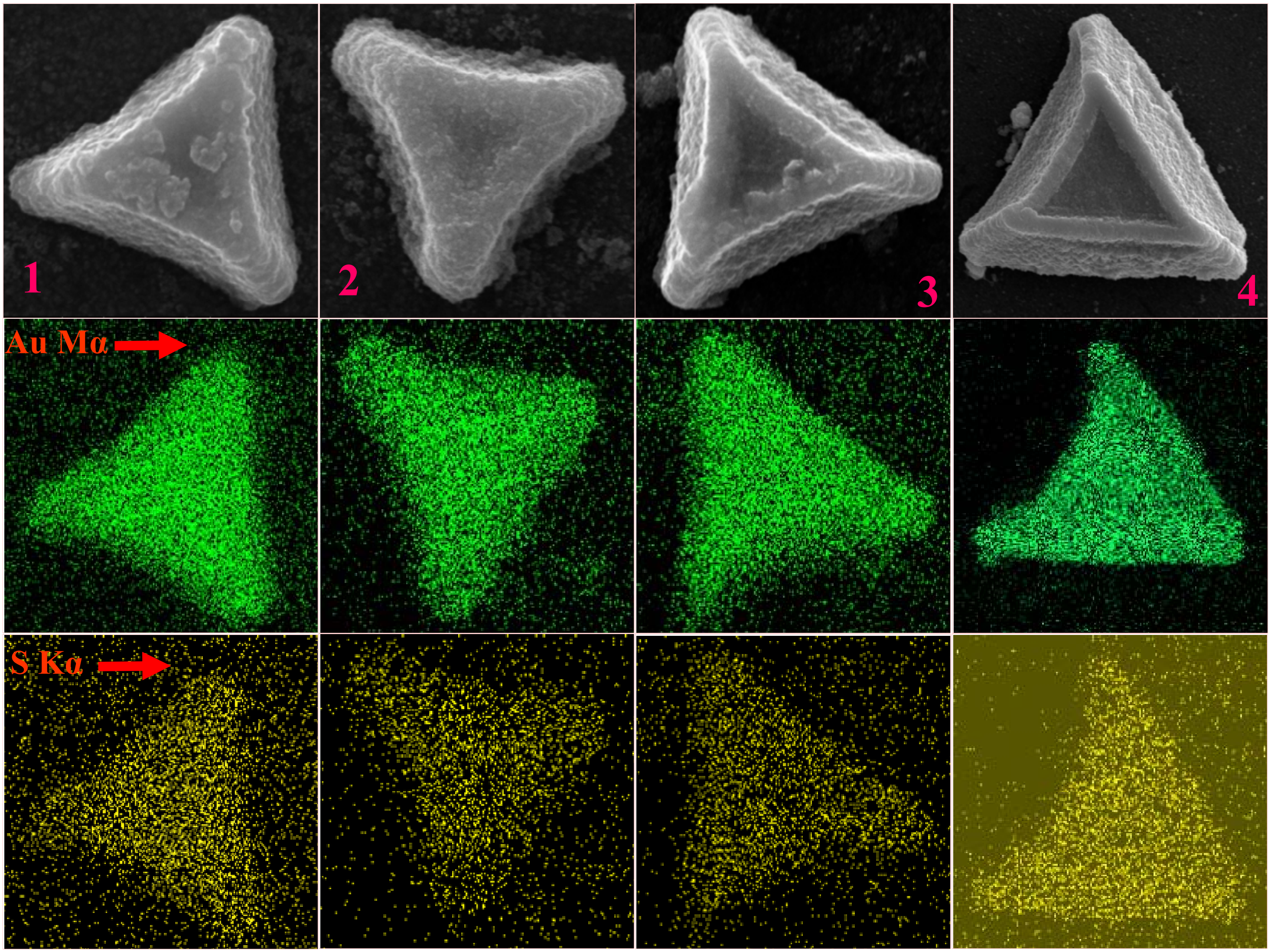

1
(a)
(b)
(c)
2
(a)
(b)
(c)

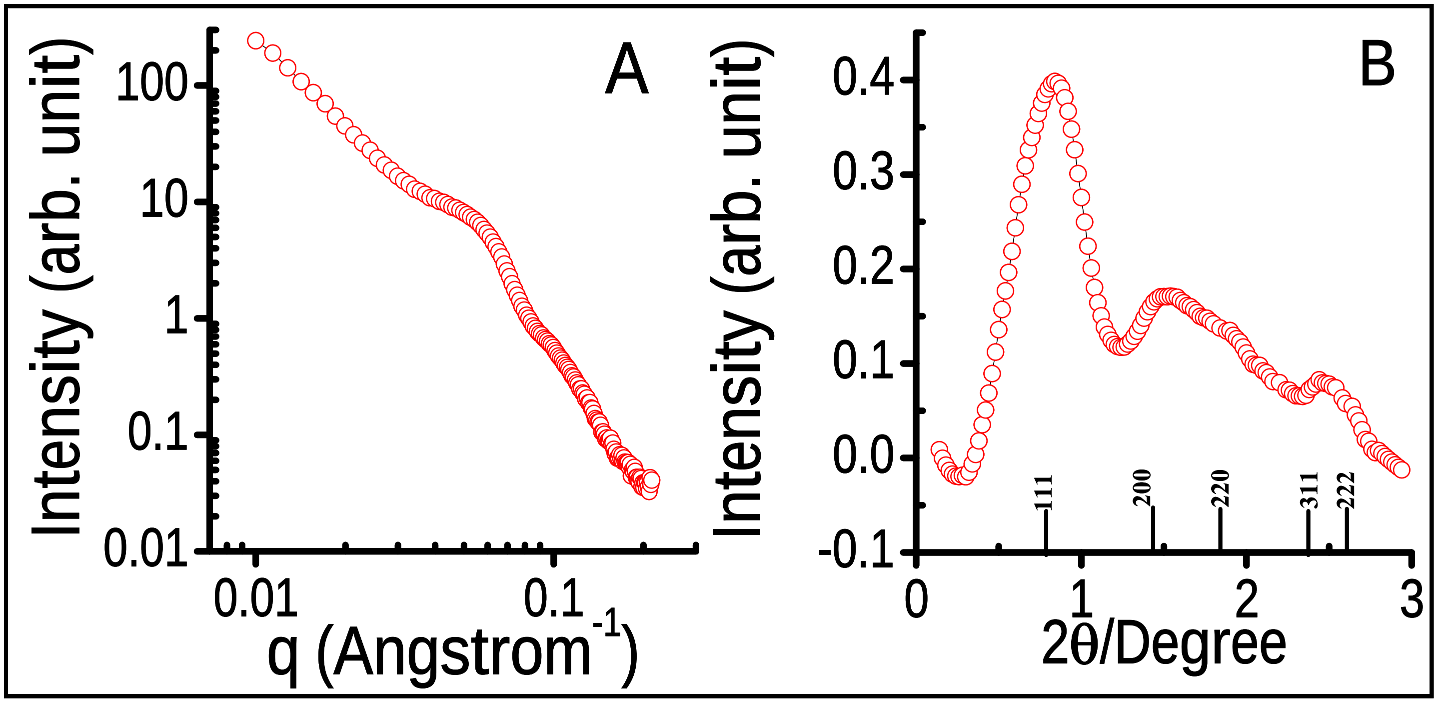


Fluorescence image
Overlay structure
a
b
c
d
e
f
g
h
a
b
c
d
e
f
g
h

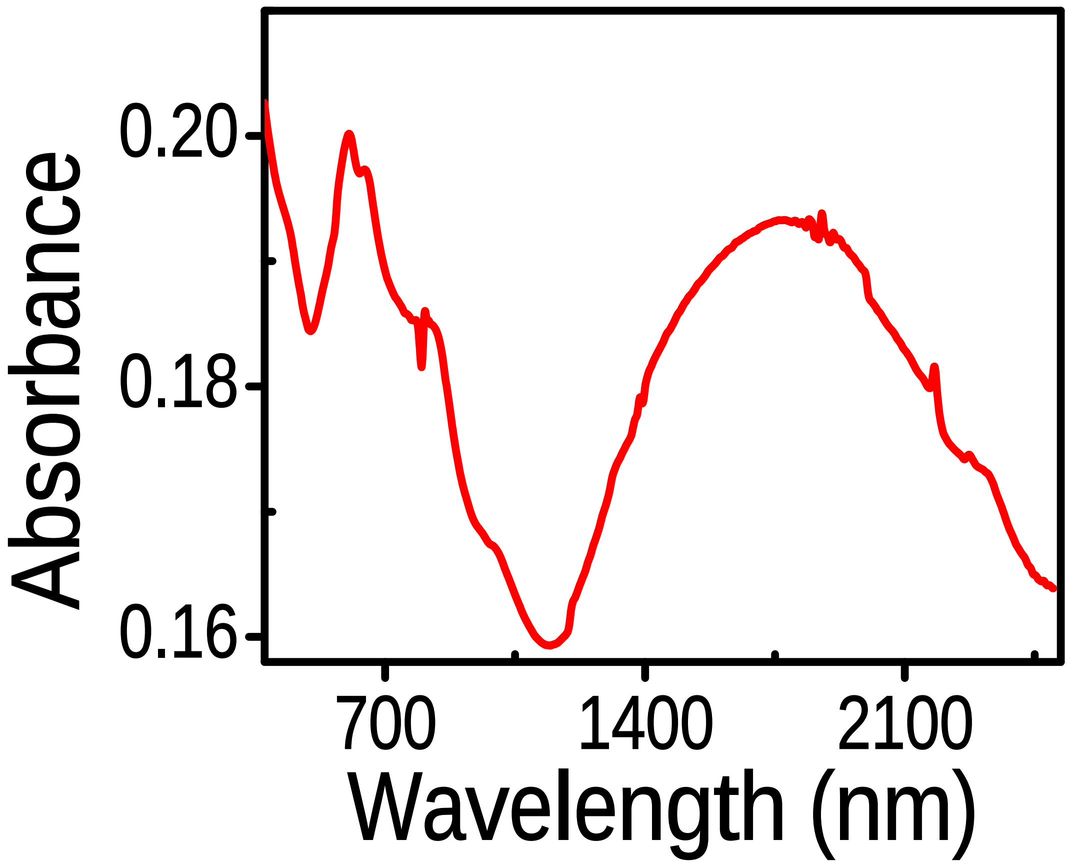


Fluorescence image
Overlay structure
a
d
a
d
b
e
b
e
c
f
c
f


1
2
3
4
Au Mα
S Kα

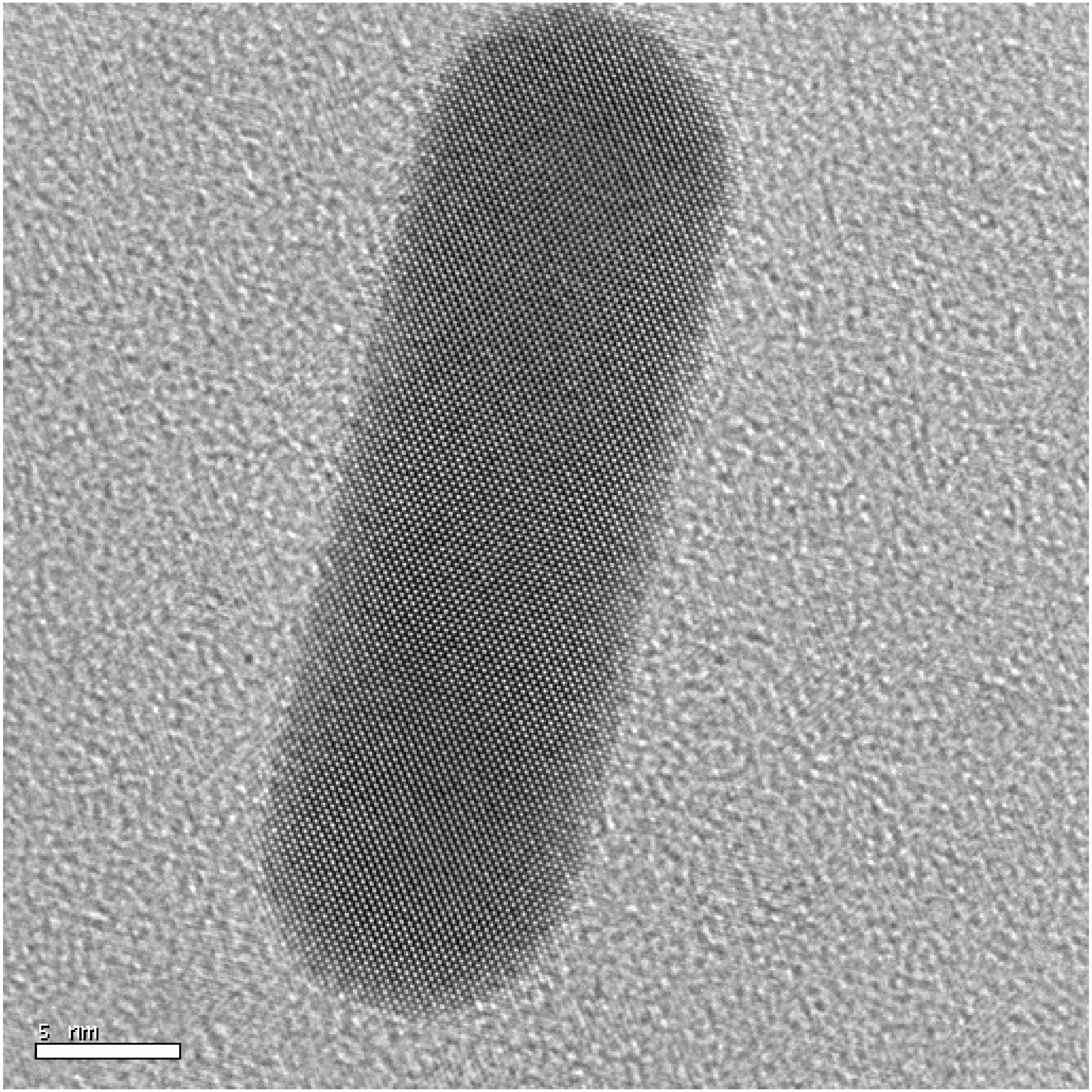


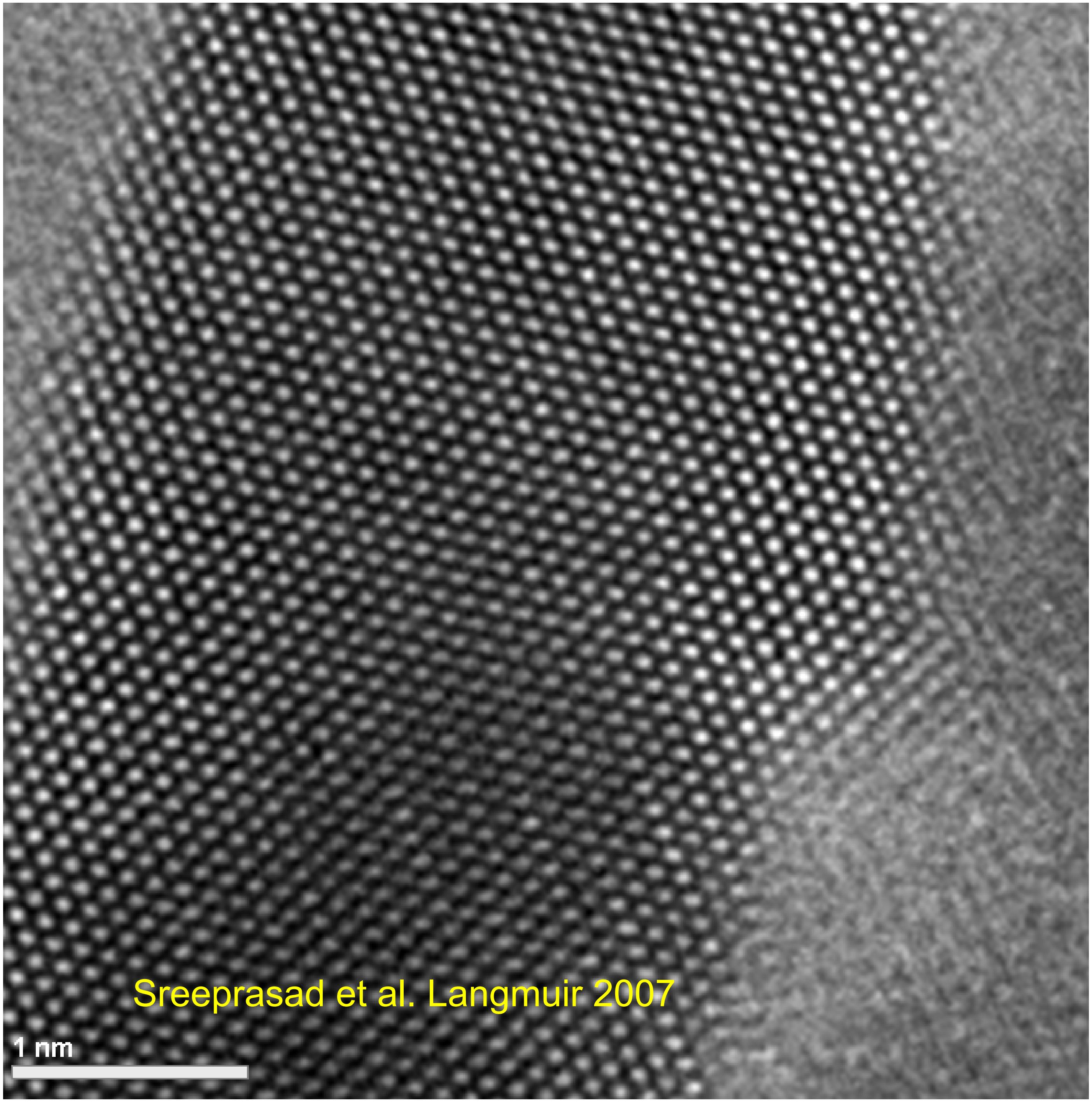
Measured in CNR Rao's lab

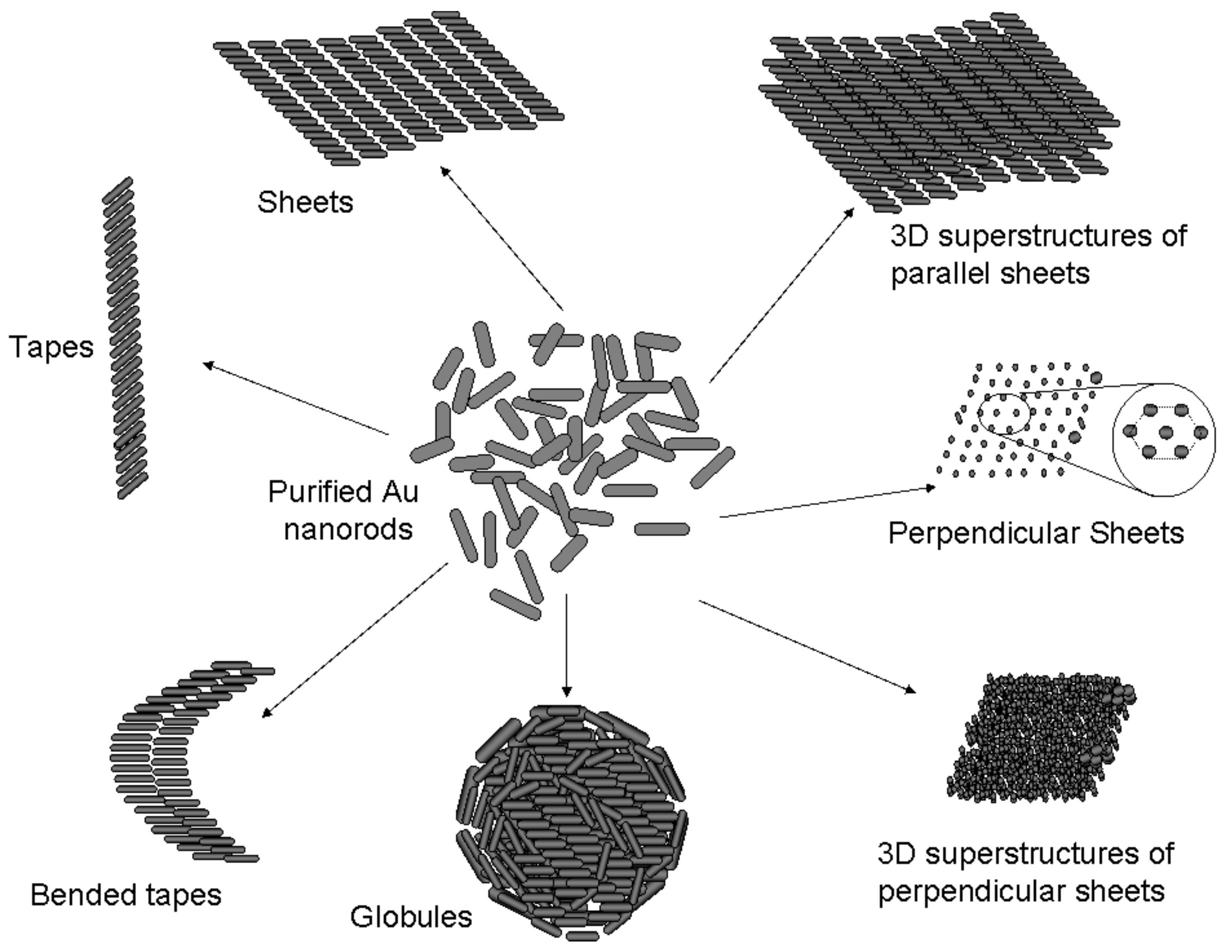


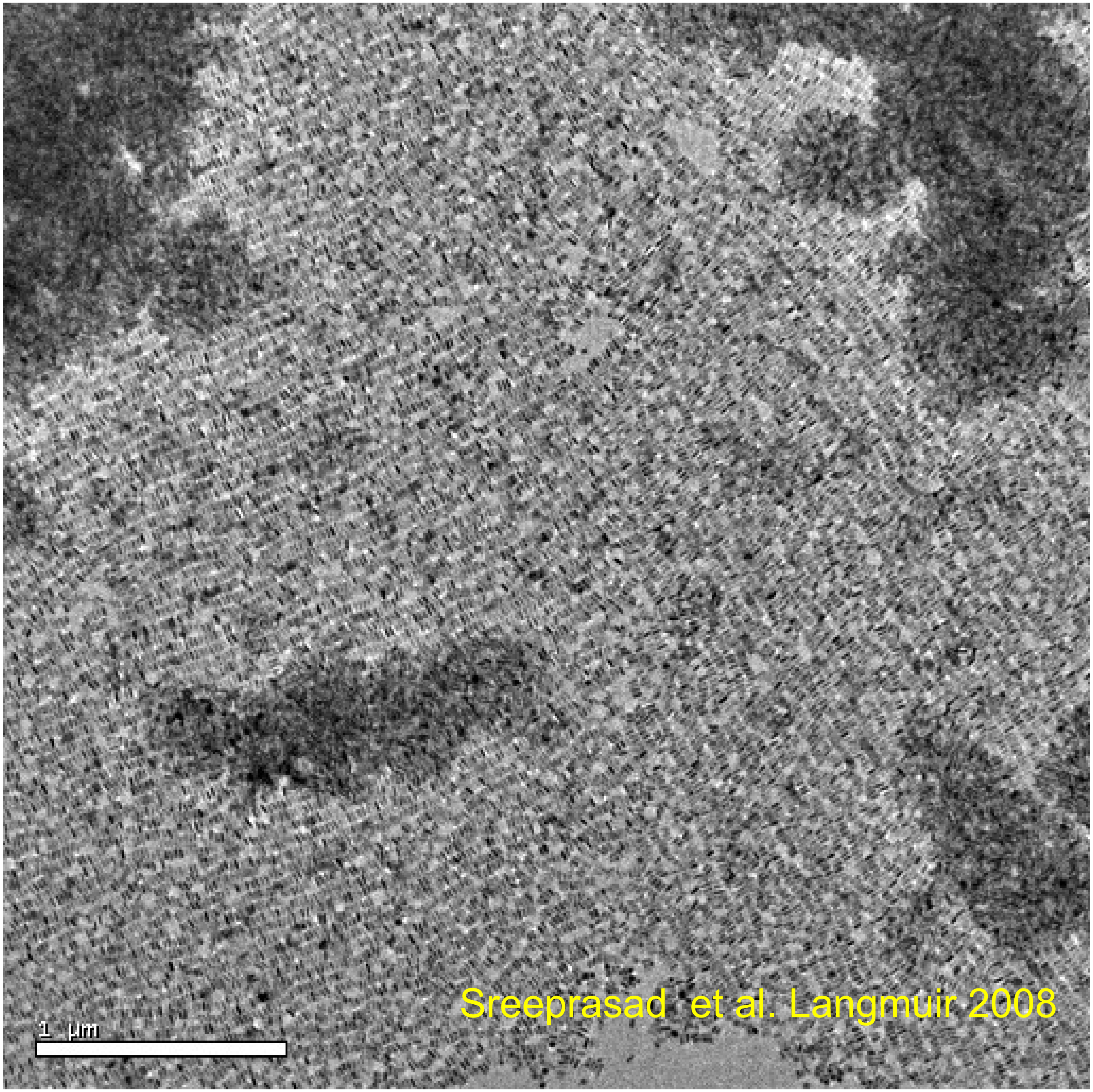
Shibu et al. Submitted

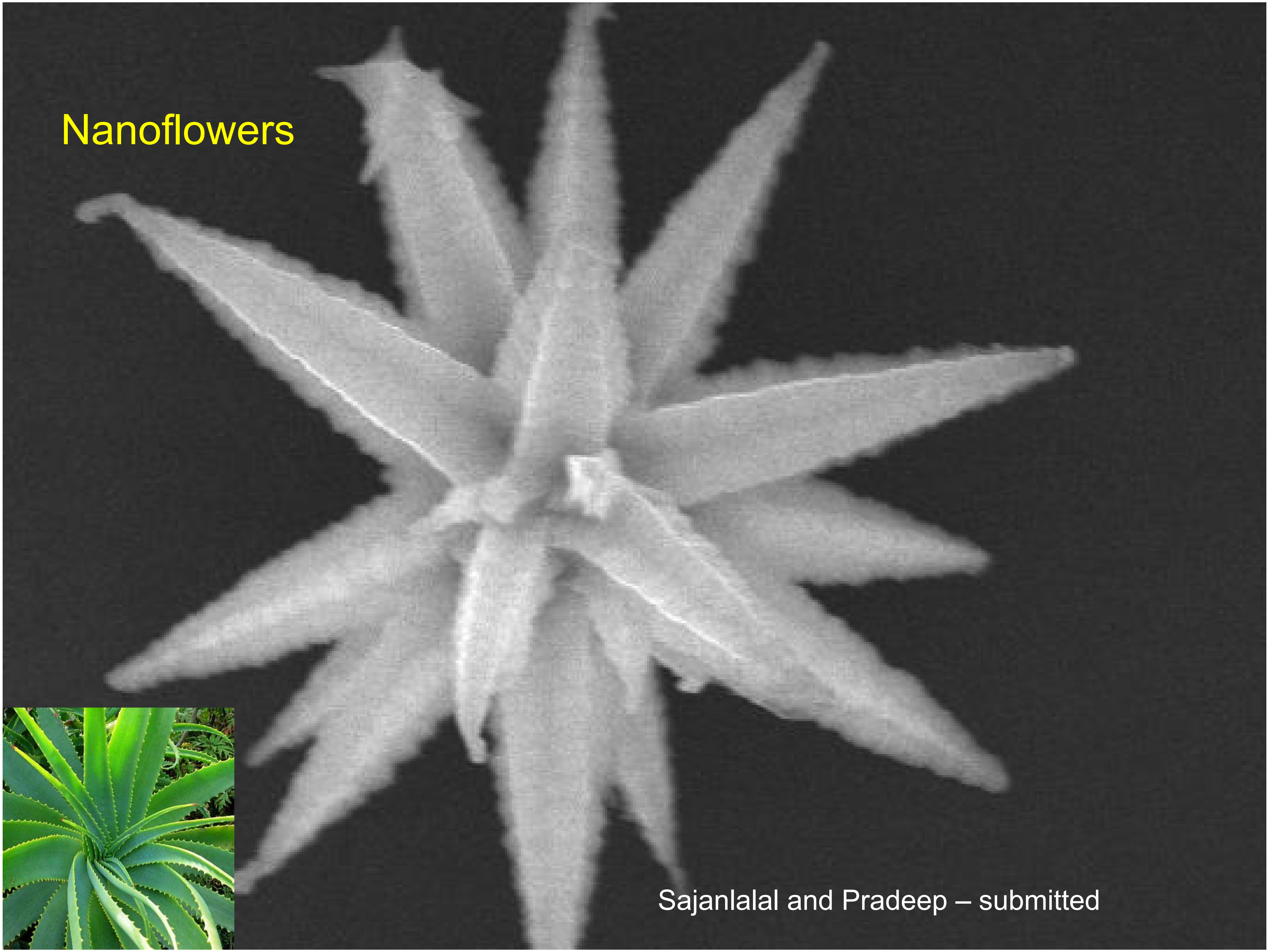
Anisotropic structures

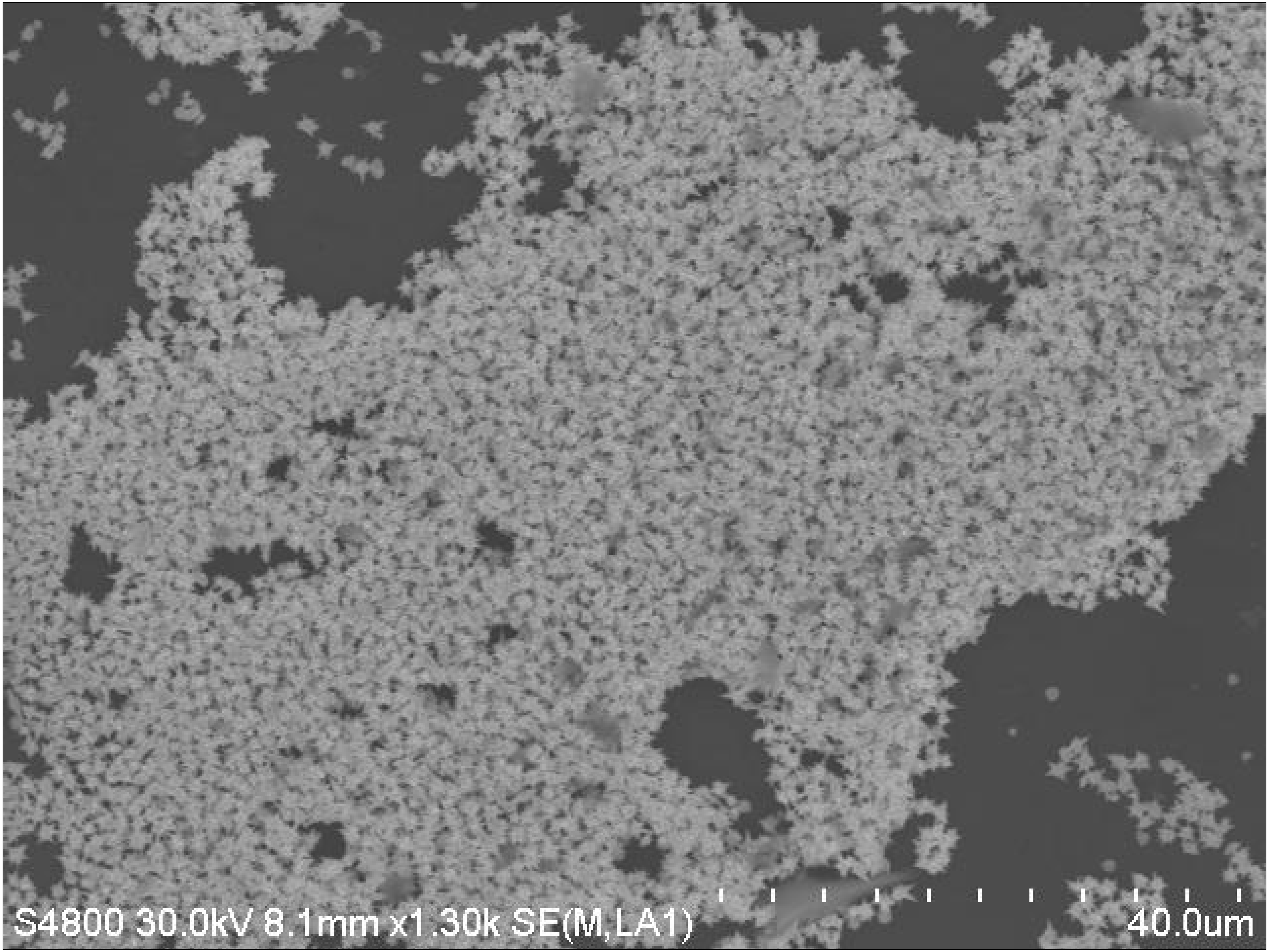

5 nm

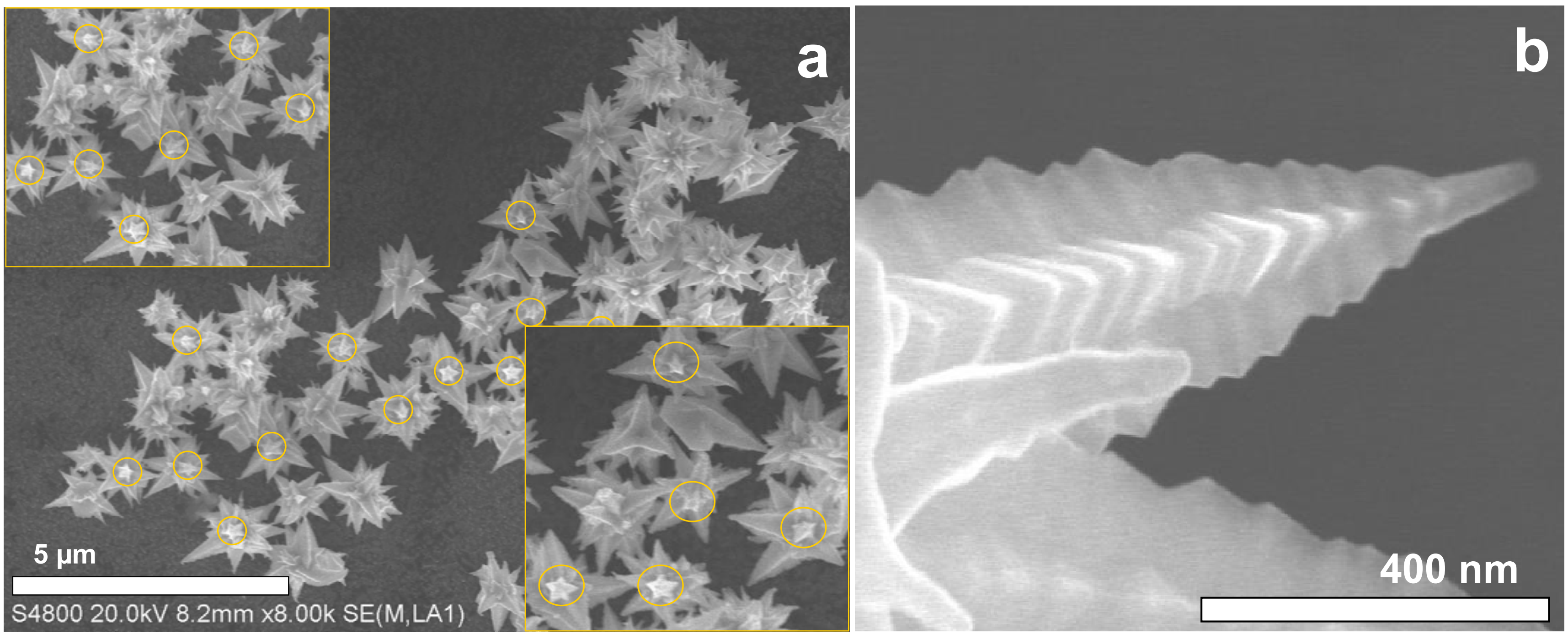

Sreeprasad et al. Langmuir 2007
1 nm

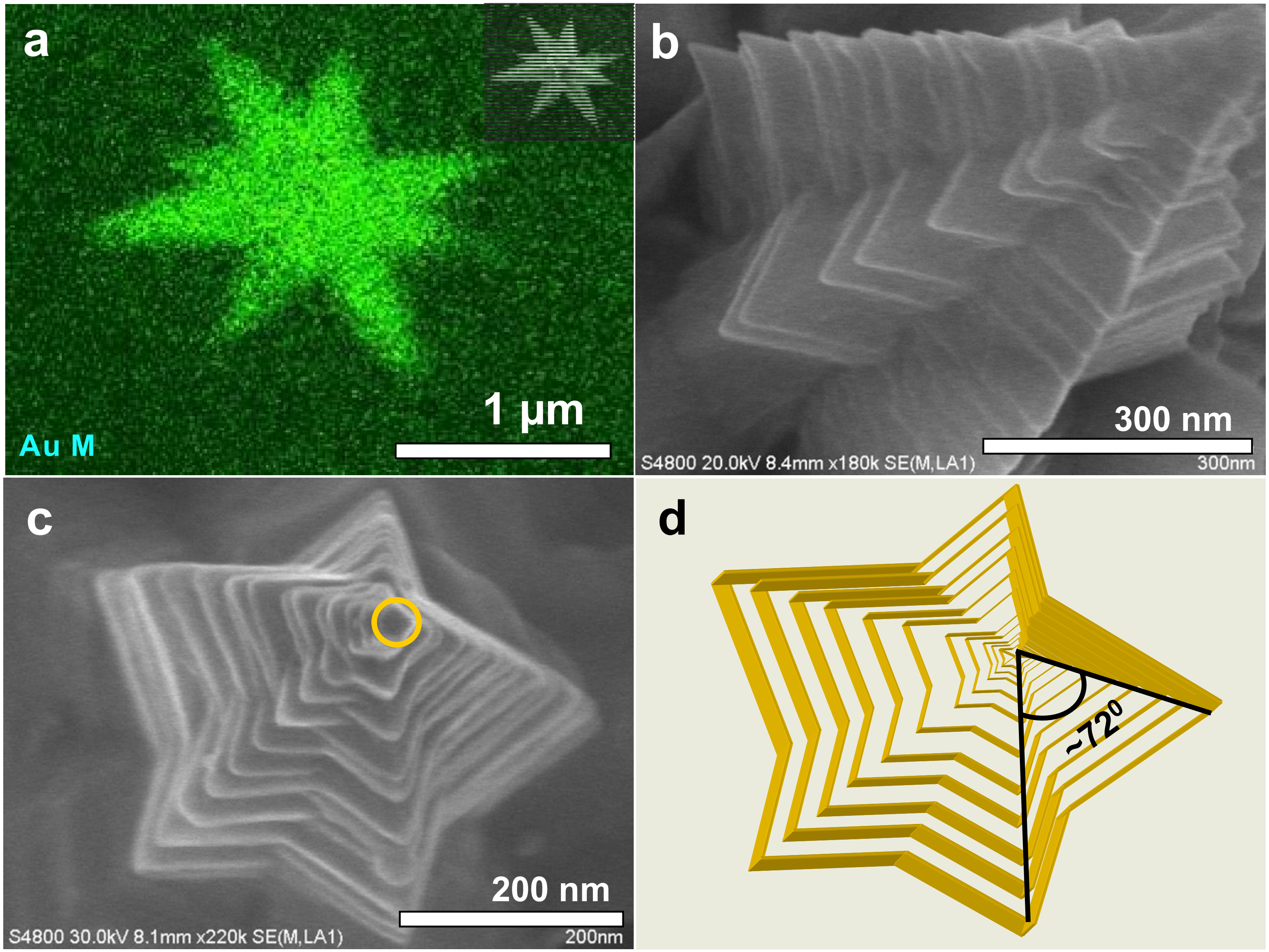

Sheets
3D superstructures of
parallel sheets
Tapes
Purified Au
nanorods
Perpendicular Sheets
Bended tapes
Globules
3D superstructures of
perpendicular sheets

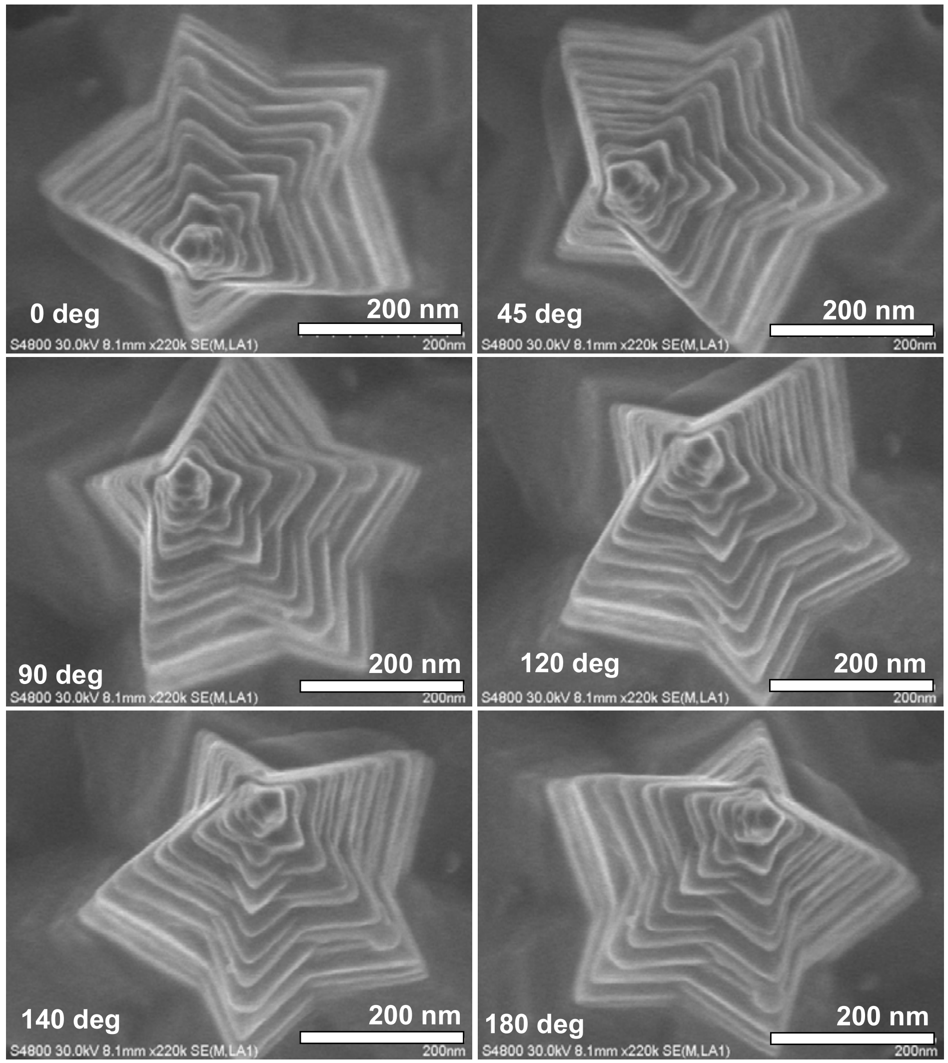

1 µm
Sreeprasad et al. Langmuir 2008

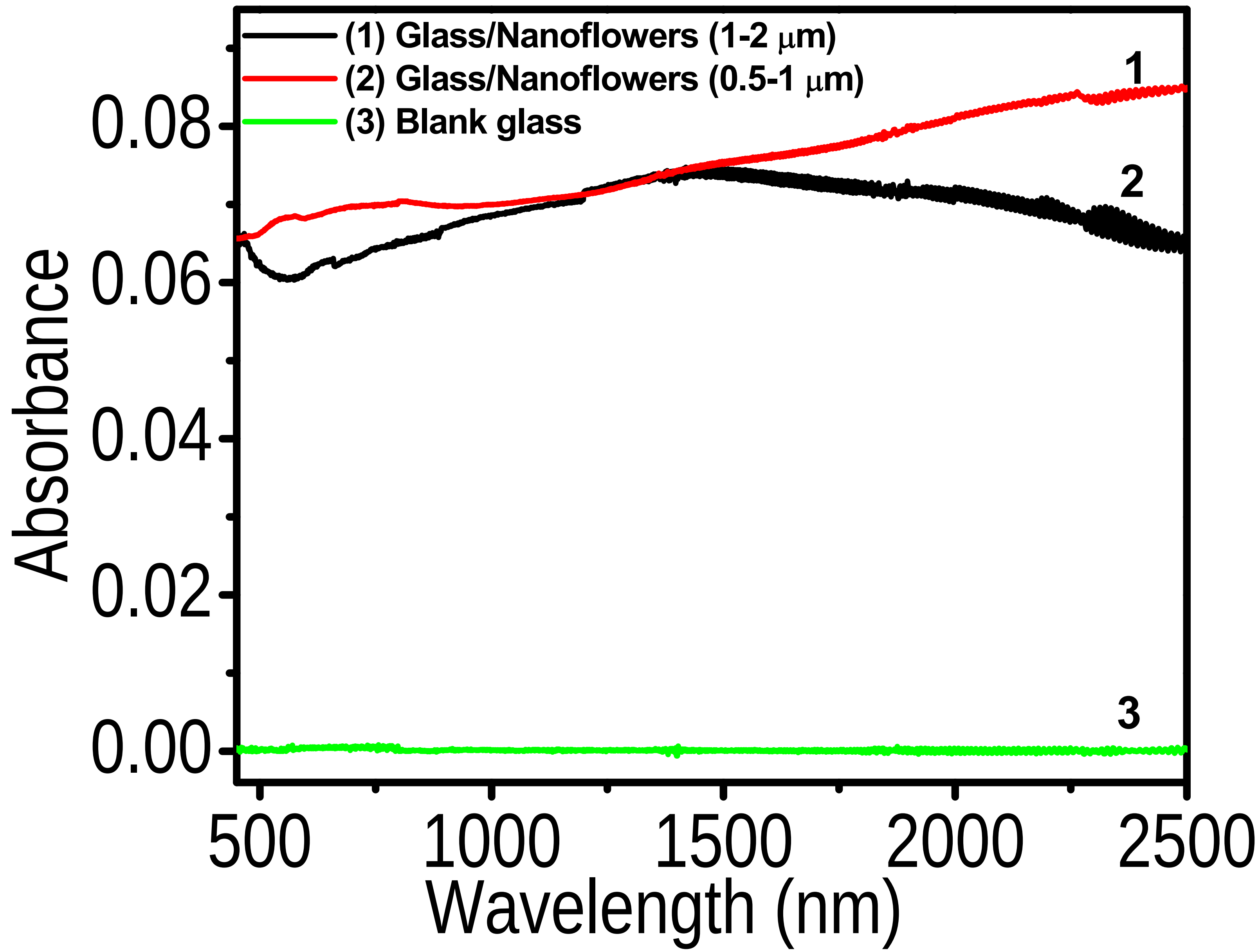

Nanoflowers
Sajanlalal and Pradeep – submitted


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

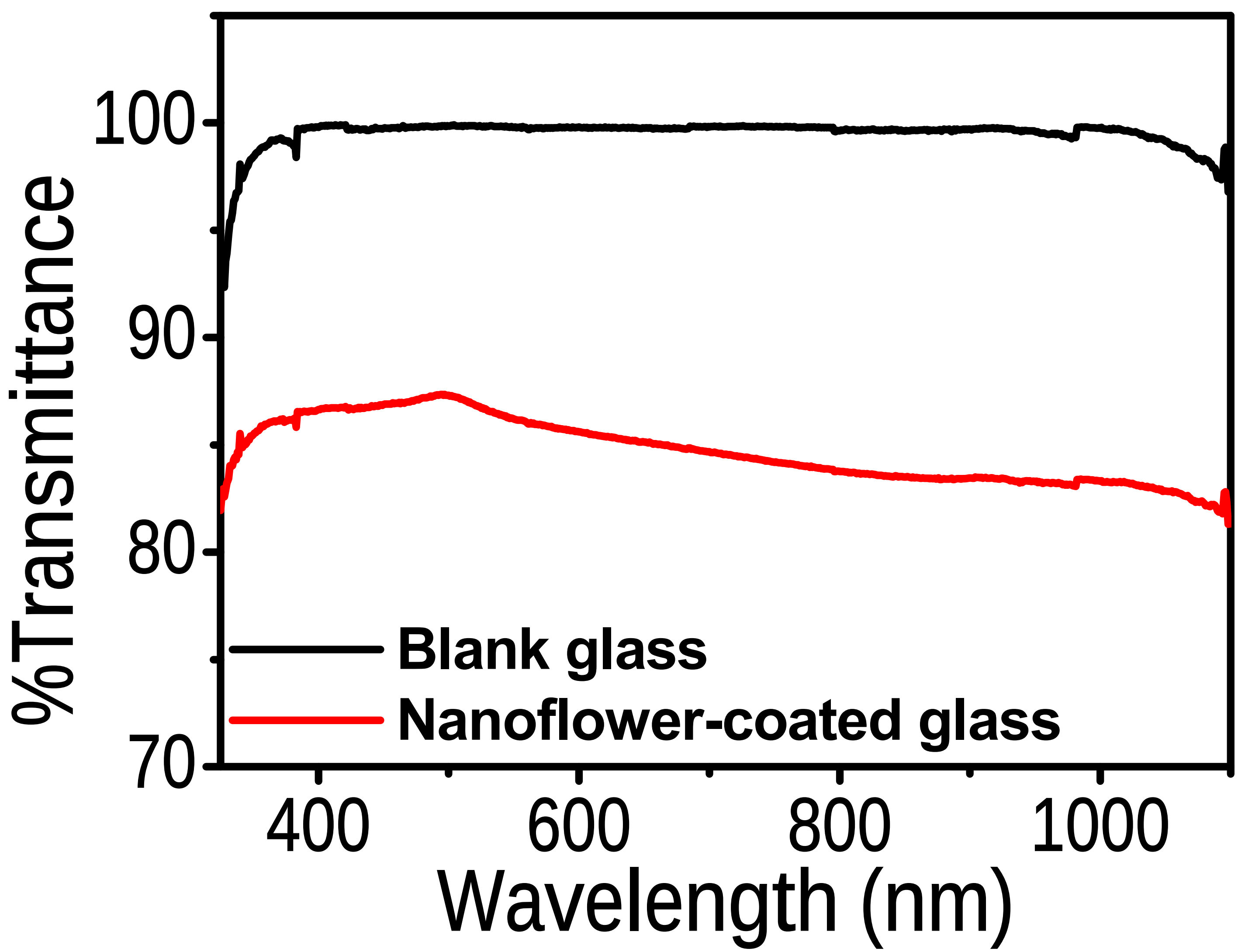

a
5 μm
S4800 20.0kV 8.2mm x8.00k SE(M,LA1)
b
400 nm


a
1 µm
Au M
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°

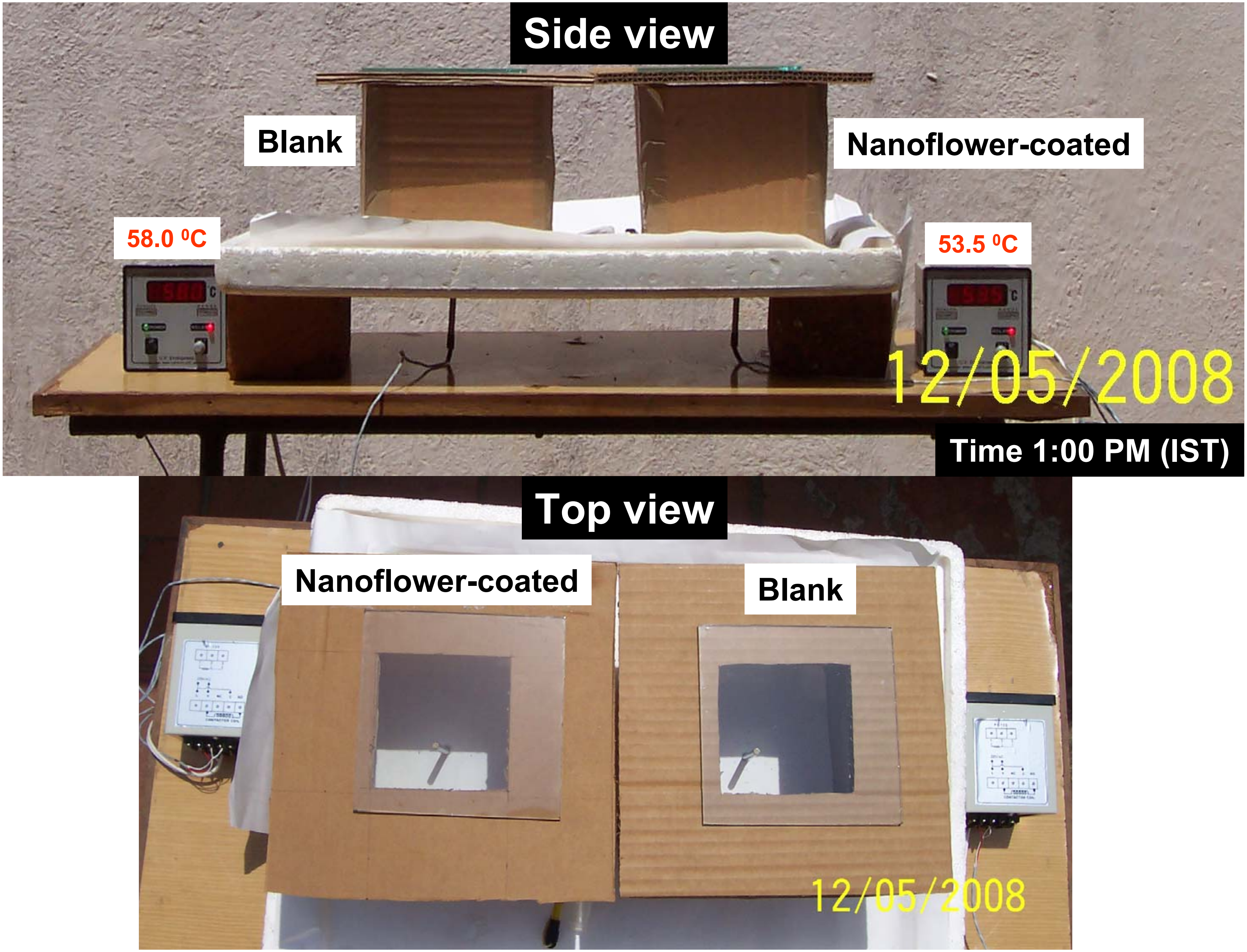

0 deg
200 nm
S4800 30.0kV 8.1mm x220k SE(M,LA1)
200nm
45 deg
200 nm
S4800 30.0kV 8.1mm x220k SE(M,LA1)
200nm
90 deg
200 nm
S4800 30.0kV 8.1mm x220k SE(M,LA1)
200nm
120 deg
200 nm
S4800 30.0kV 8.1mm x220k SE(M,LA1)
200nm
140 deg
200 nm
S4800 30.0kV 8.1mm x220k SE(M,LA1)
200nm
180 deg
200 nm
S4800 30.0kV 8.1mm x220k SE(M,LA1)
200nm



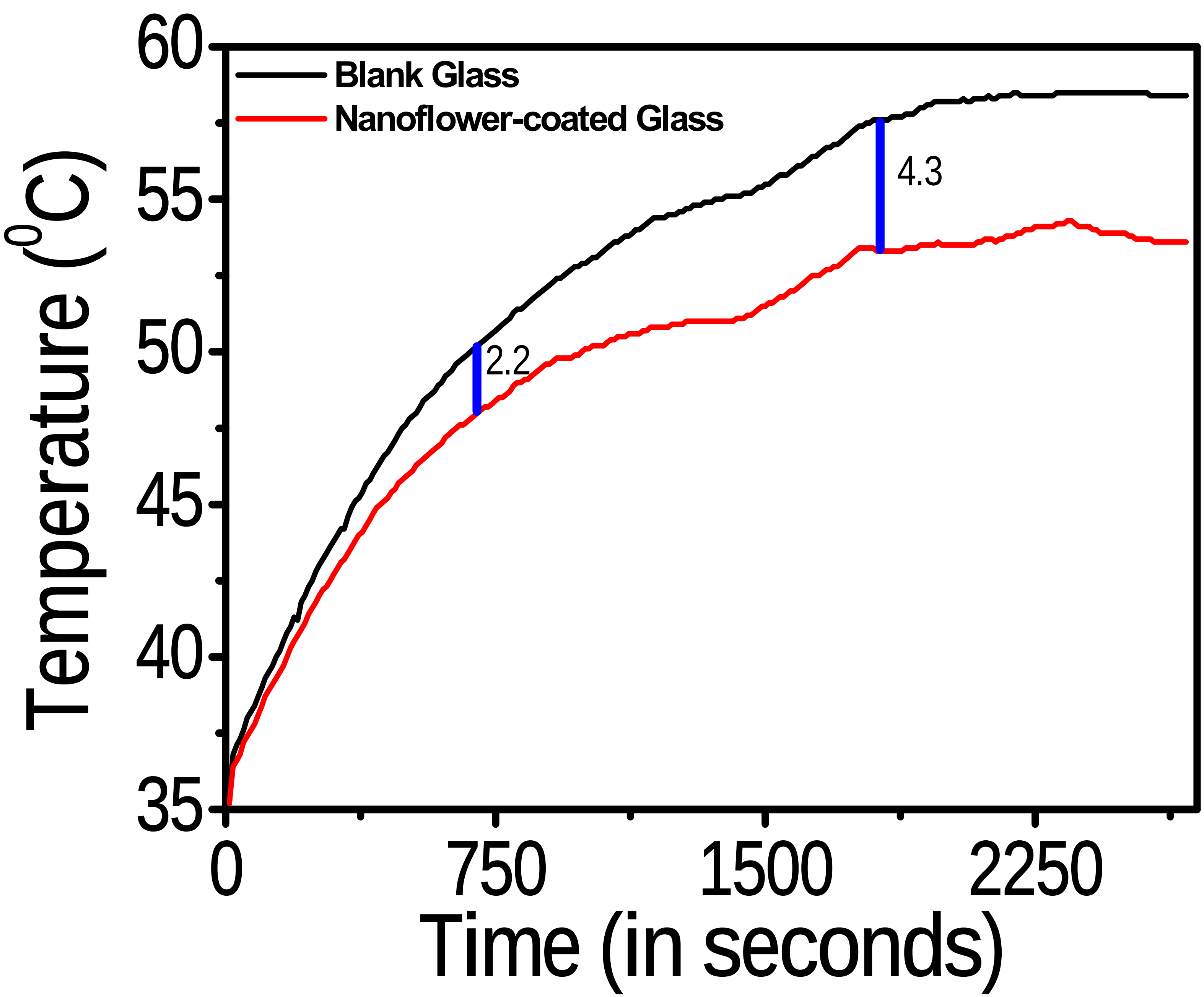
(1) Glass/Nanoflowers (1-2 μm)
(2) Glass/Nanoflowers (0.5-1 μm)
(3) Blank glass
1
2
3
Absorbance
0.00
0.02
0.04
0.06
0.08
500
1000
1500
2000
2500
Wavelength (nm)



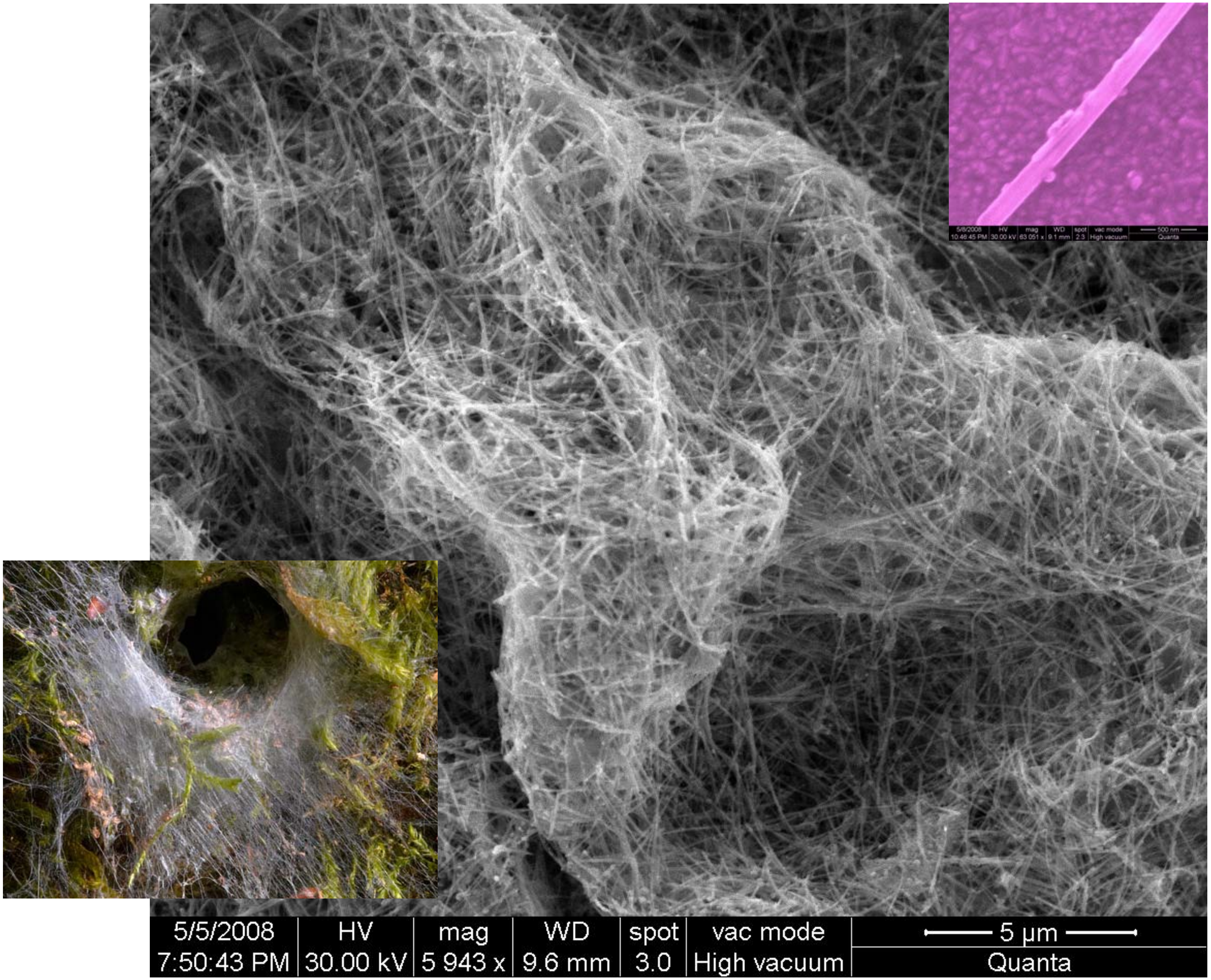
100
90
80
70
%Transmittance
400
600
800
1000
Wavelength (nm)
Blank glass
Nanoflower-coated glass

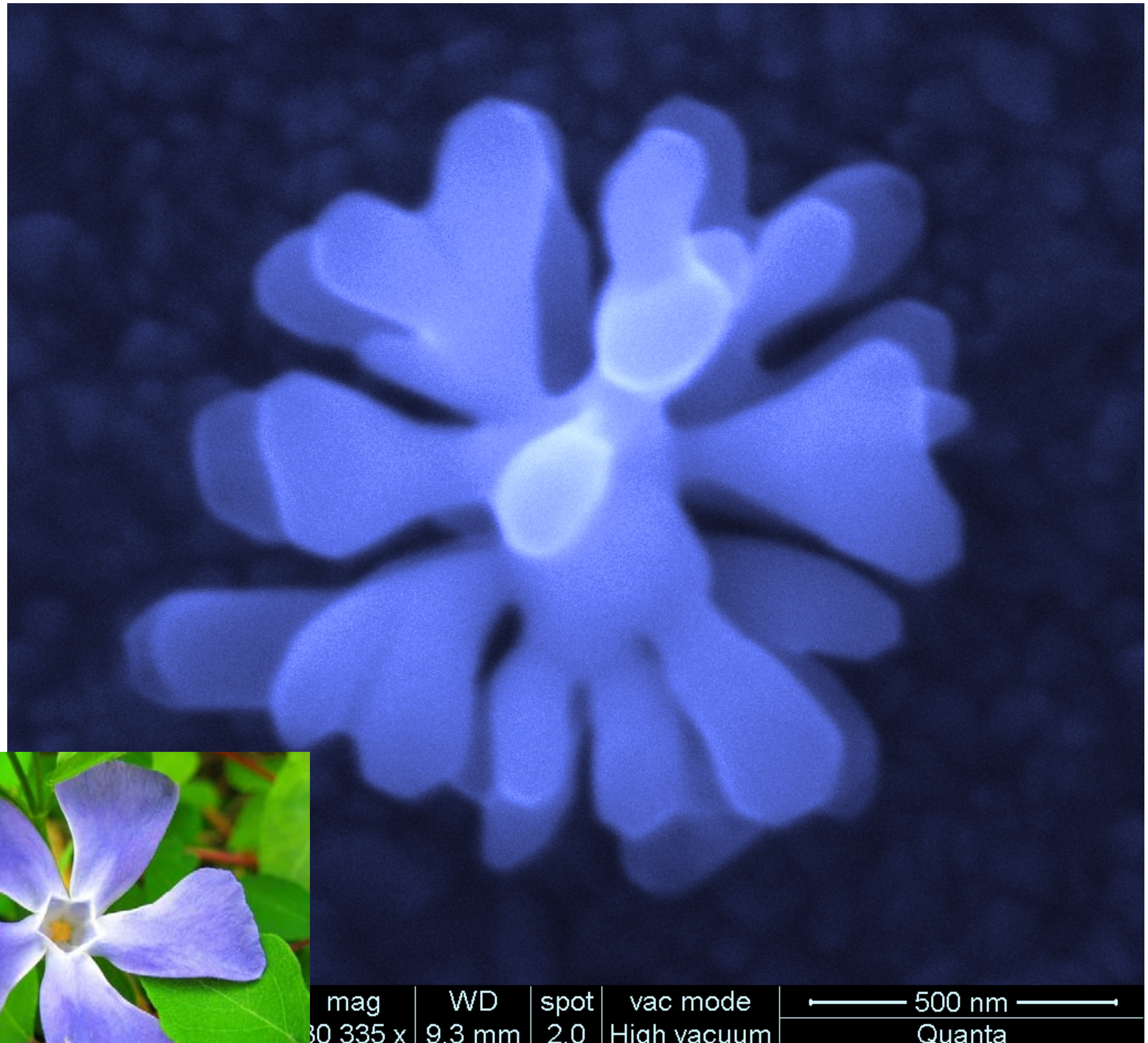


Side view
Blank
Nanoflower-coated
58.0 0C
53.5 0C
12/05/2008
Time 1:00 PM (IST)
Top view
Nanoflower-coated
Blank
12/05/2008



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

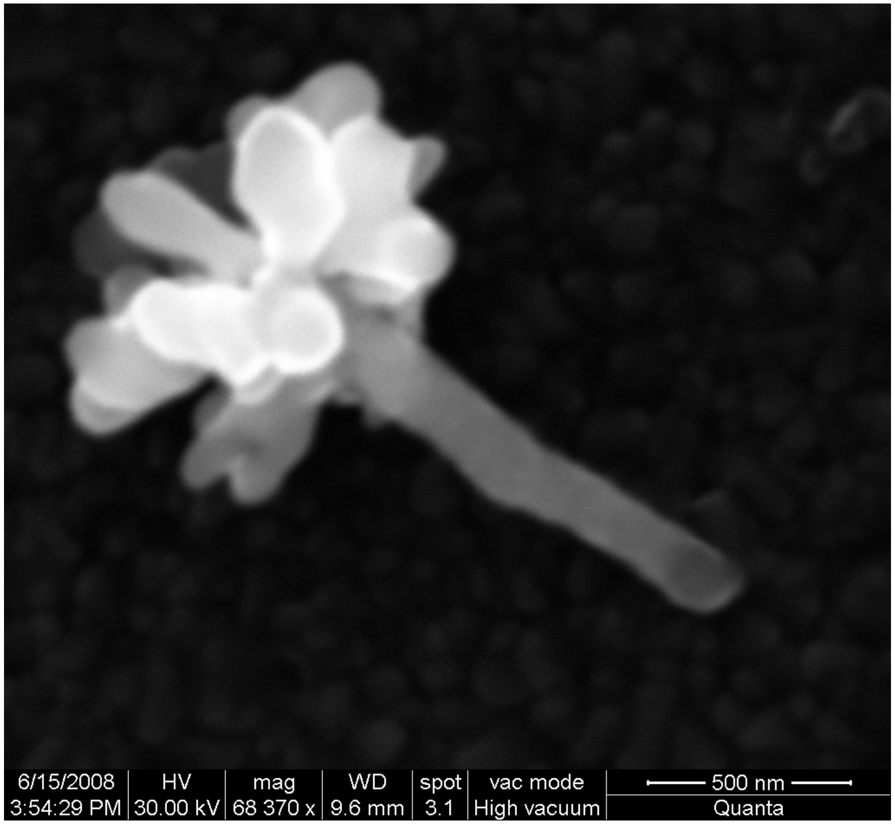

5/5/2008
7:50:43 PM
HV
30.00 kV
mag
5 943 x
WD
9.6 mm
spot
3.0
vac mode
High vacuum
5 μm
Quanta

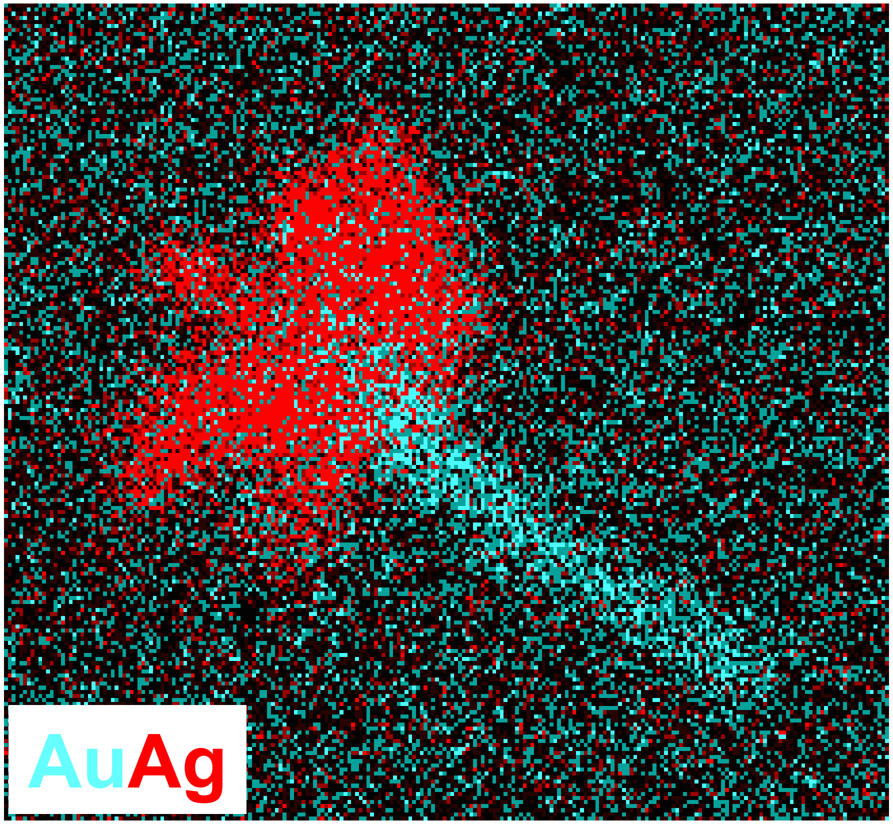


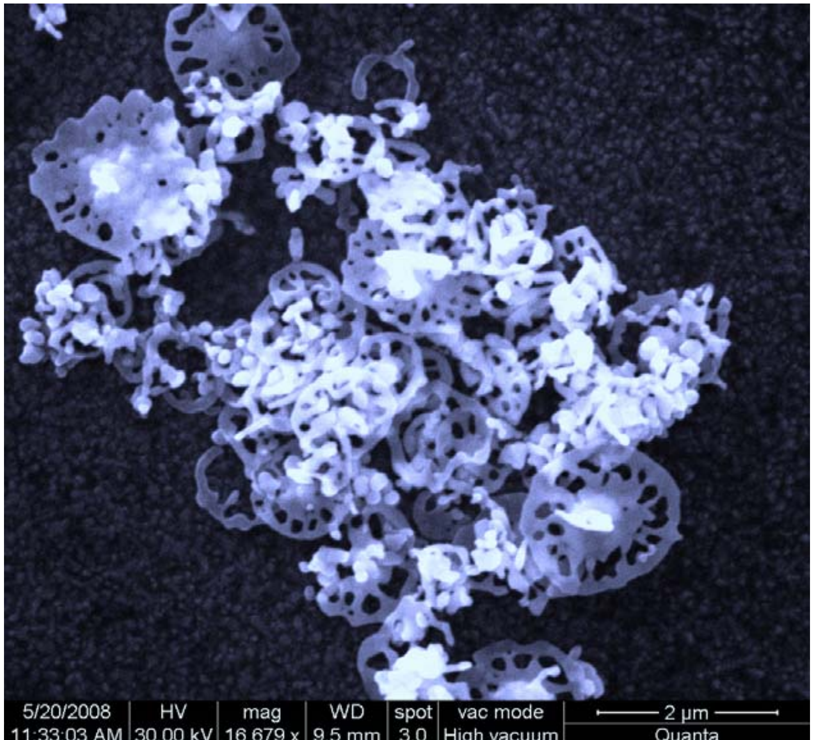
http://www.hermann-uwe.de/files/images/blue_flower.preview_0.jpg

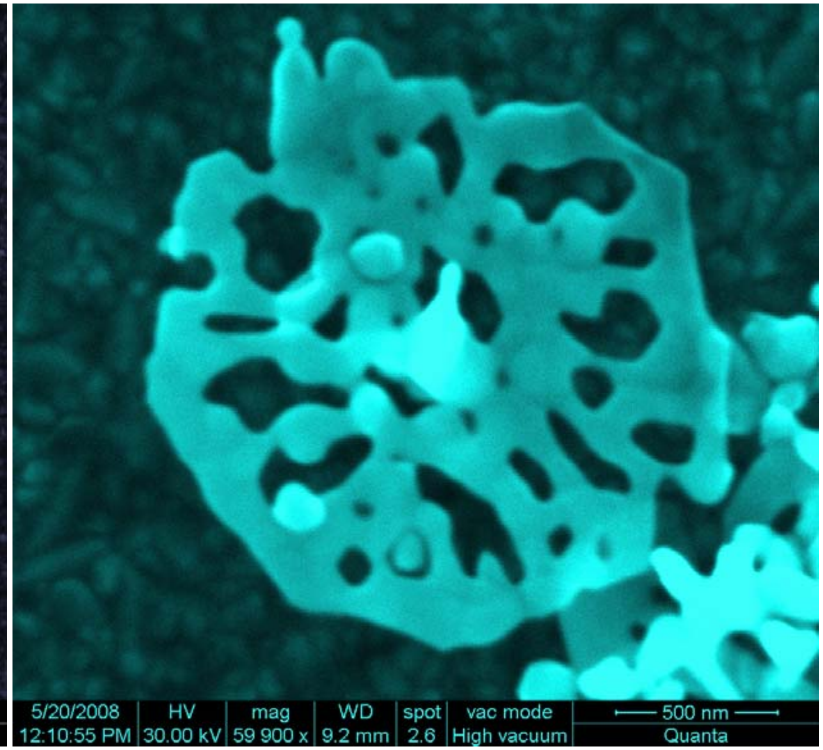
http://www.diabloflowerz.co.uk/flowers/single%20stem.jpg

EDAX Image


6/15/2008 3:54:29 PM
HV 30.00 kV
mag 68 370 x
WD 9.6 mm
spot 3.1
vac mode High vacuum
500 nm
Quanta


AuAg

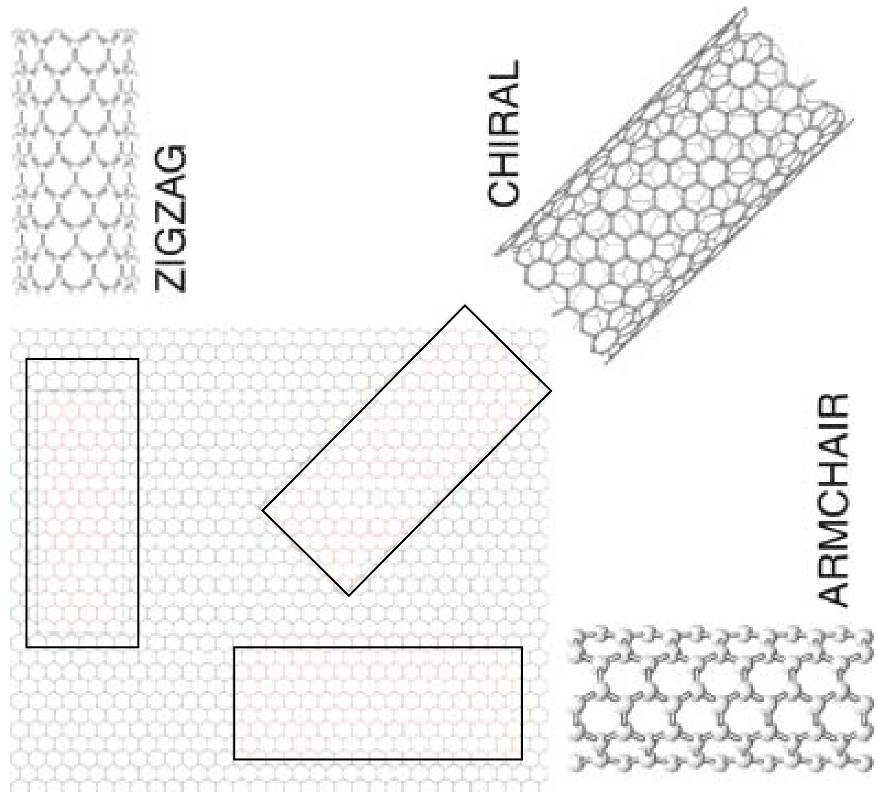




http://veggieplatter.blogspot.com/2007/09/roasting-papads-fryums-in-microwave.html

3

Visible emission from single walled carbon nanotubes



(n,m) indices

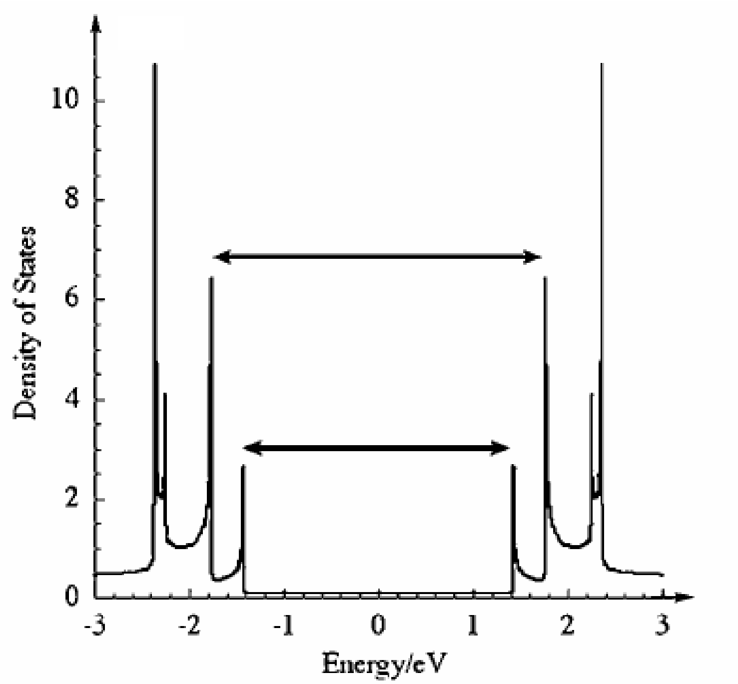
Metallic

Semiconducting

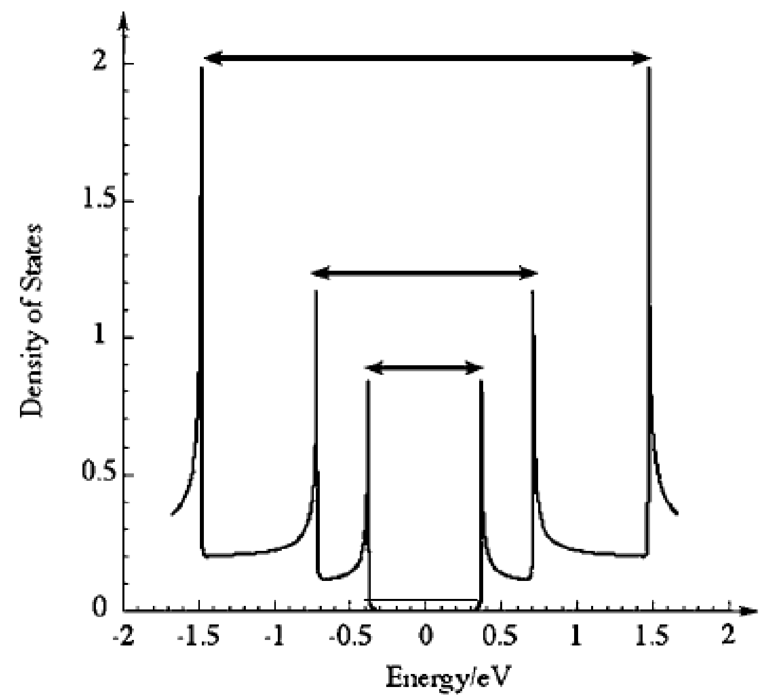
http://www.photon.t.u-tokyo.ac.jp/~maruyama/

Electrical transport properties

- Semiconducting : (n-m) ≠ 3*l.* Eg = 1.7 – 2.0 eV
- Metallic : (n-m) = 3*l.* E_g = 0.0 – 0.5 eV

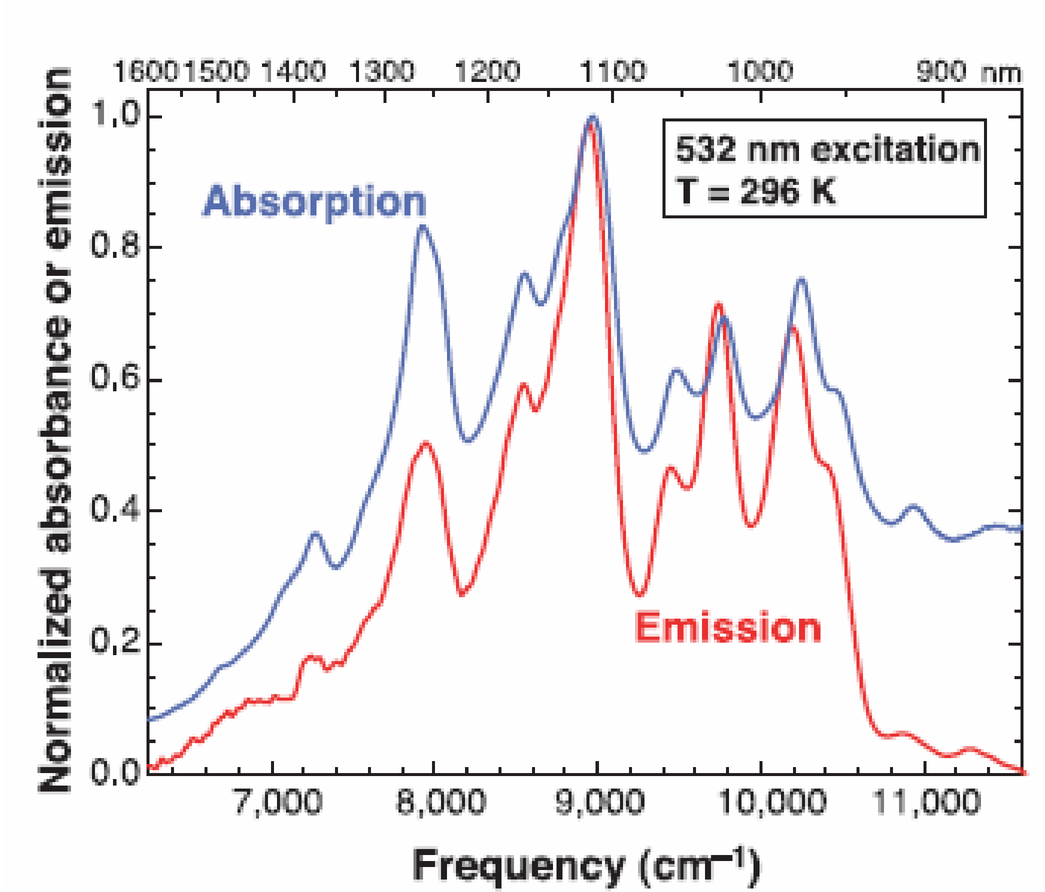


Semiconducting



Metallic

A. Hartschuh *et al.*, *Chem. Phys. Chem.* ***6****, 577 (2005)*



Emission spectrum (red) of individual fullerene nanotubes suspended in SDS micelles in D_2O excited by 8 ns, 532-nm laser pulses, overlaid with the absorption spectrum (blue) of the sample in this region of first van Hove band gap transitions.

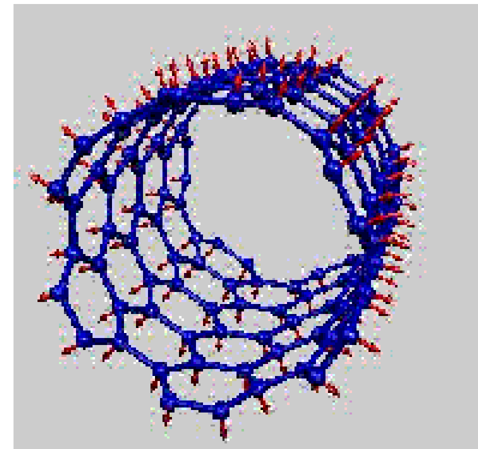
M. J. O'Connell *et al.*, *Science **297**, 593 (2002).*

Vibrational Properties

(A) Radial Breathing Mode (RBM)

Diameter dependent

$$\omega_{RBM}(cm^{-1}) = \frac{224.8}{d_t(nm)} + 12.5$$



(B) Tangential G band

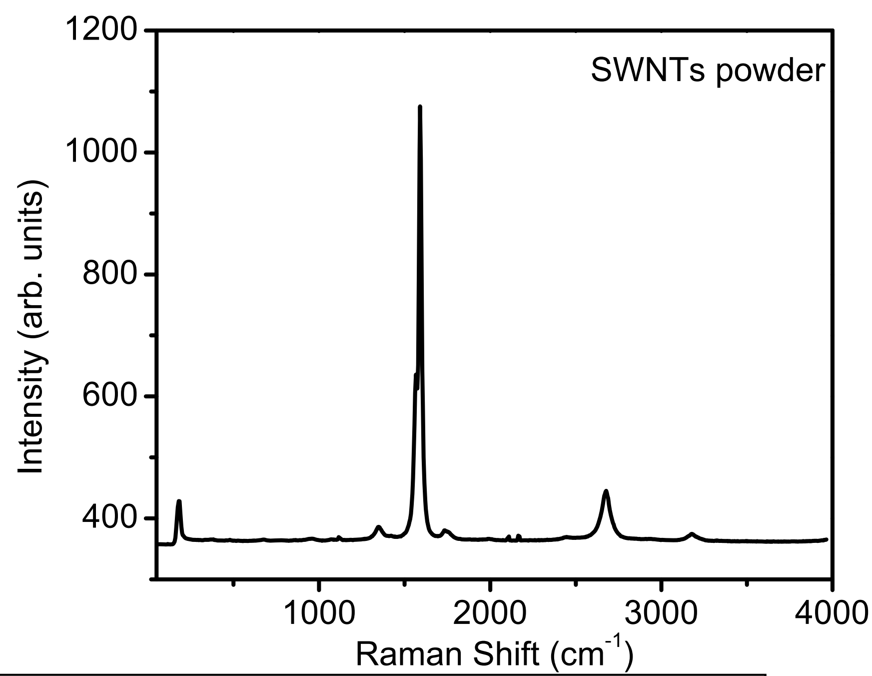
In-plane vibrations

(C) D-band

Defect centered

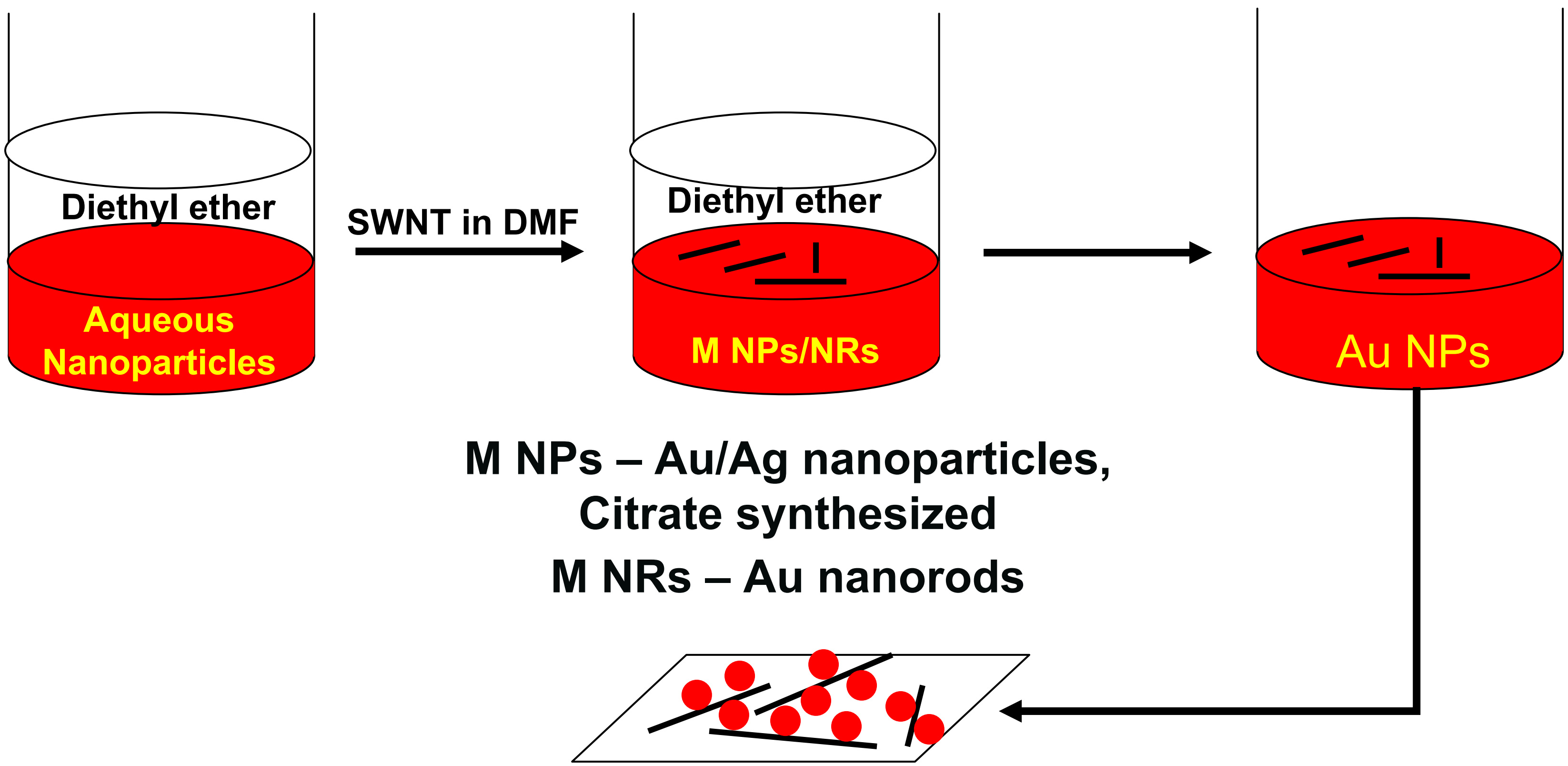
(D) G` band

Occurs at $2\omega_D$

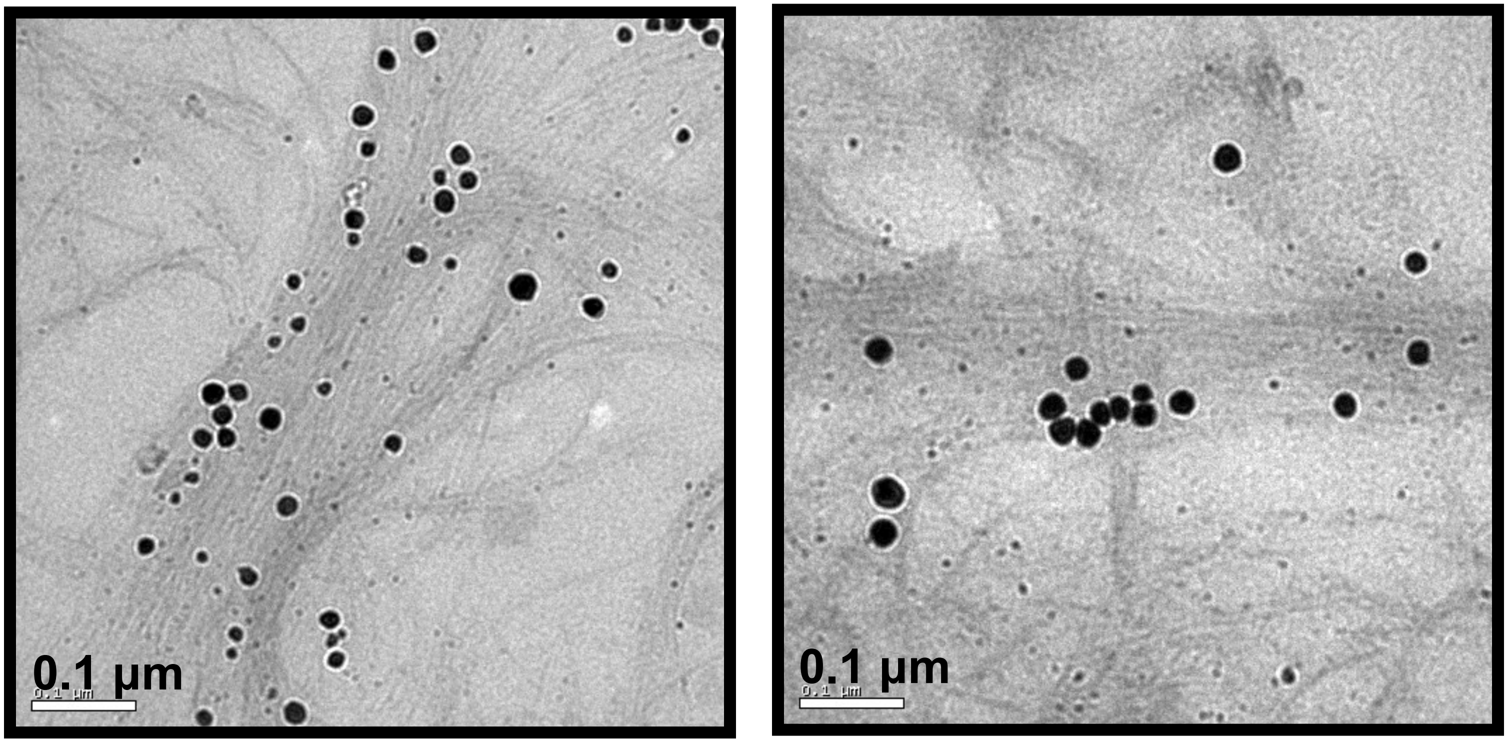


Science, **1997**, *275*, 187. & *http://www.photon.t.u-tokyo.ac.jp/~maruyama/*

Preparation of composite

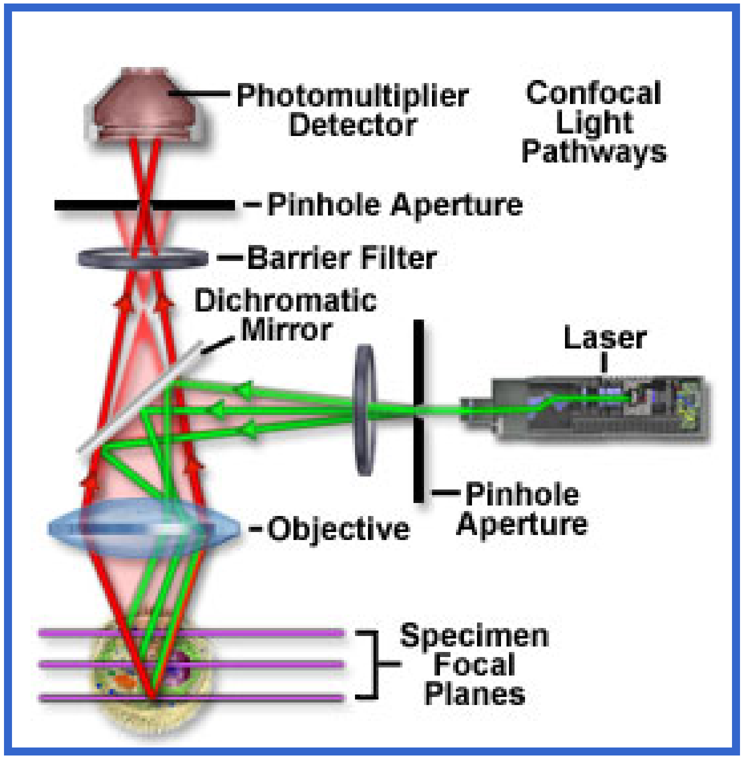


Transmission Electron Microscopy

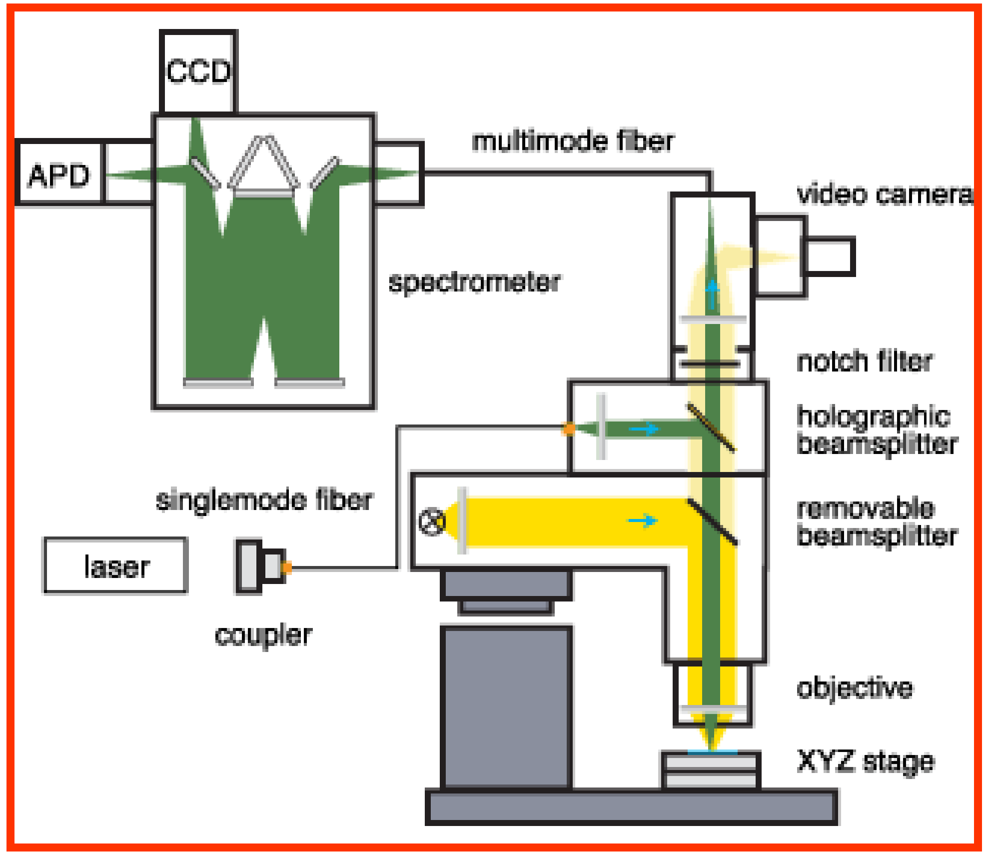


TEM images of Au-SWNTs composite acquired at 100 keV.

Instrumentation – Confocal Raman



Concept of confocality

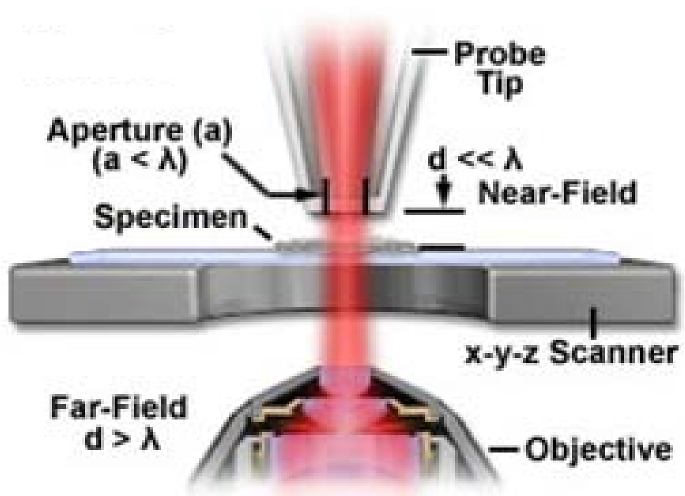


Raman Instrument

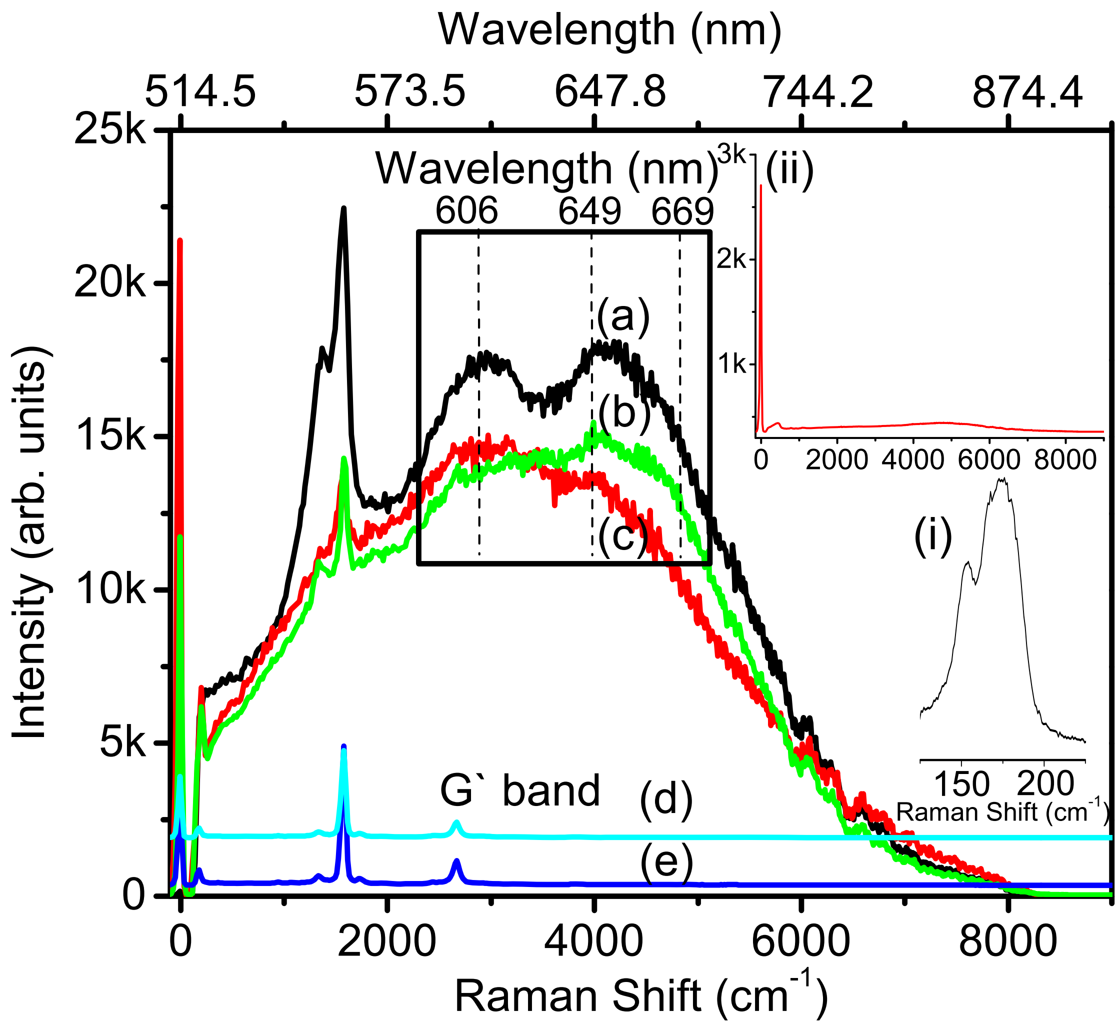
Scanning Near-field Optical Microscopy

- **Resolution is limited by wavelength of light used.**
- **Near-filed microscopy was first proposed by Synge in 1928.**

"Resolutions below the diffraction limit can be obtained when the tip-sample distance is smaller than the aperture diameter. In such a case, the aperture diameter controls the resolution and not the wavelength of light used[2]"

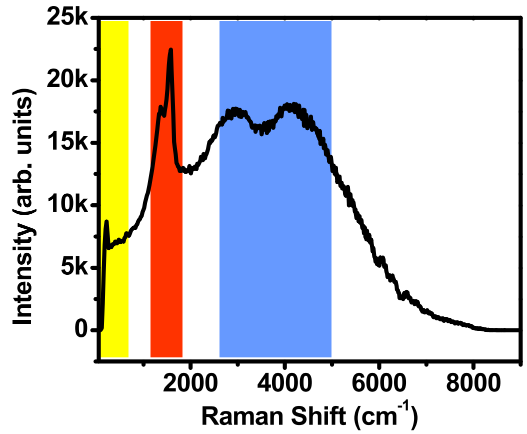


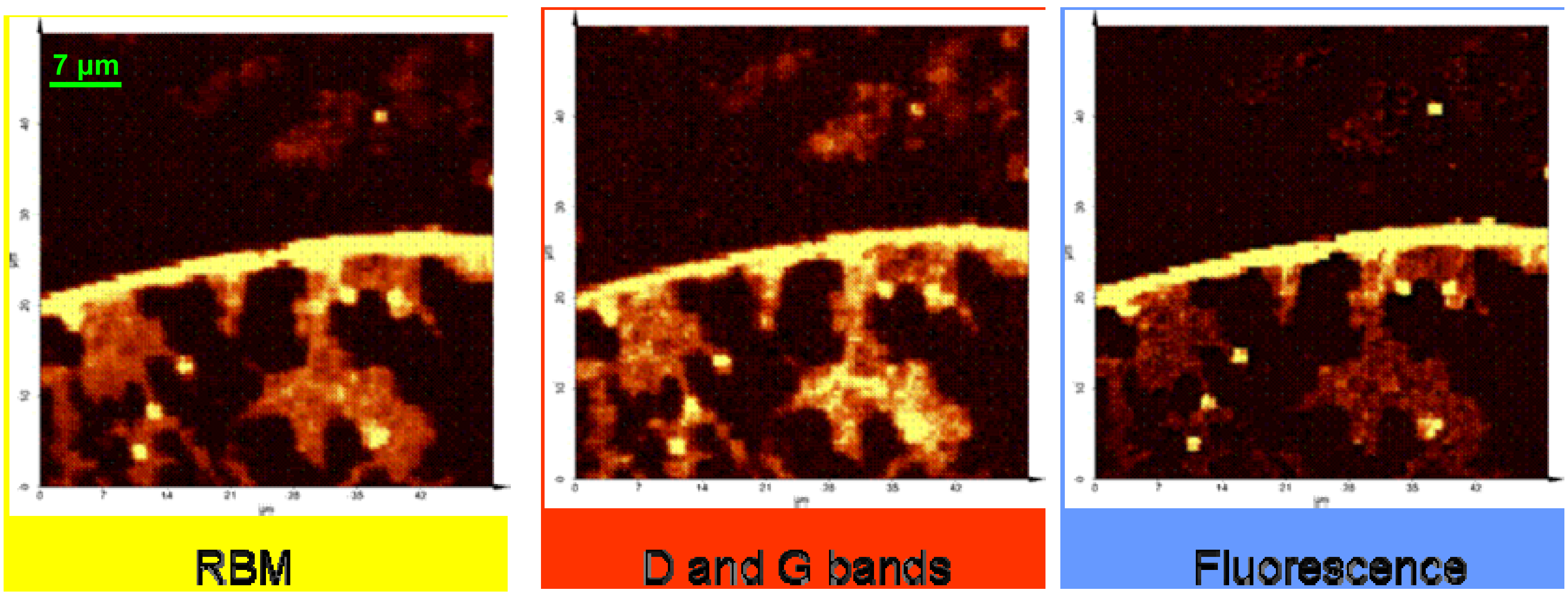
1. *www.olympusmicro.com*
2. E.H. Synge, *Phil.Mag.* **6**, 356 (1928)



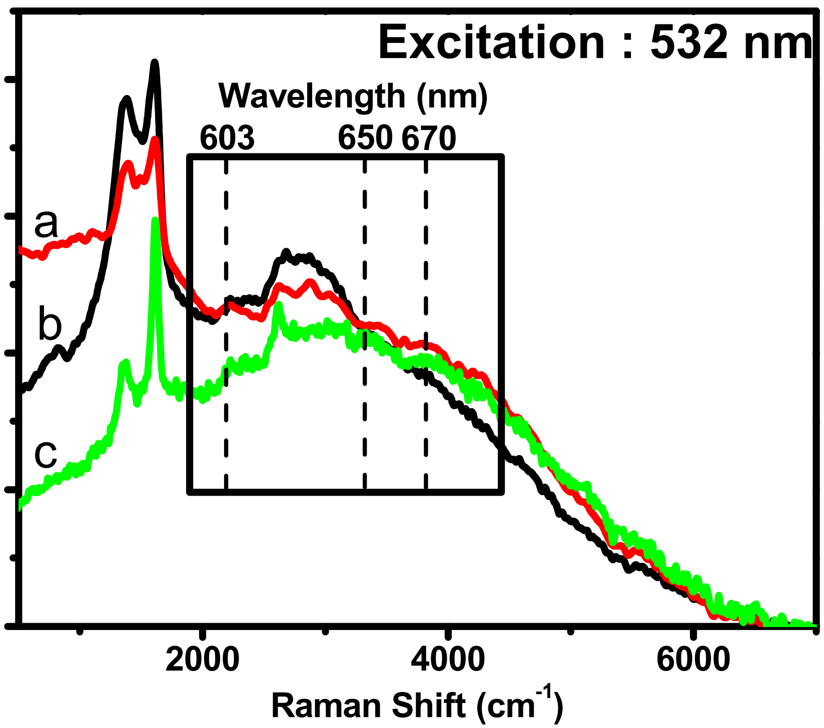
Raman Spectra of (a) Ag-SWNTs composite, (b) Au-SWNTs composite, (c) AuNR-SWNTs composite, (d) pristine SWNTs, (e) Pristine SWNTs treated with trisodium citrate and (f) Au nanorods.

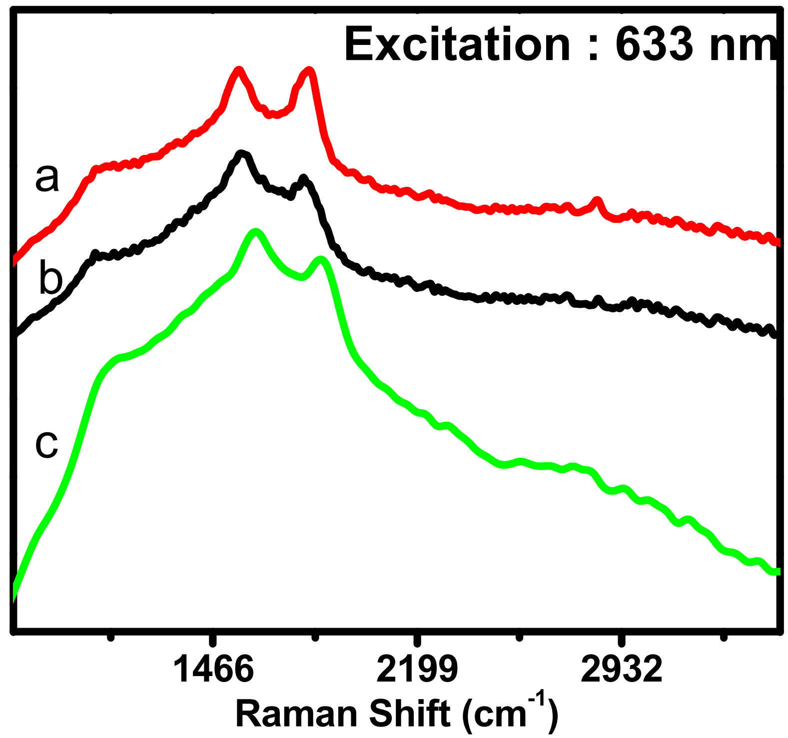
Raman Spectral imaging



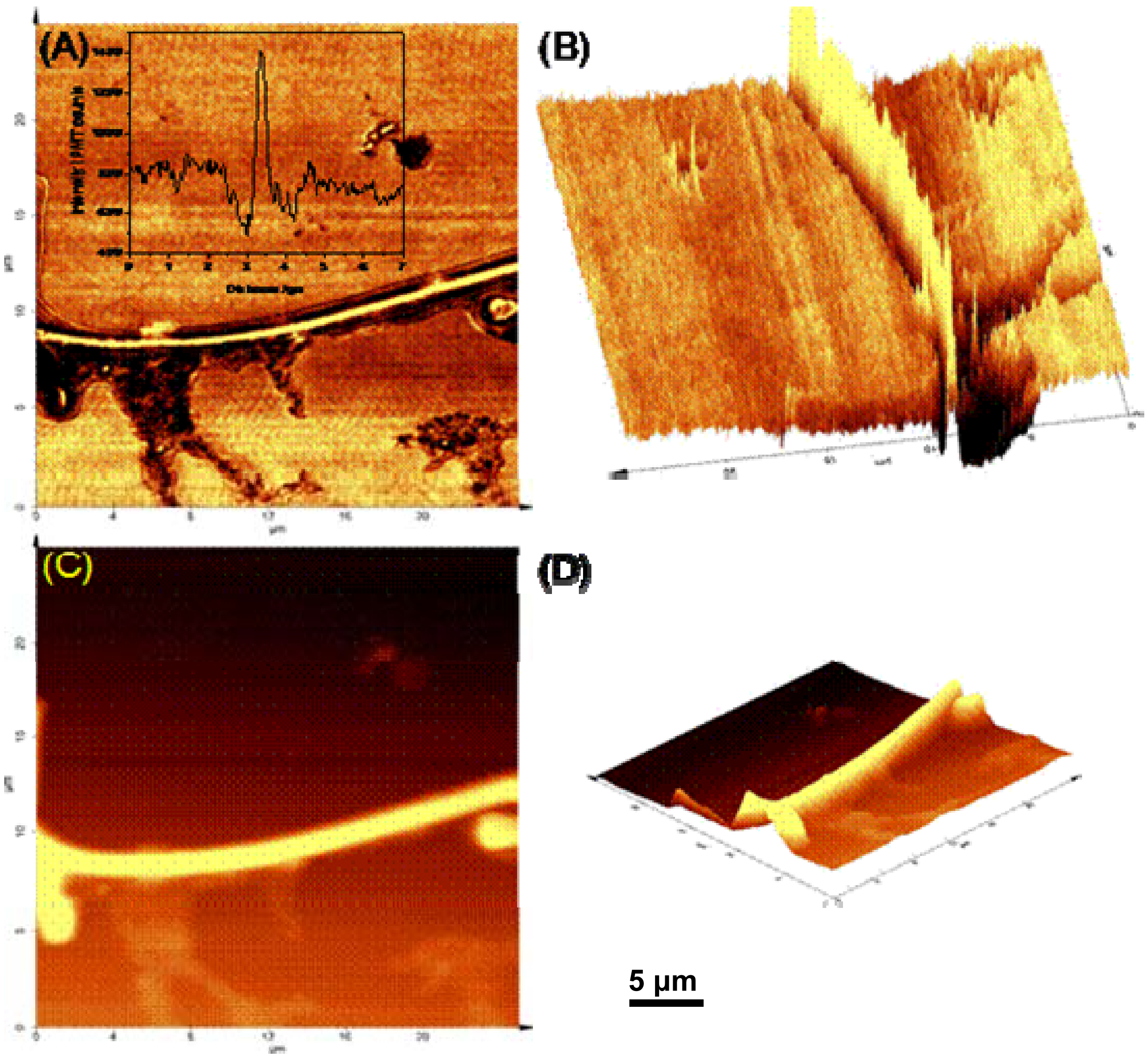


Varying excitation sources

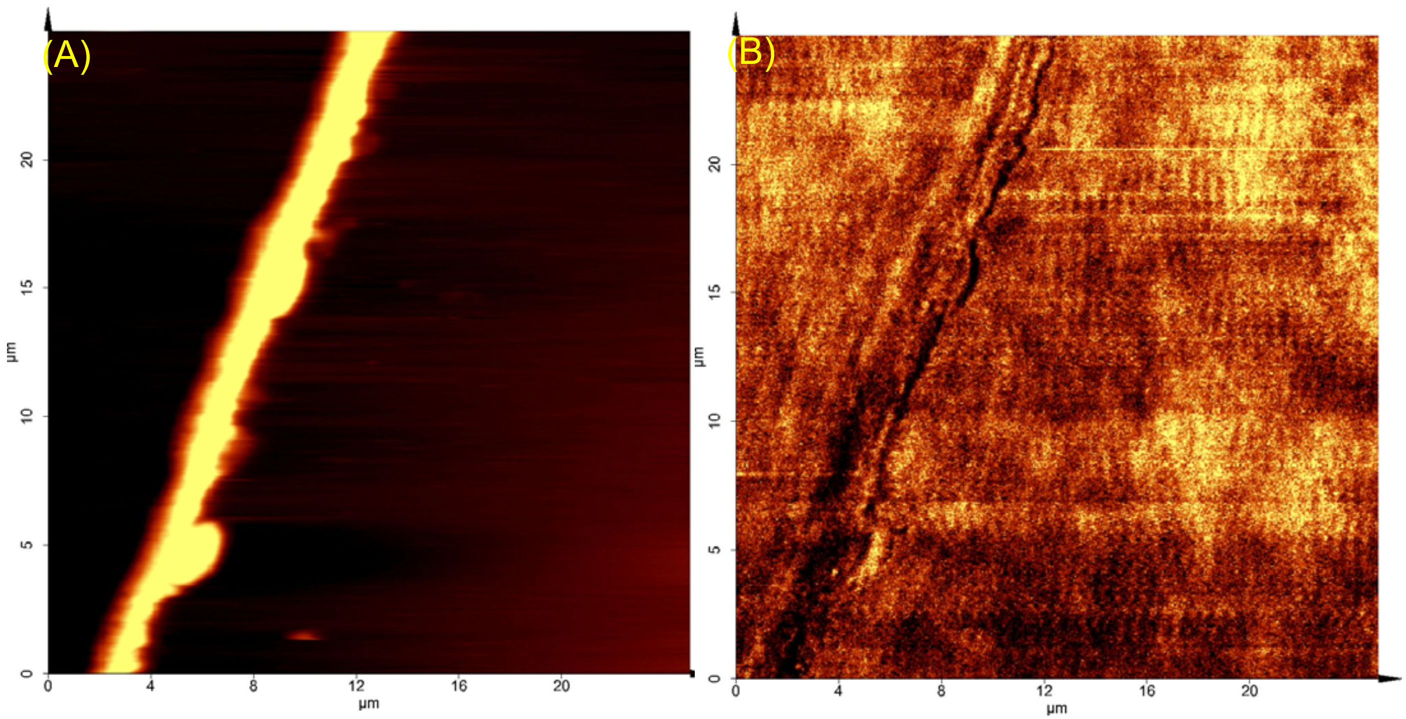




Raman Spectra acquired with (A) 532 nm Nd-YAG and (B) 633 nm He-Ne as excitation sources. Traces (a), (b) and (c) correspond to Ag-SWNTs composite, Au-SWNTs composite and AuNR-SWNTs composite, respectively.

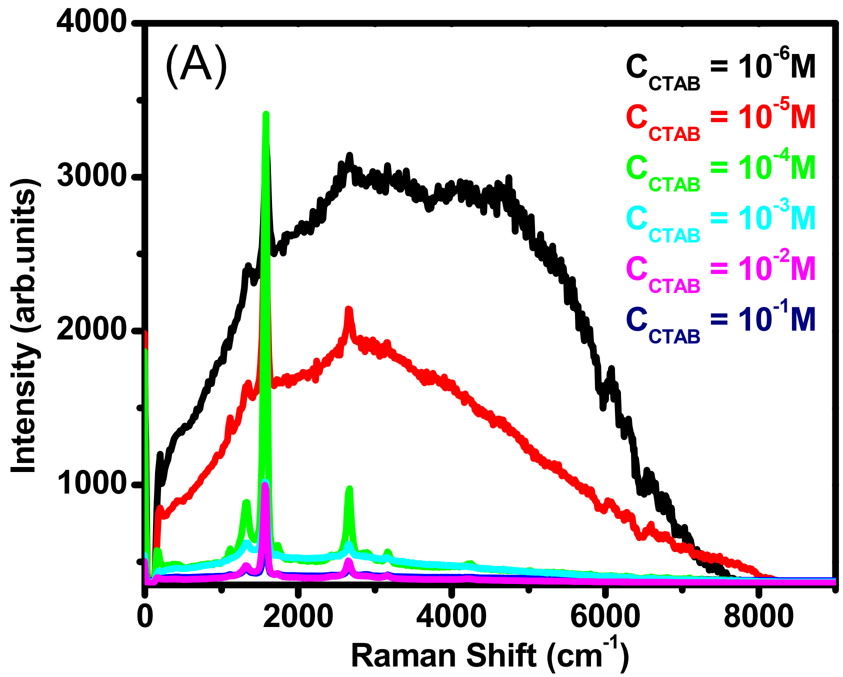


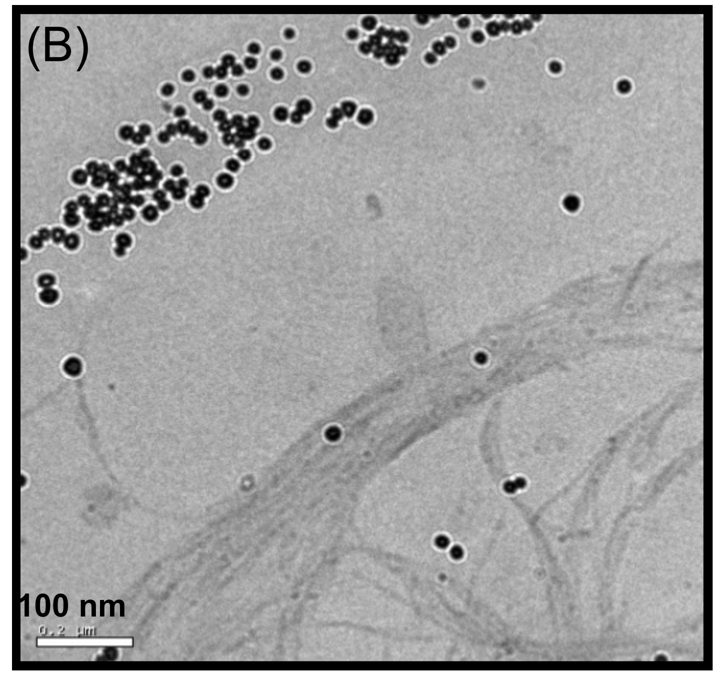
(A) SNOM images of Au-SWNT composite along with the (C) topography. (B) and (D) are their three dimensional representations.



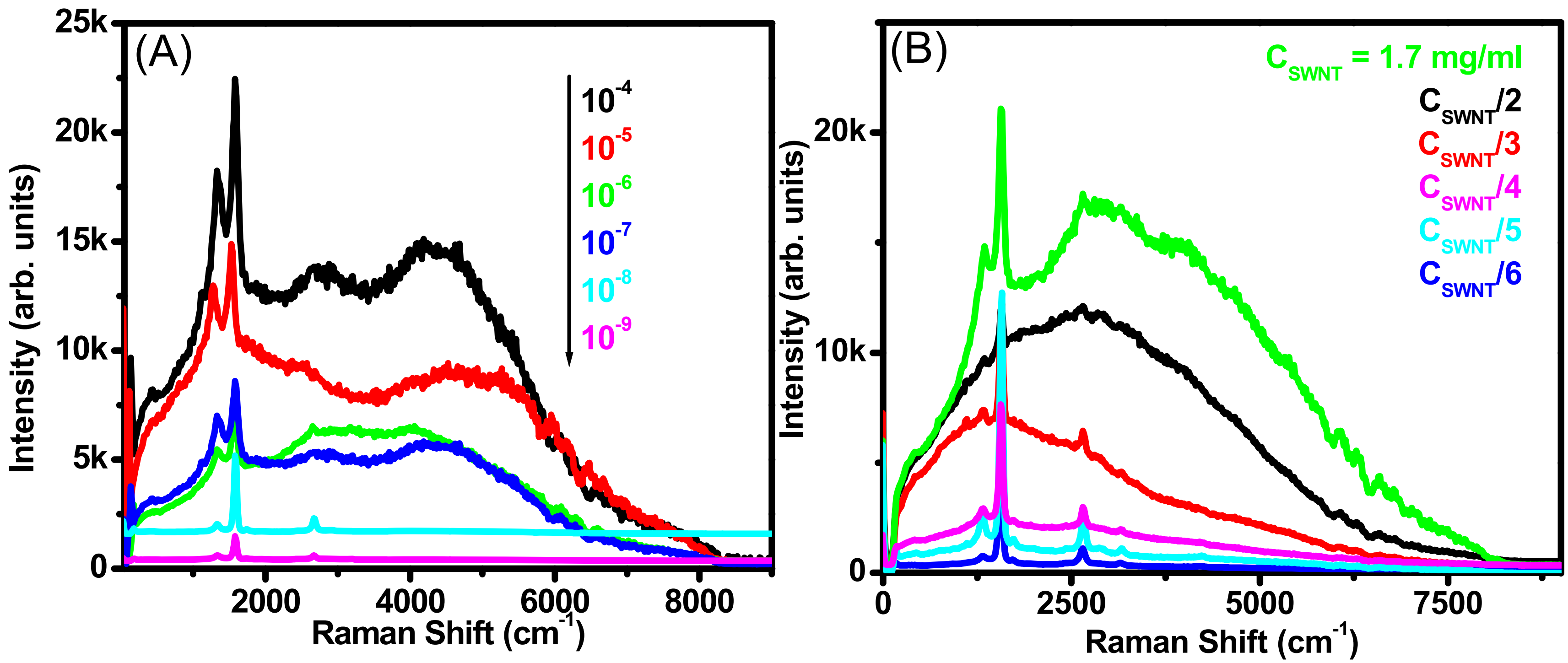
Transmission SNOM images of pristine SWNT based on (A) topography and (B) light intensity.

Supporting experiments

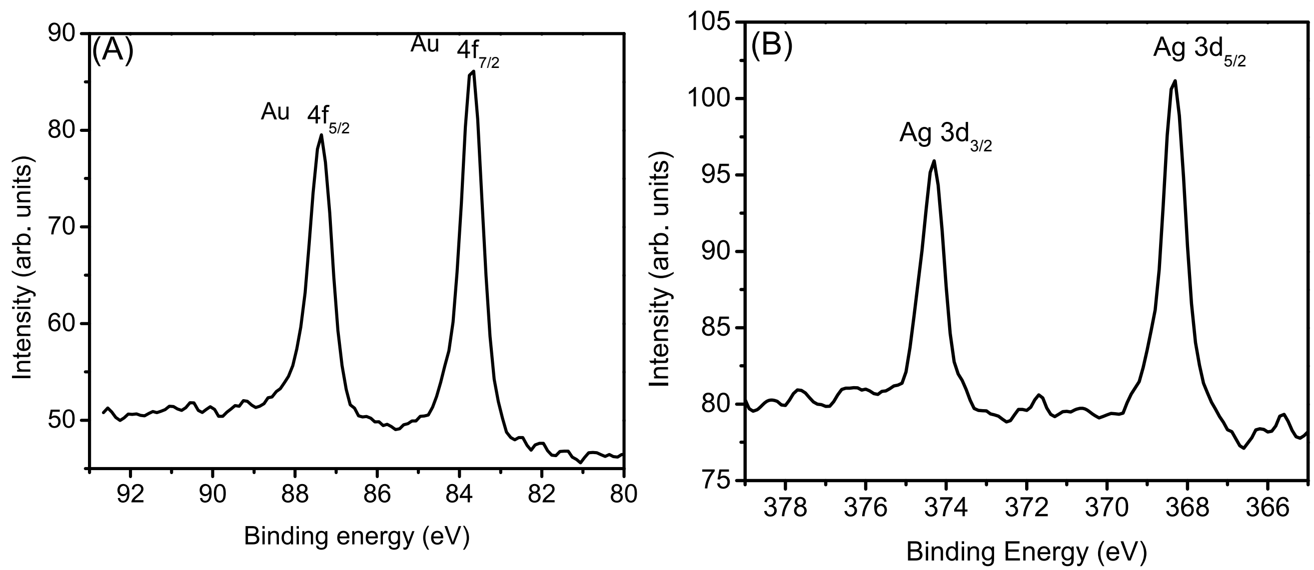




(A) Raman spectra of Ag-SWNT composite measured as a function of CTAB concentration. (B) TEM image of Au-CTAB-SWNT at C_{CTAB} = 10^{-4}M



Raman spectra of Ag-SWNT composite, measured as a function of (A) concentration of Ag nanoparticles, (B) SWNT concentration.



XPS spectra of (A) Au-SWNT and (B) Ag-SWNT composites in the Au 4f and Ag 3d regions, respectively

(n,m) indexing

$$\omega_{RBM} = \frac{C_1}{d_t} + C_2, \text{ where } C_1 \text{ and } C_2 \text{ are constants}$$

$$d_t = \frac{\sqrt{3}a_{c-c}}{\pi}\sqrt{n^2 + nm + m^2}$$

(n,m)	**RBM (cm^{-1},Theoretical)**	**d_t (nm)**	
(10,10)	175	1.37	E_{11}^{m}
(18,0)	168	1.43	
(13,7)	172	1.40	
(17,0)	178	1.35	E_{23}^{s} / E_{32}^{s}
(11,9)	175	1.37	
(12,8)	174	1.38	

So what happens to the metallic SWNTs present in the composite?

Separation protocol

SWNT + isopropyl amine + THF

Ultrasonicate, 1h

SWNT dispersion

Centrifuged @ 40,000 g, 16^0C, 12h

Centrifugate

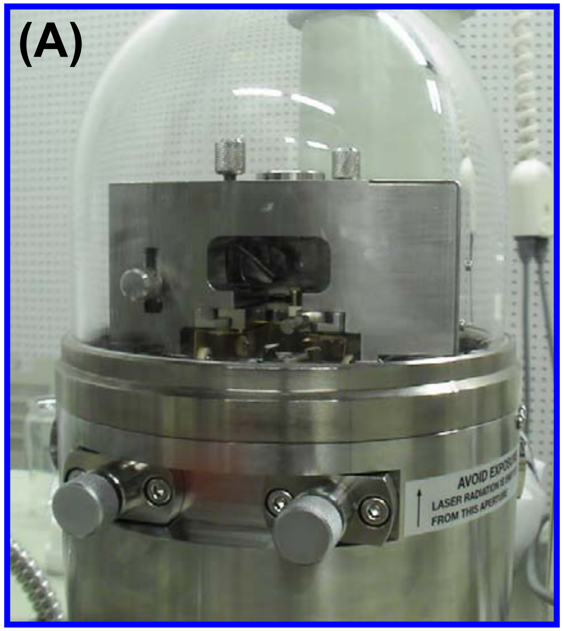
mSWNT

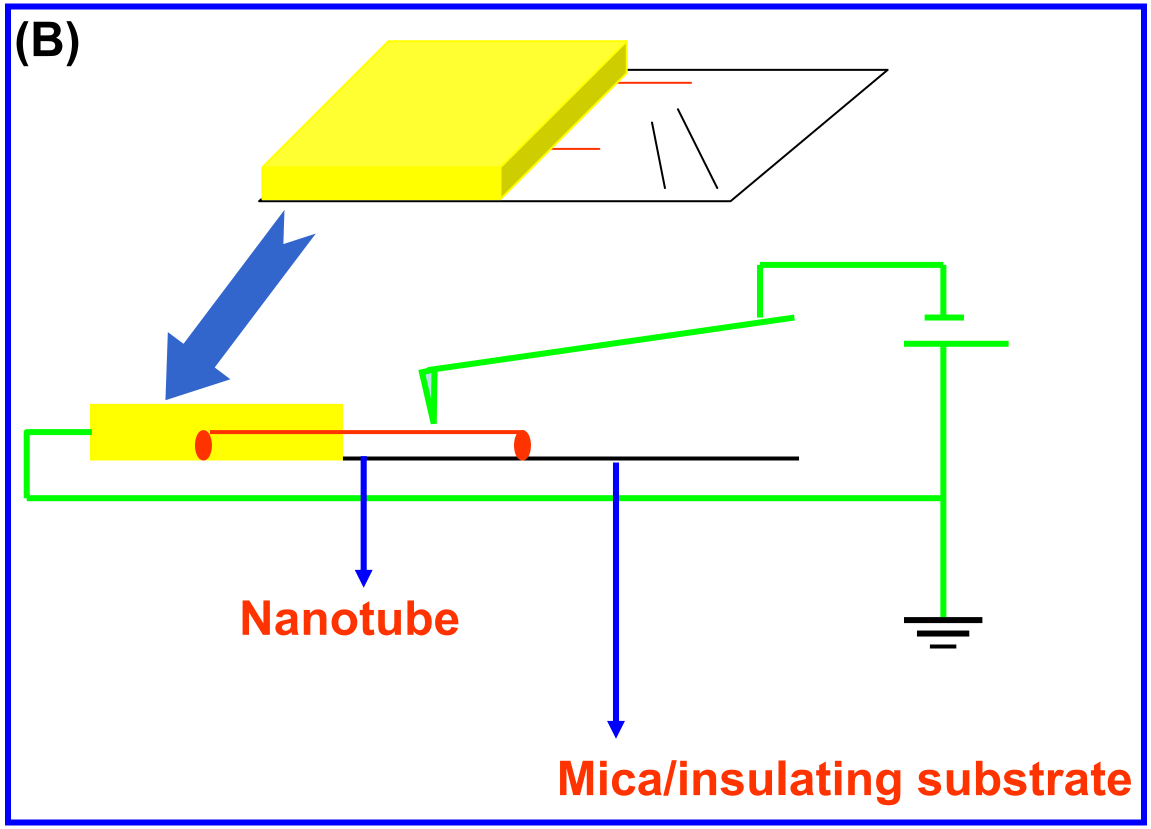
Residue

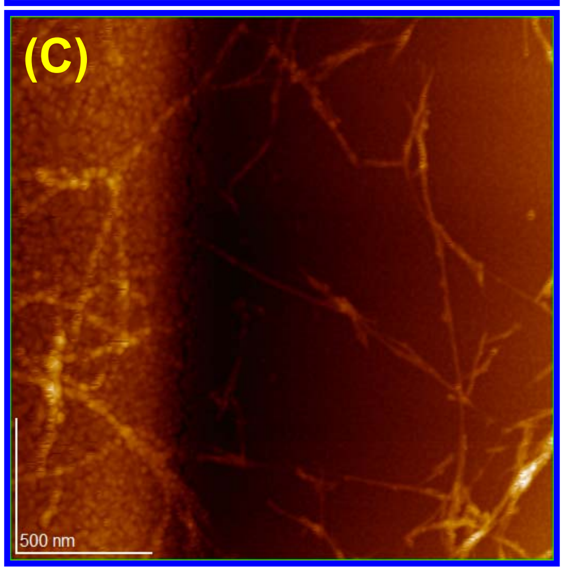
Alkyl amines stabilize metallic SWNT

Maeda, S., *et al J. Am. Chem. Soc.*, **2005**, *127*, 10287.

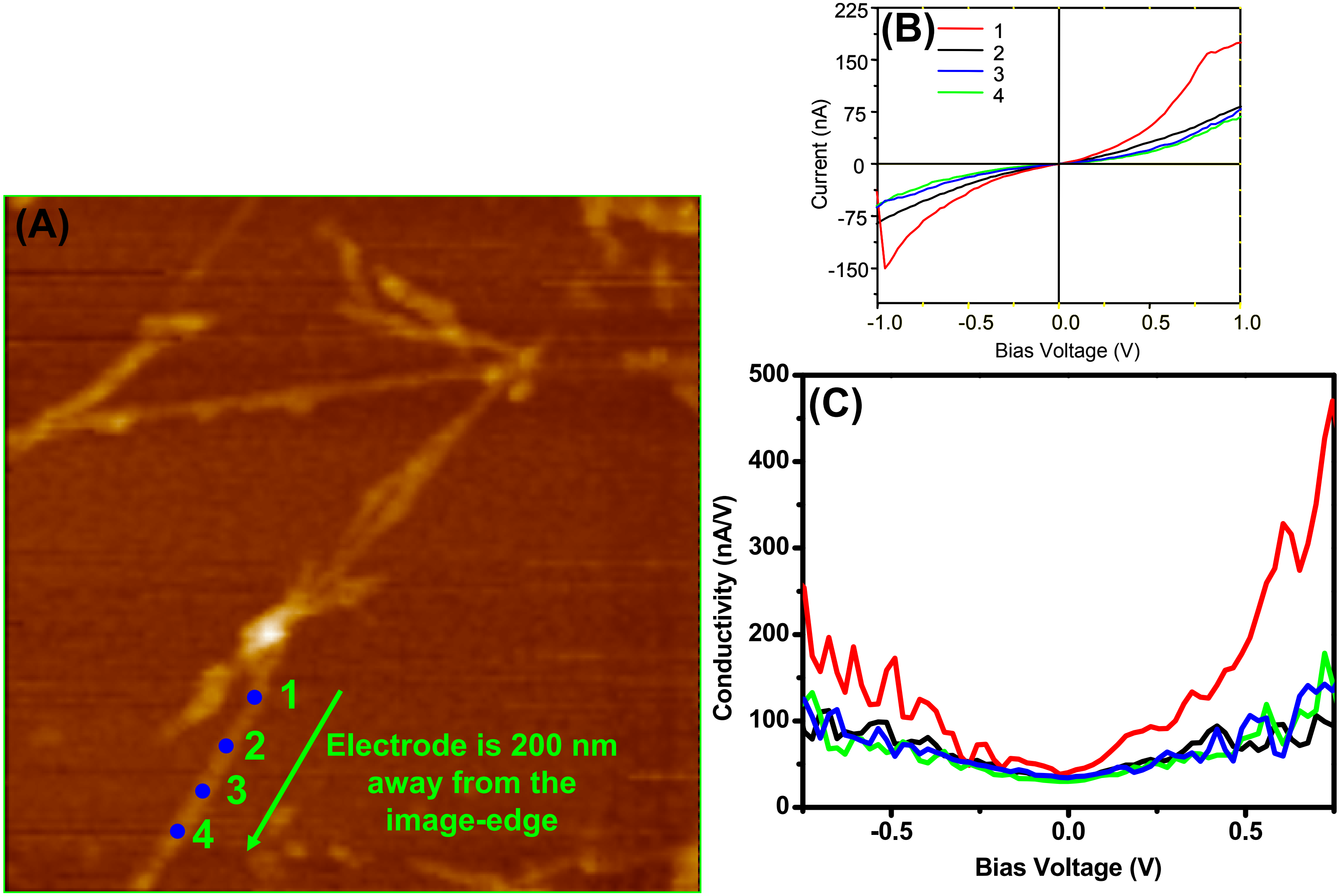
Measurement geometry



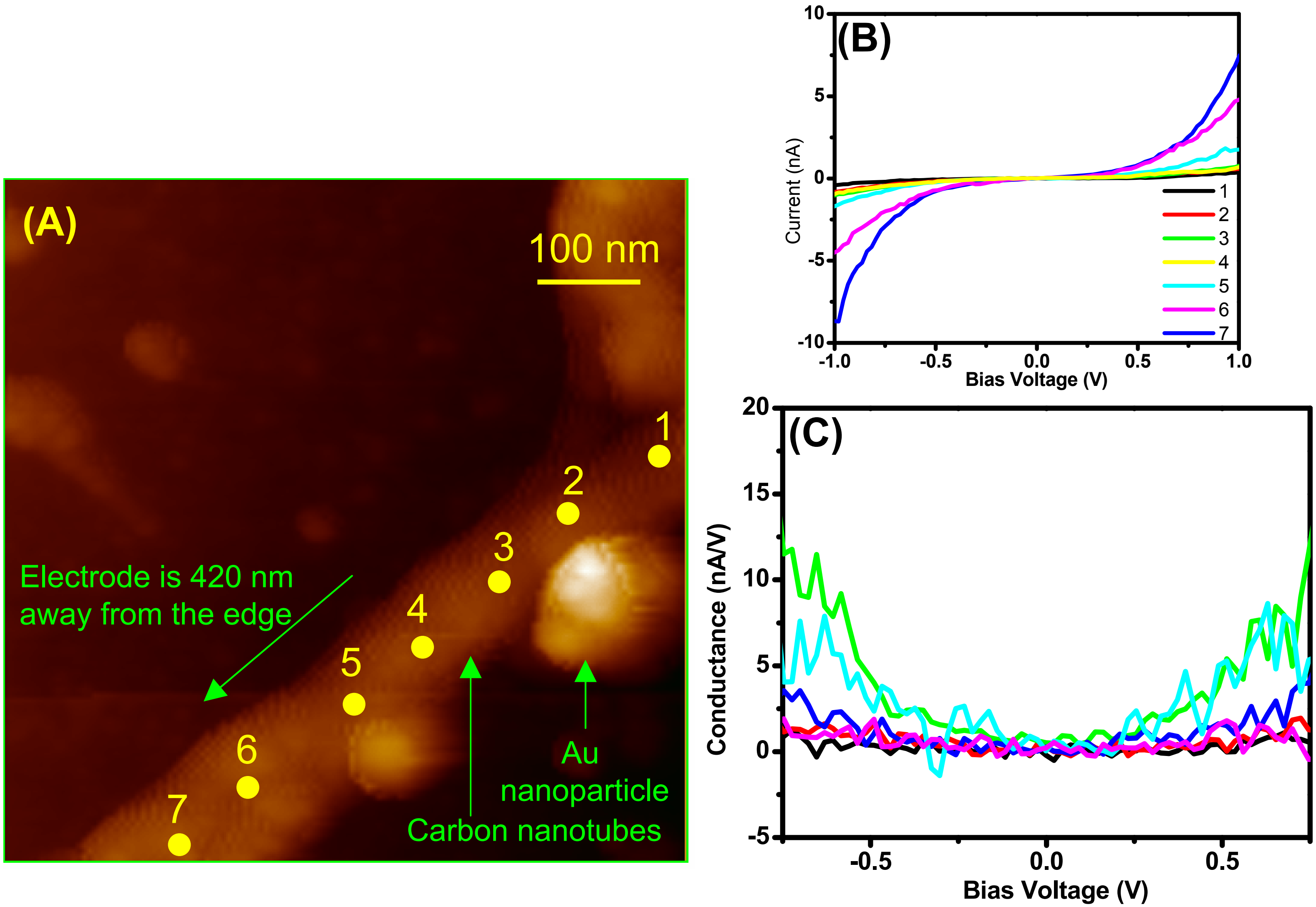




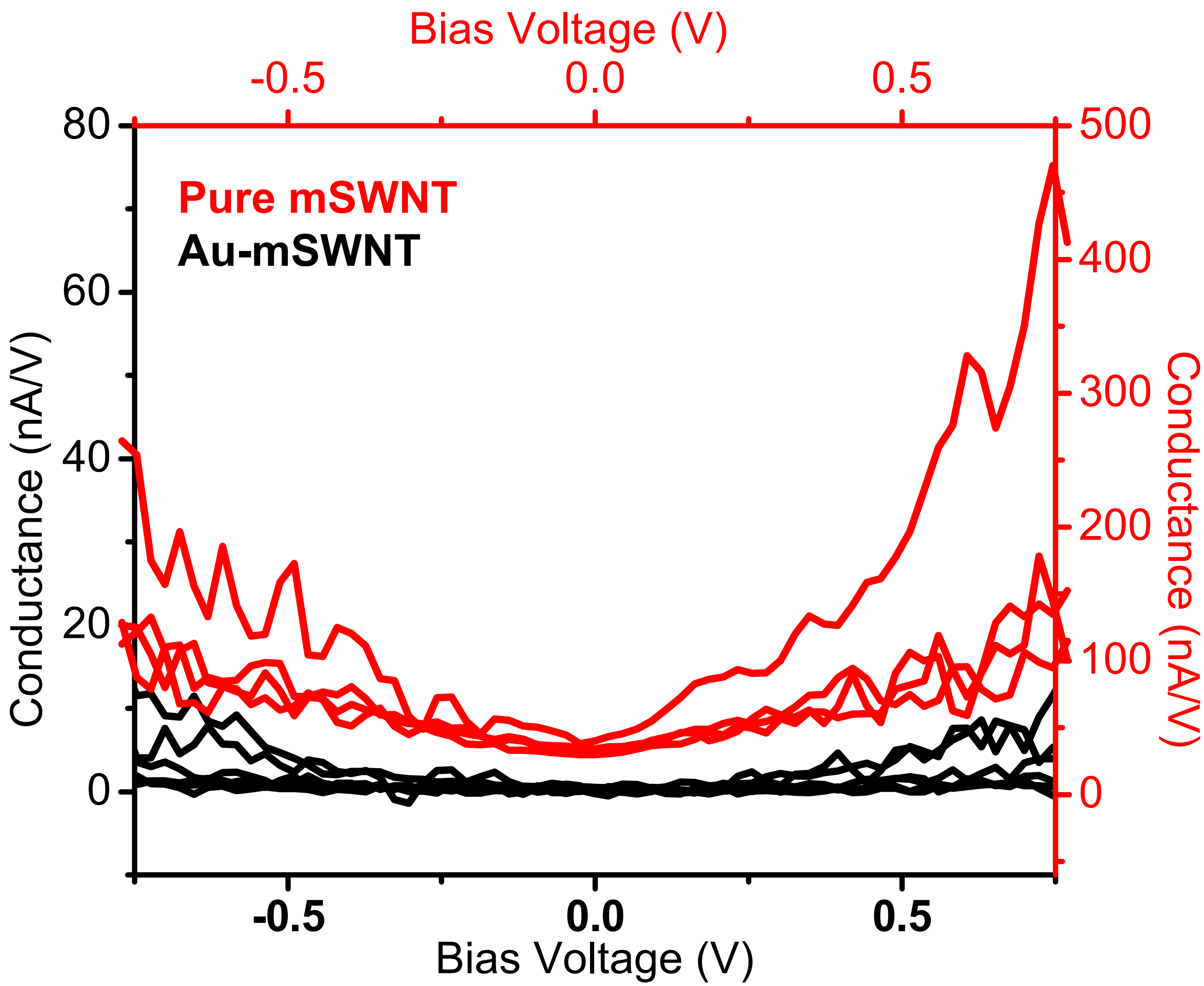
(A) Photograph of the scanning head, (B) schematic of the PCI-AFM measurement and (C) representative AFM image of pristine SWNTs



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

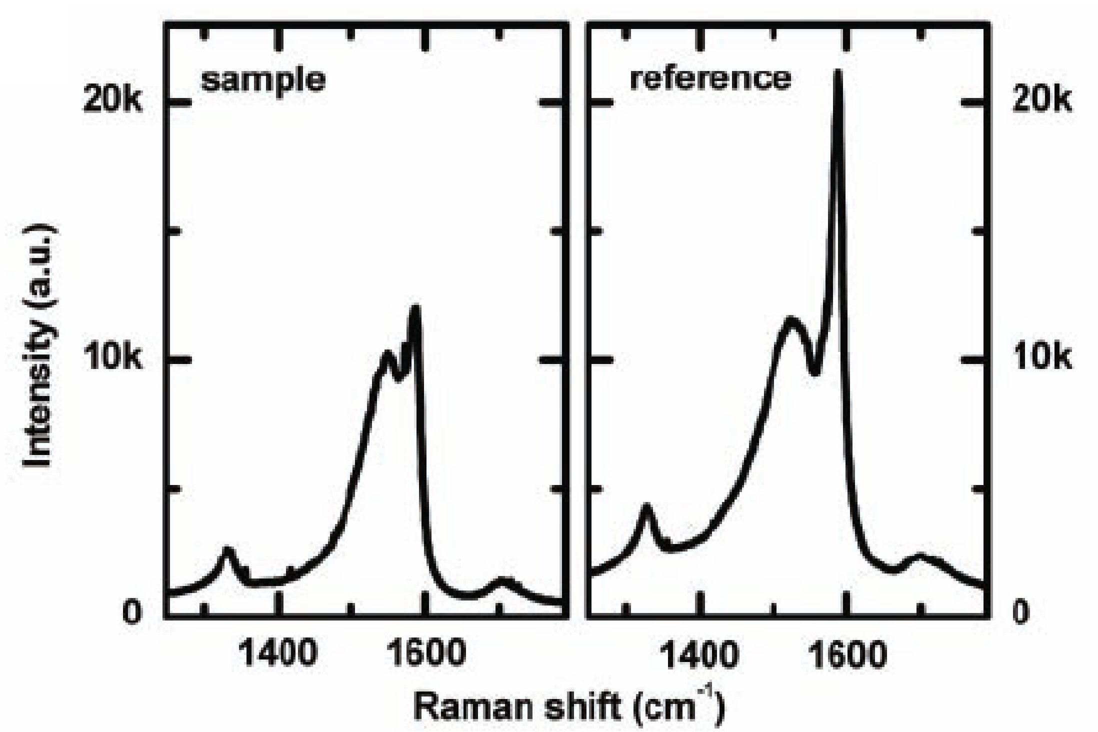


(A) PCI-AFM image of Au-mSWNT with (B) the corresponding I-V curves and (C) Plot of conductance versus bias voltage.



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

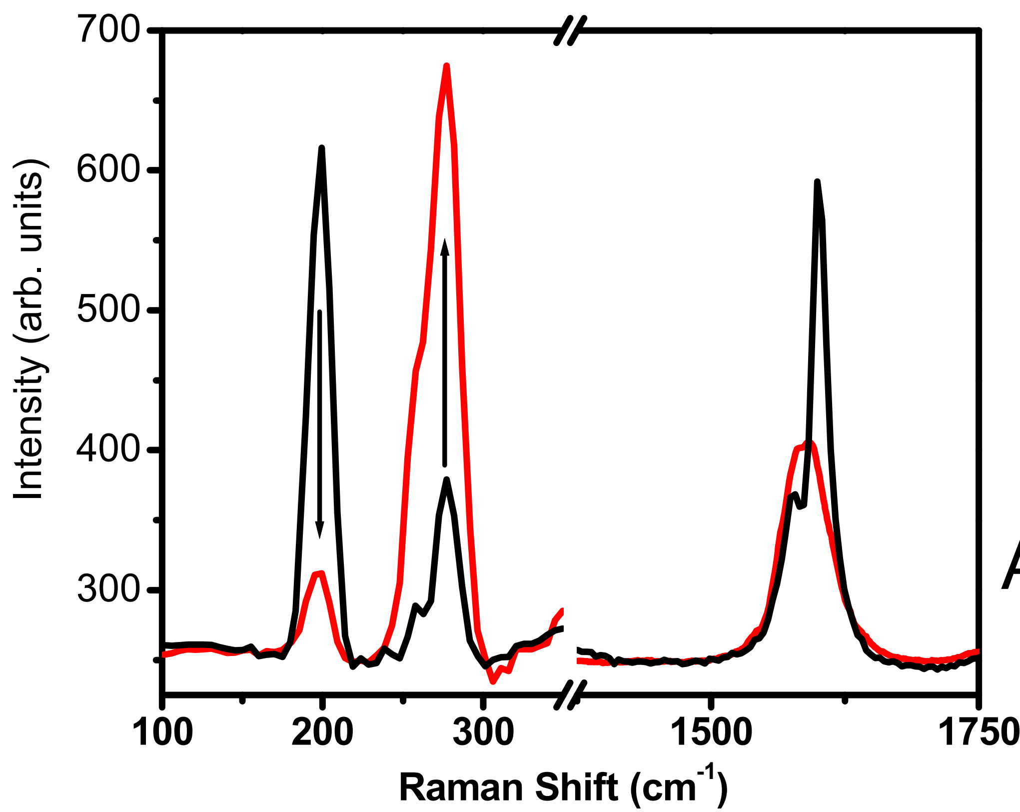
G-band line shapes of metallic and semiconducting SWNT



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

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

Confocal Raman investigations



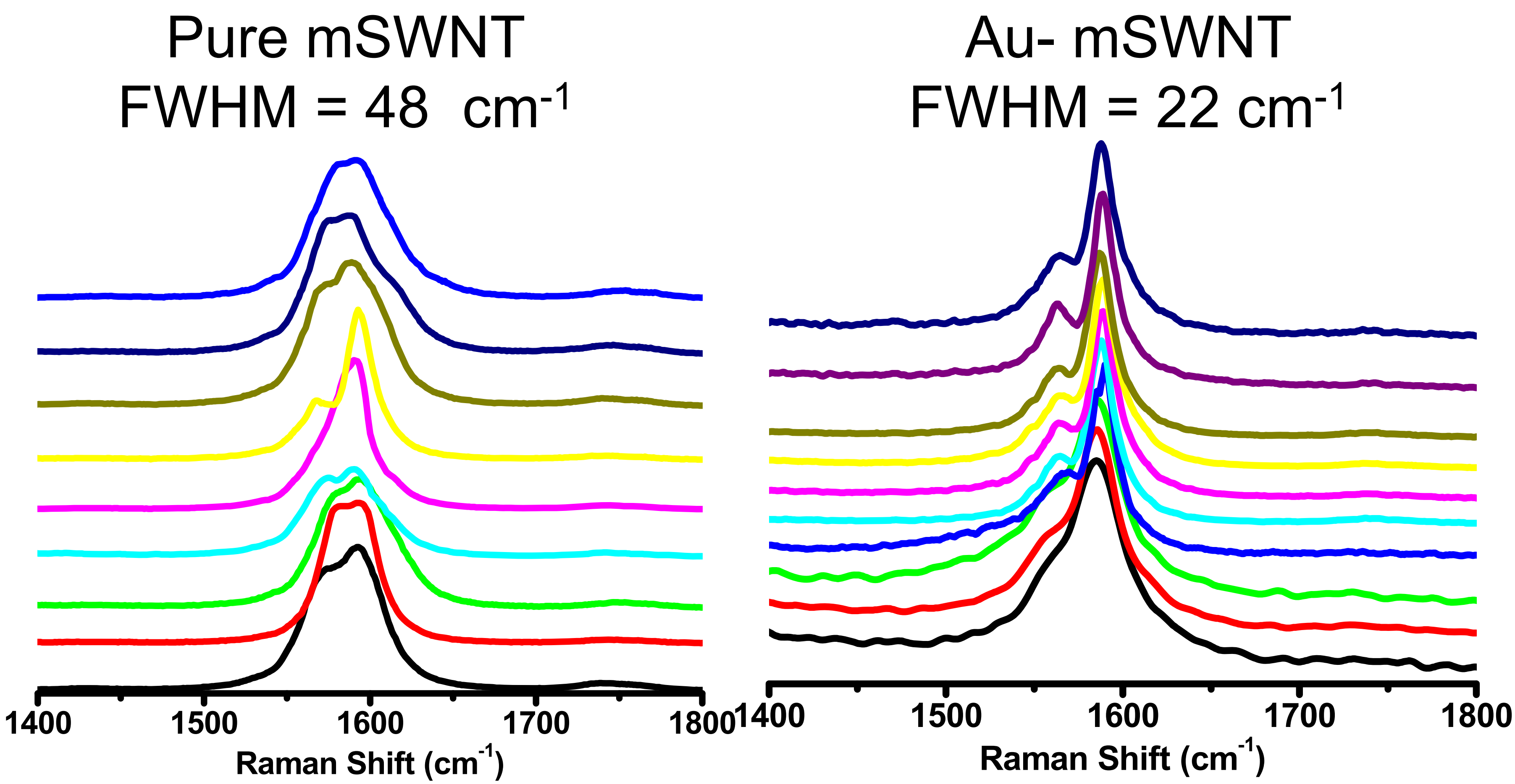
$A_s/A_m = 65.0$

$A_s/A_m = 0.14$

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

What we know:

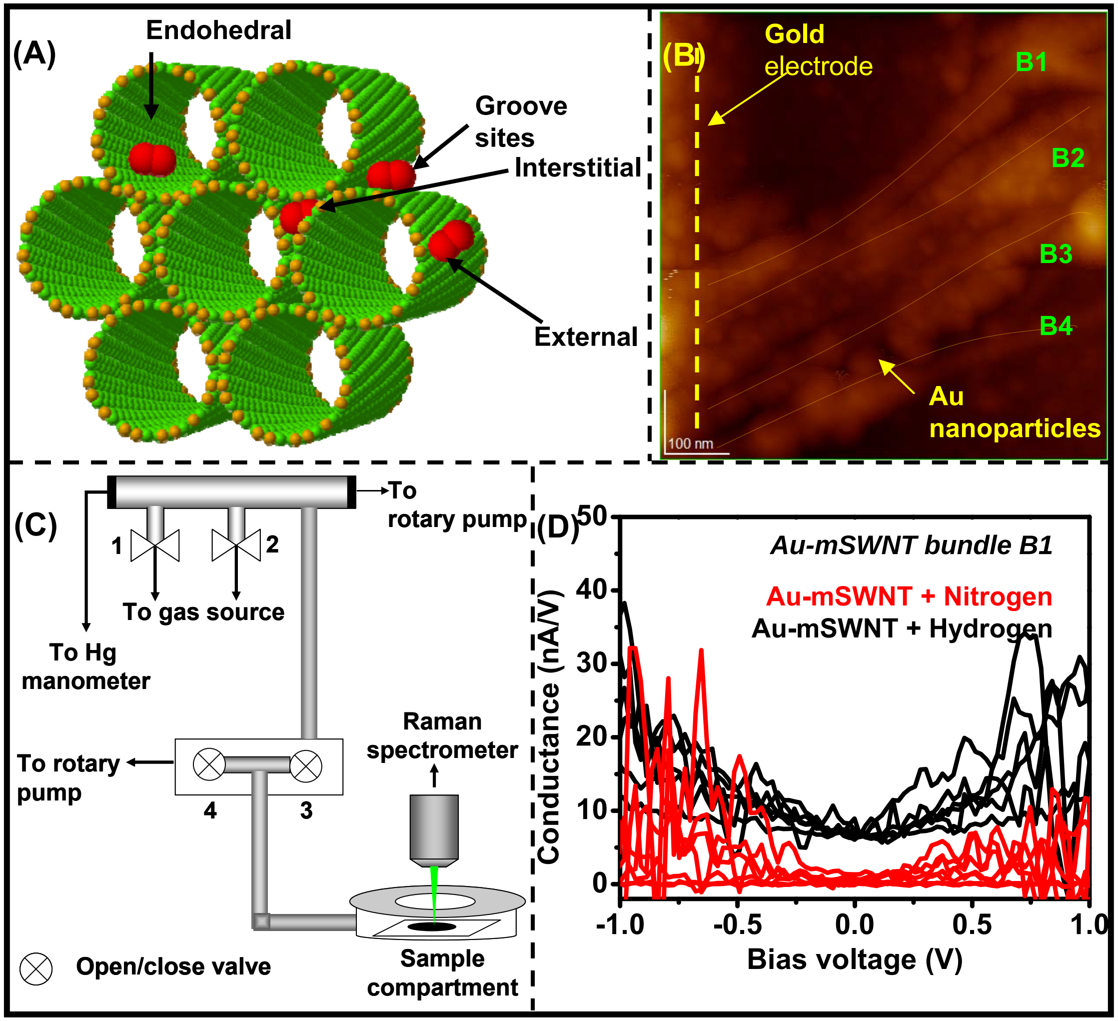
Metallicity of SWNT is destroyed by interaction with nanoparticles.

PCI-AFM and confocal Raman confirm this M-S transition.

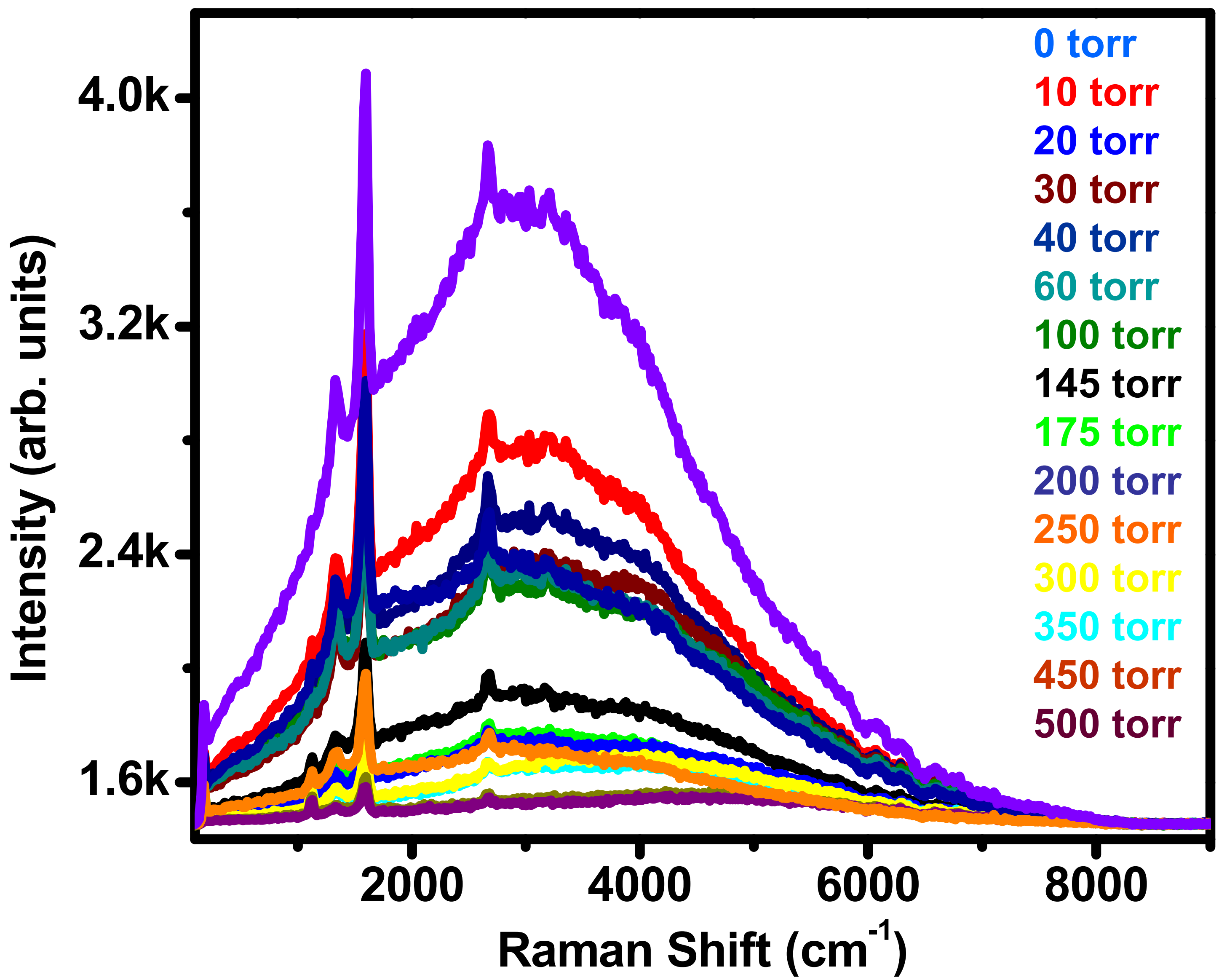
mSWNT fluoresce when their metallicity is destroyed.

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

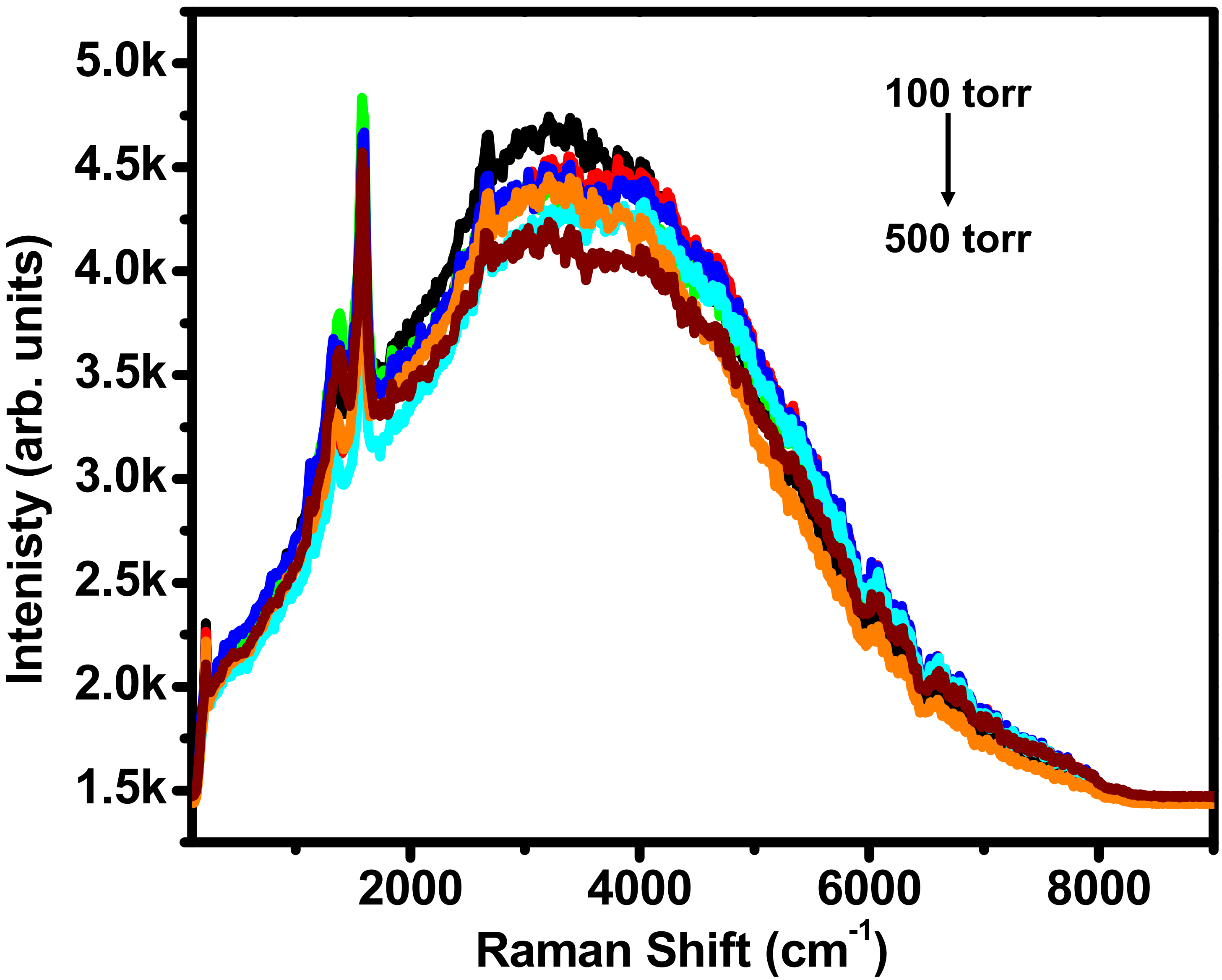
C. Subramaniam and T. Pradeep Patent applications 2006, 2007



(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).

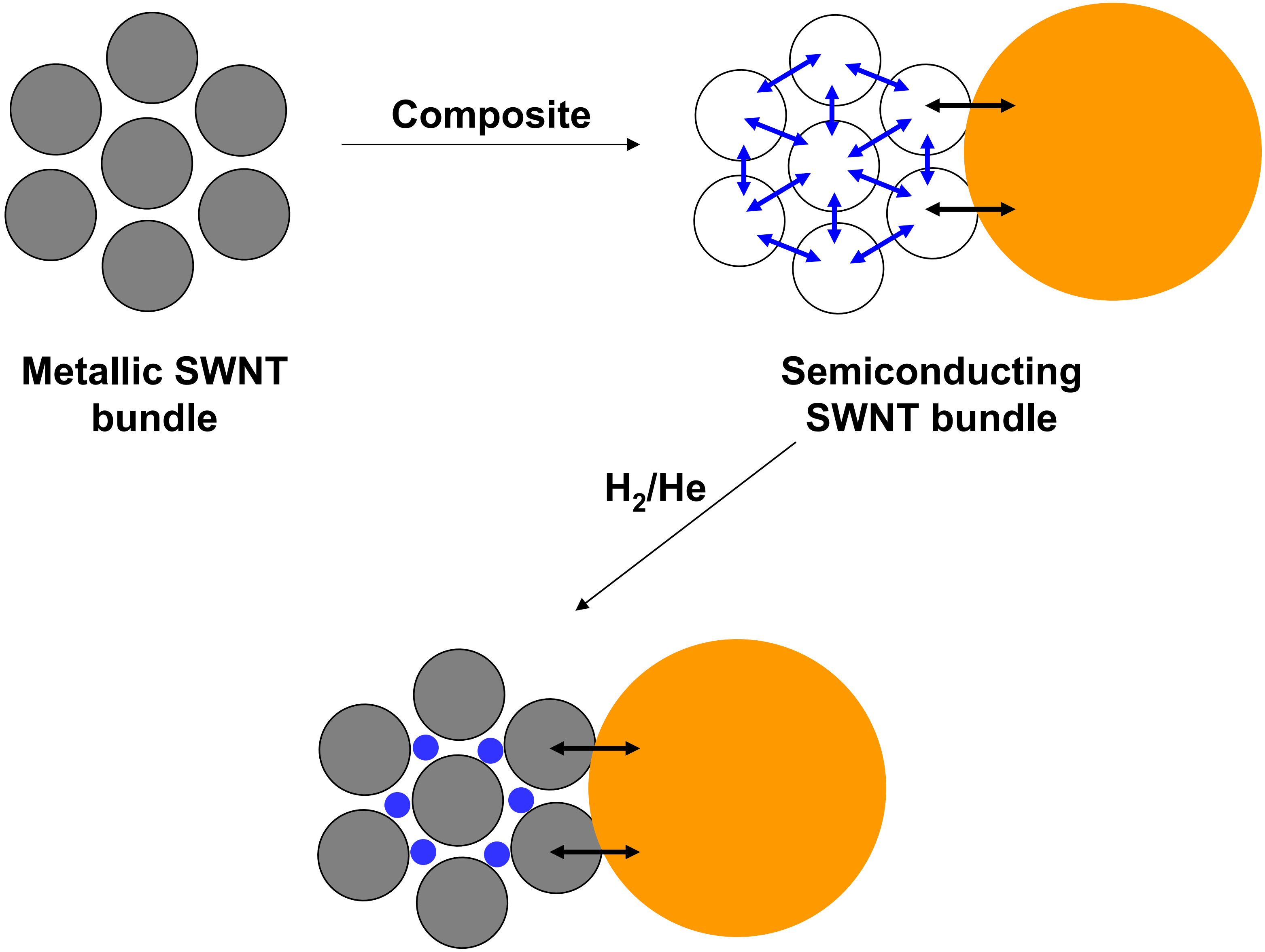


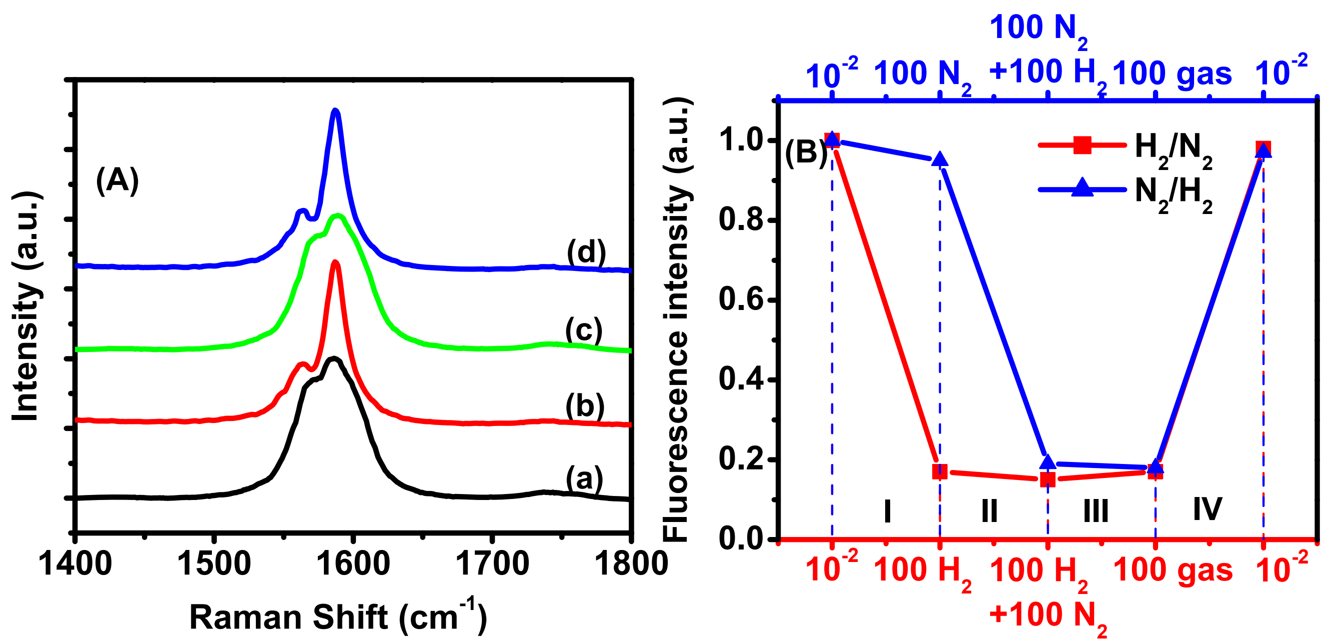
Au-SWNTs exposed to H_2 gas at various partial pressures.



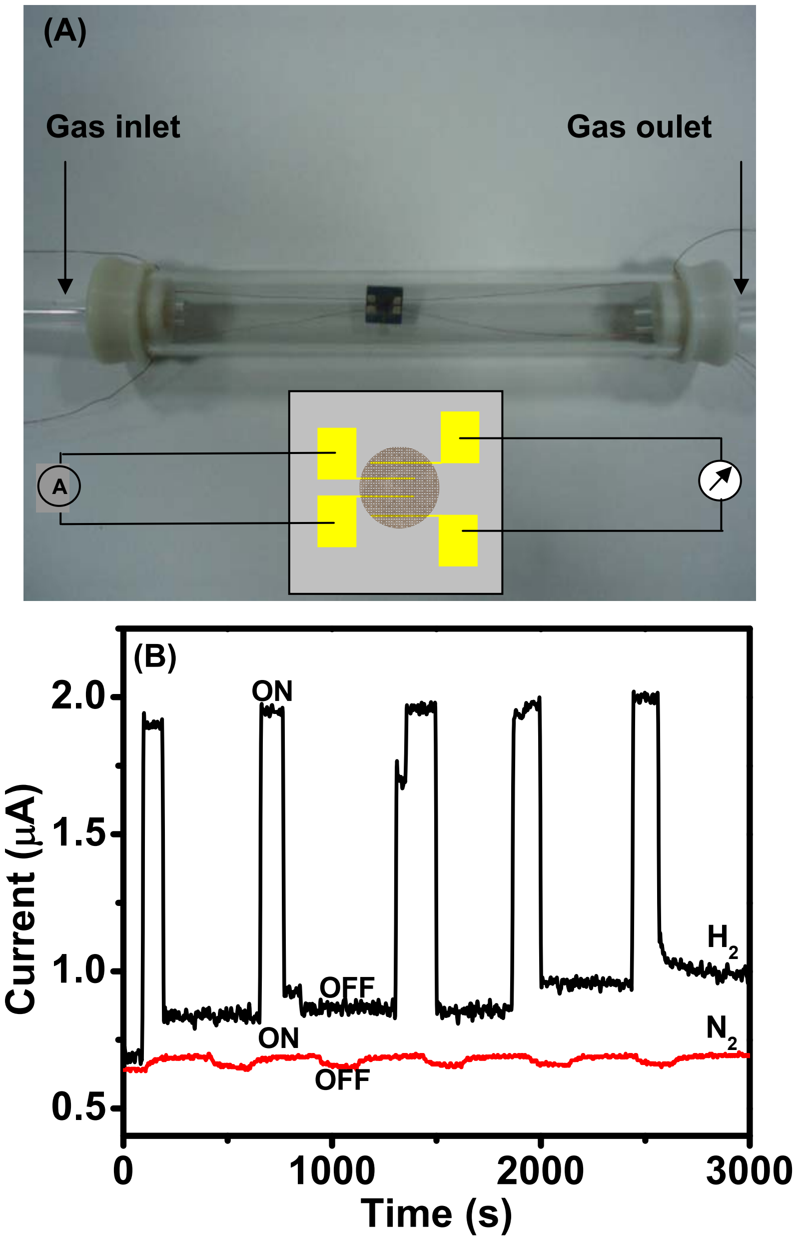
Au-SWNTs exposed to N_2 gas at various partial pressures.

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.

Summary and conclusions

New materials for infrared absorption

Infrared filters can be developed with novel nanomaterials

Visible emission in carbon nanotube composites

This happens when nanoparticles bind nanotubes which makes a metal-semiconductor transition

This emission can be used for gas sensing

Other possibilities with M-S transition

C. Subramaniam and T. Pradeep Patent application 2008

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

IIT Madras

Thank you all