# Visible light emission and metal-semiconductor transition in single walled carbon nanotube-noble metal nanoparticle composites

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# Acknowledgements

C. Subramaniam

Collaborators

T. Ogawa, Institute of Molecular Science, Okazaki

J. Chakrabarti, SN Bose Centre, Kolkata

Chandrabhas Narayana, JNCASR, Bangalore

Nanoscience and Nanotechnology Initiative of the DST

Confocal Raman Microscope

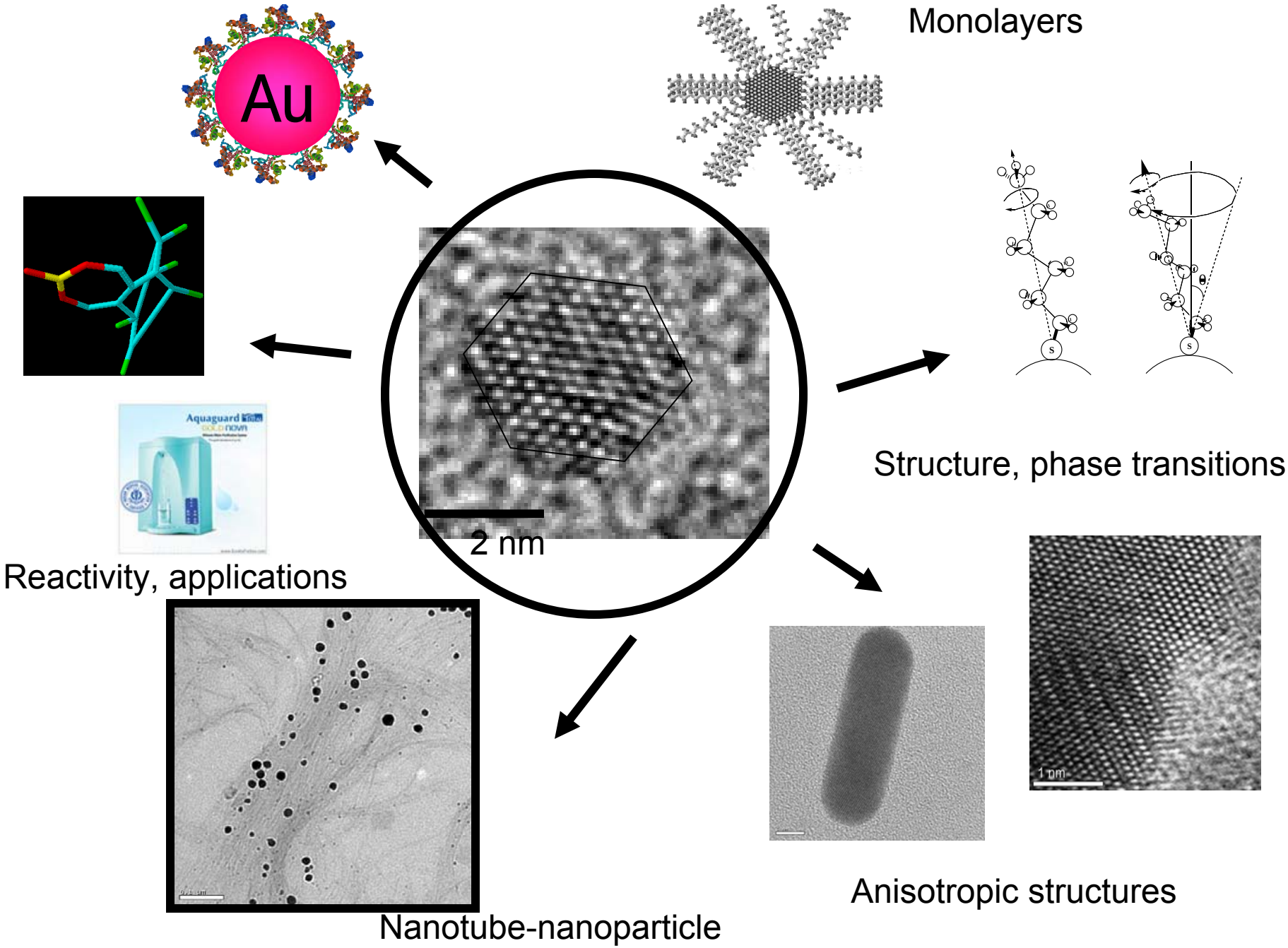
Transmission Electron Microscope

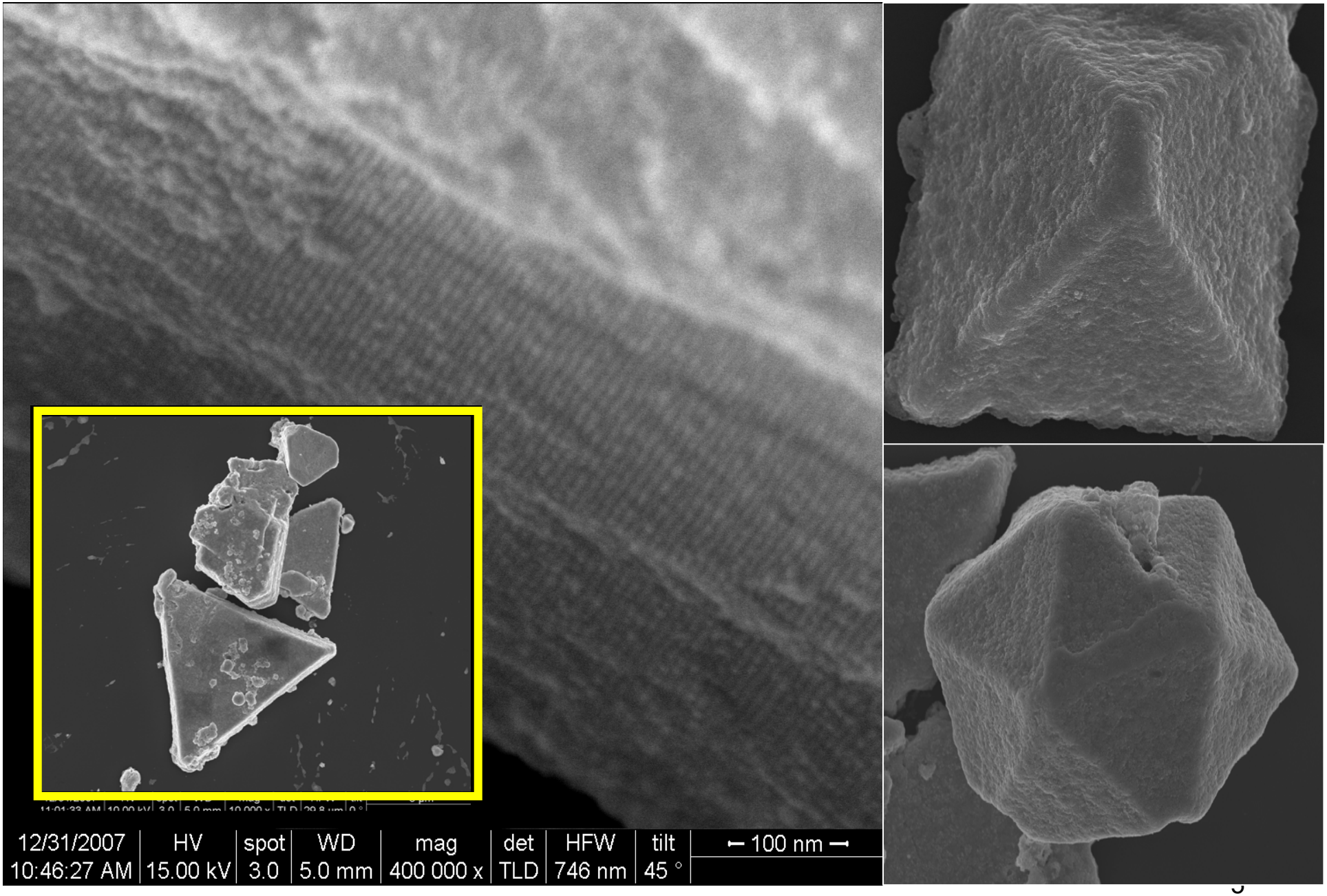
MALDI TOF MS


QTrap MS

Ultramicrotome

Nanoscience and Nanotechnology Initiative of the DST


Au
Monolayers
2 nm
Structure, phase transitions
Reactivity, applications
Aquaguard
Nanotube-nanoparticle
Anisotropic structures
1 nm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HV
15.00 kV
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WD
5.0 mm
mag
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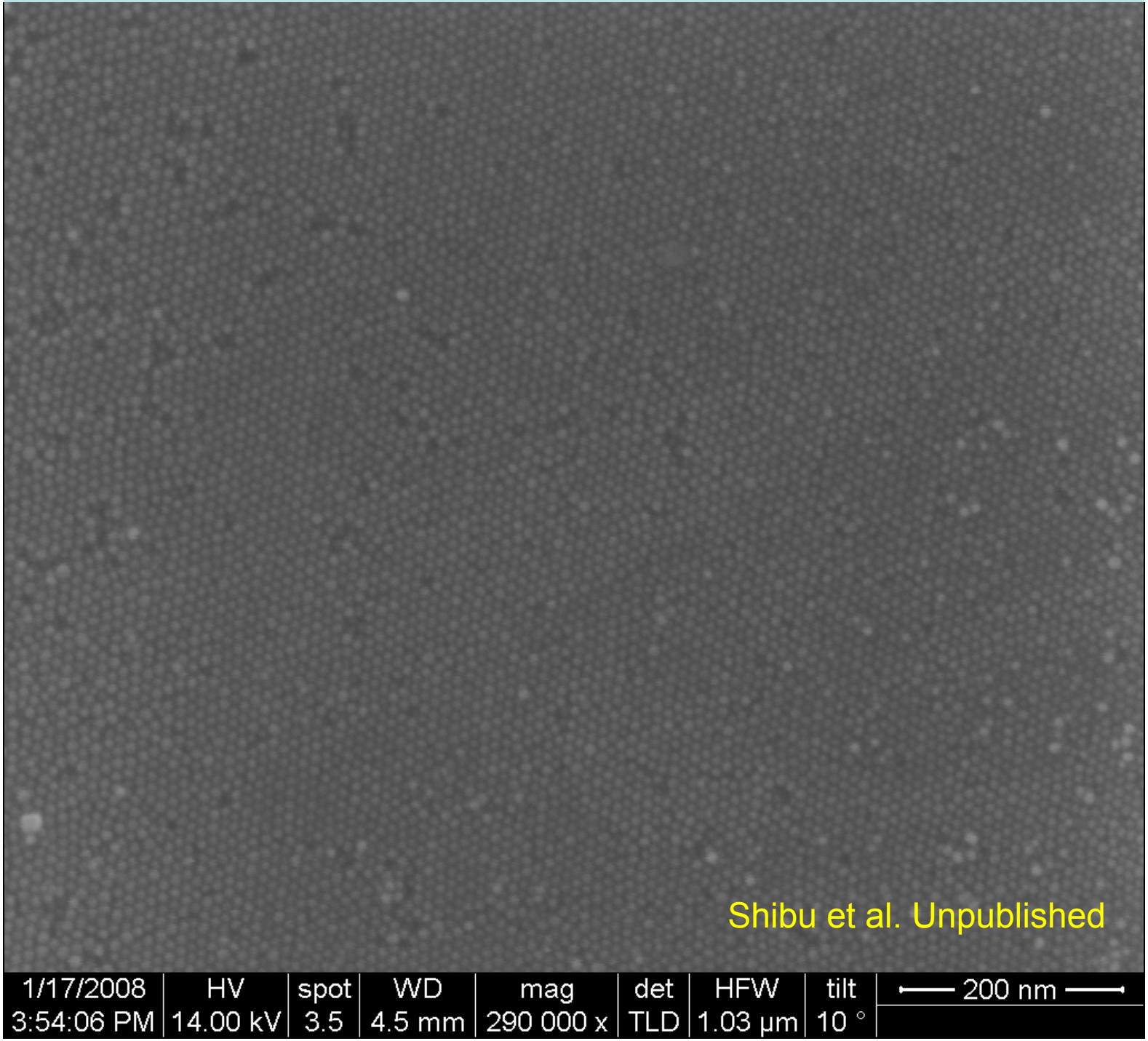
det
TLD
HFW
746 nm
tilt
45 °
100 nm


Shibu et al. Unpublished
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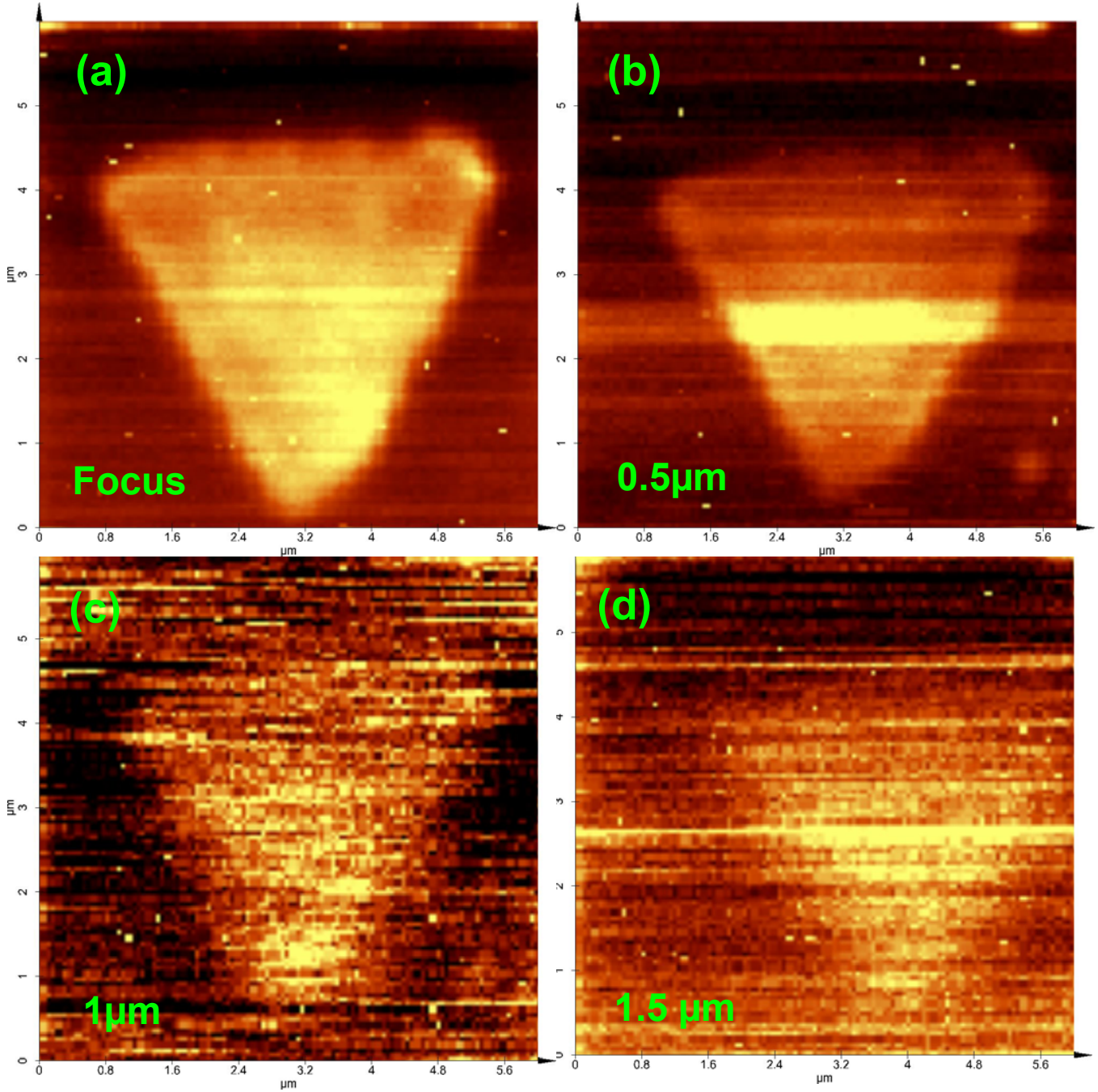
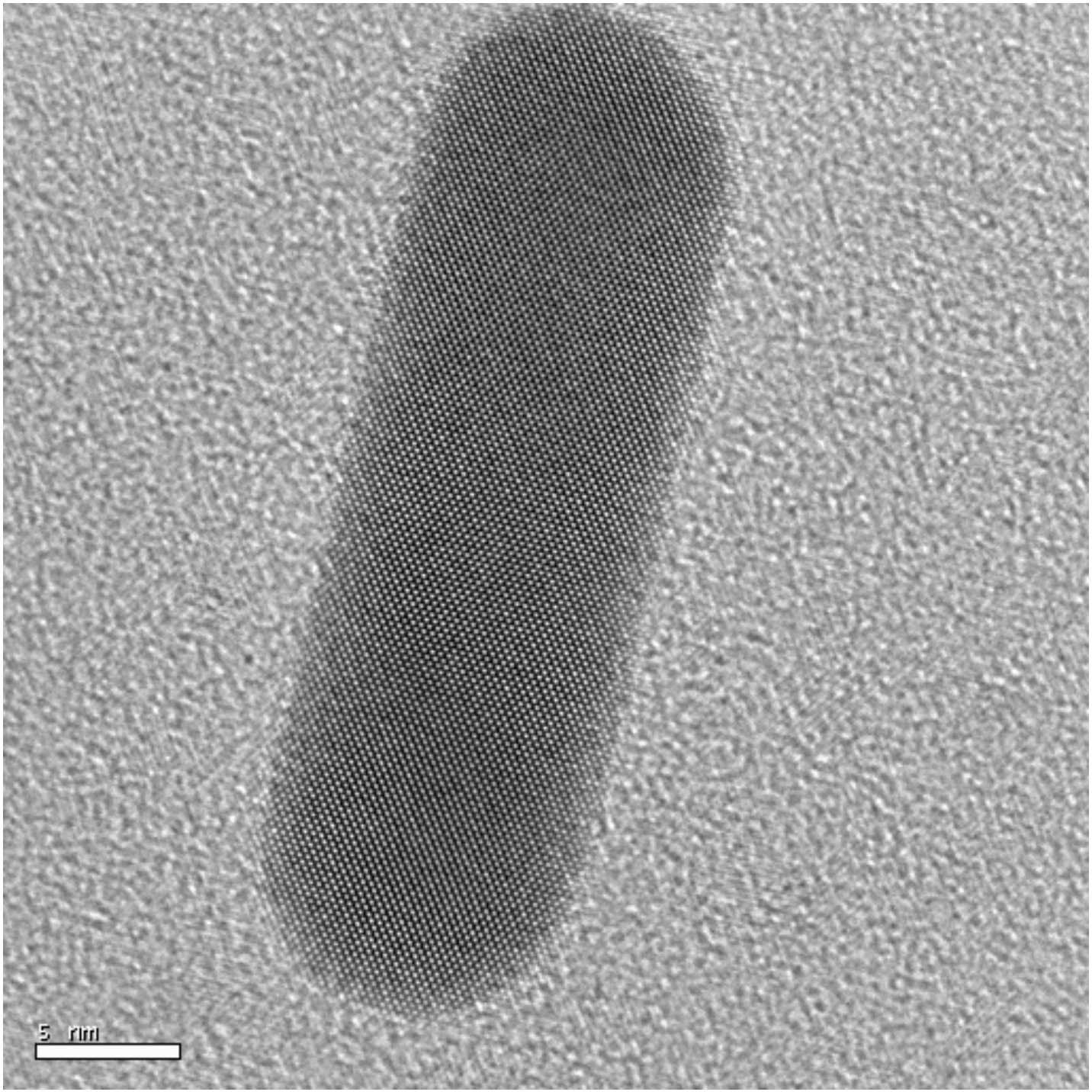
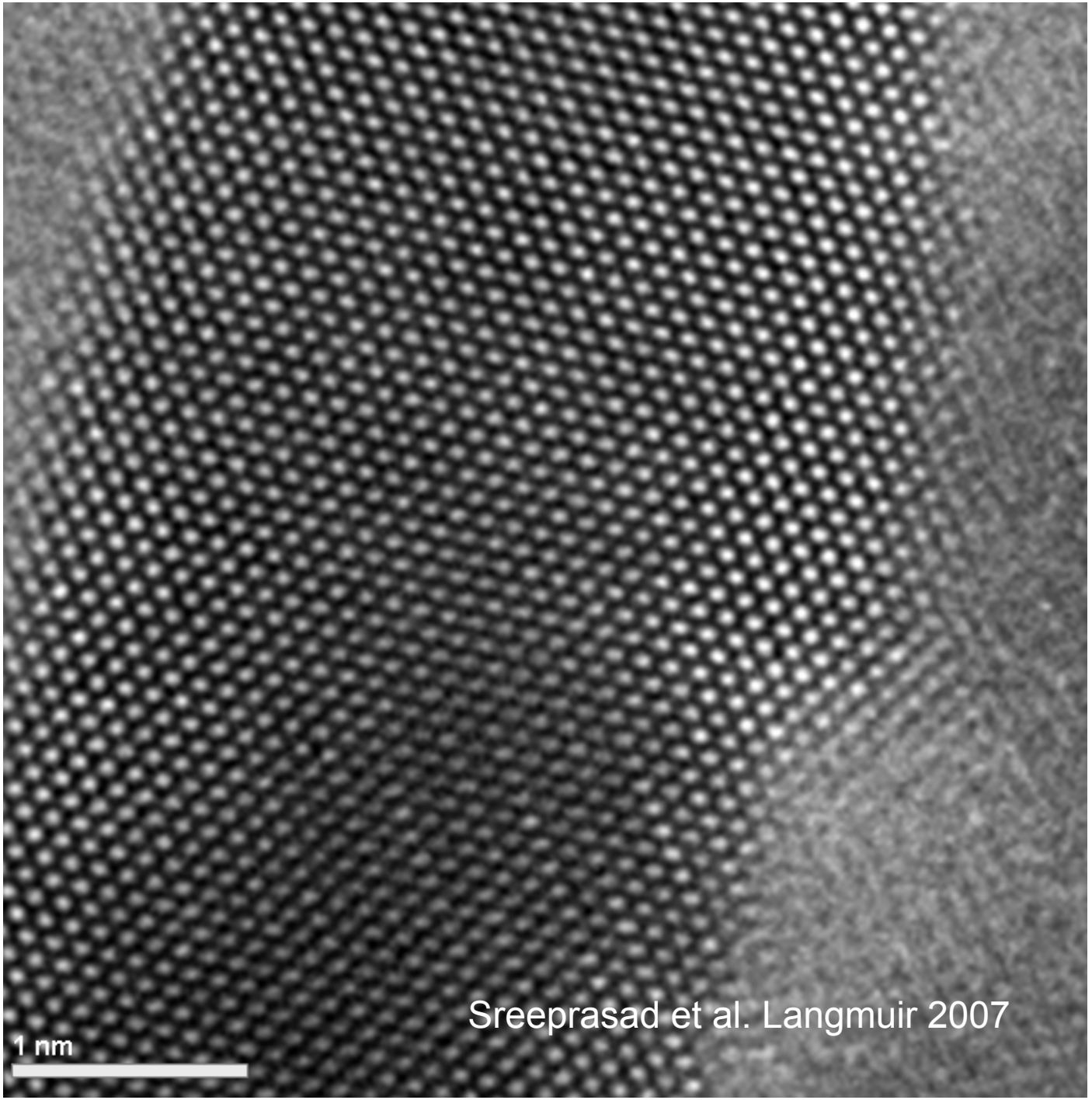
10 °
200 nm

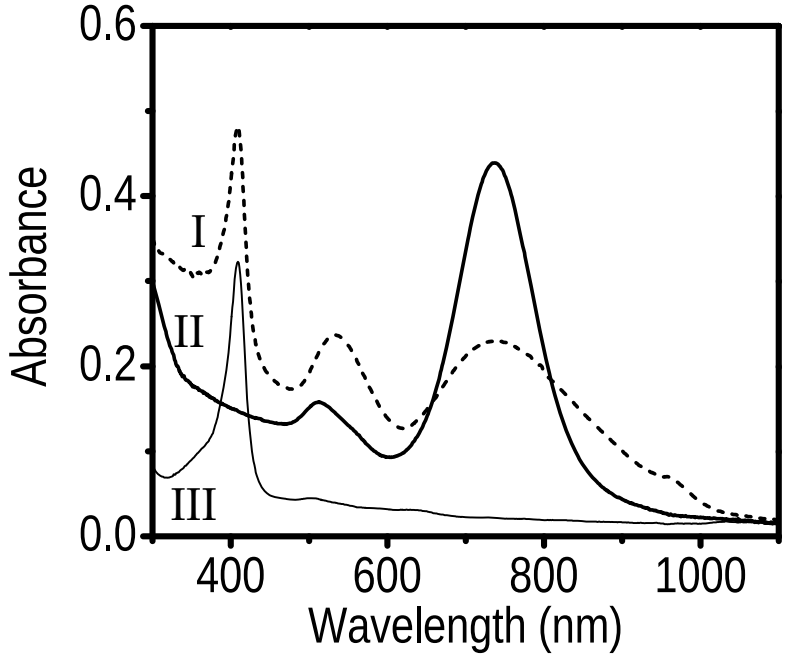


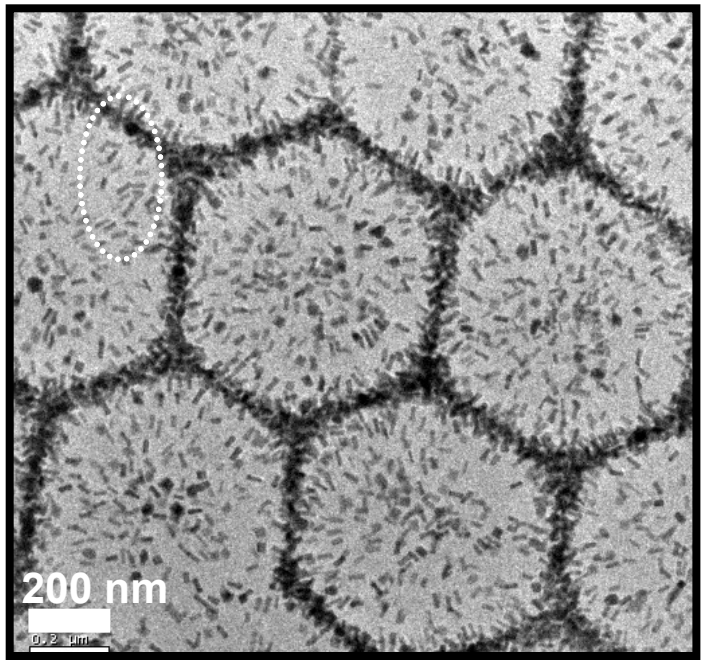

With K. Kimura, Hyogo University


5 nm

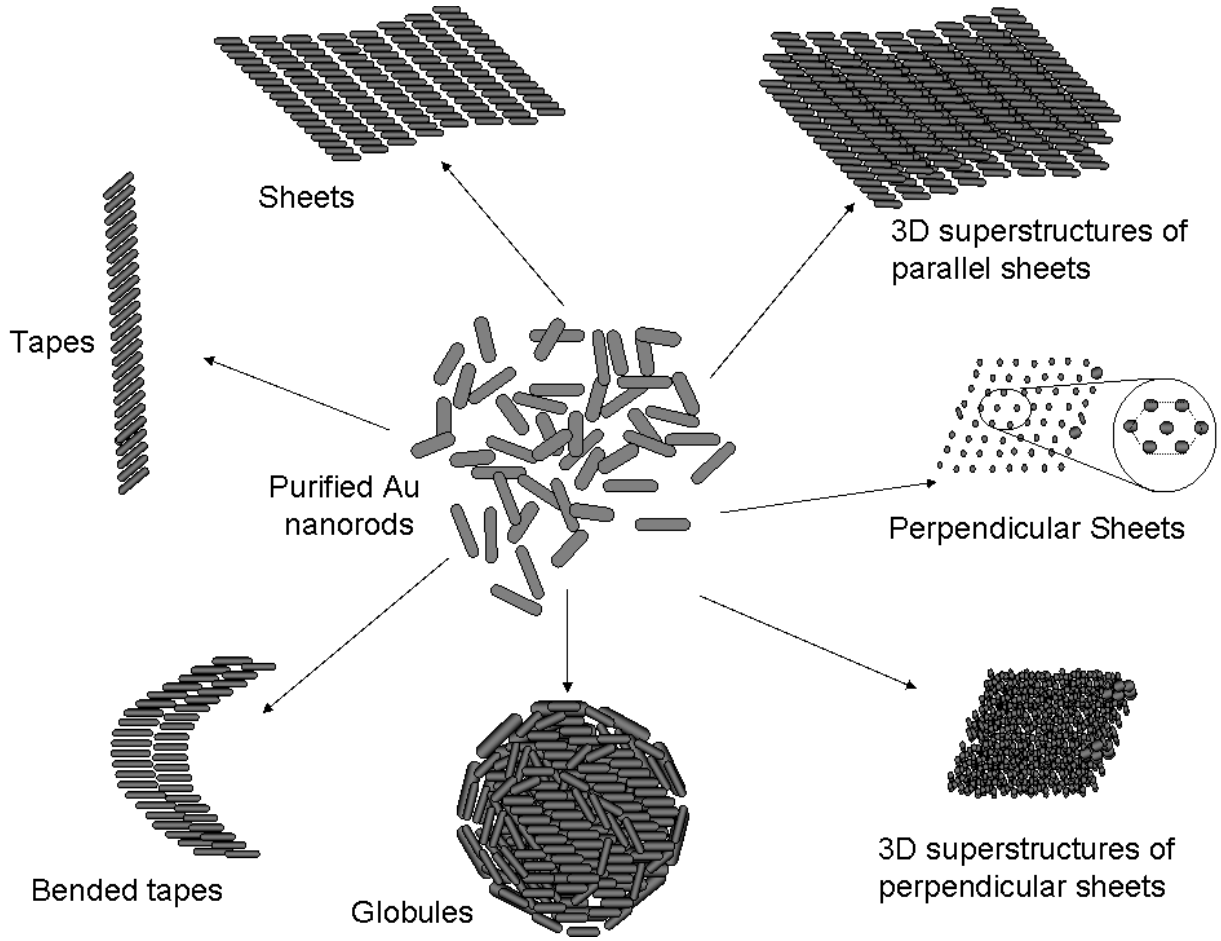


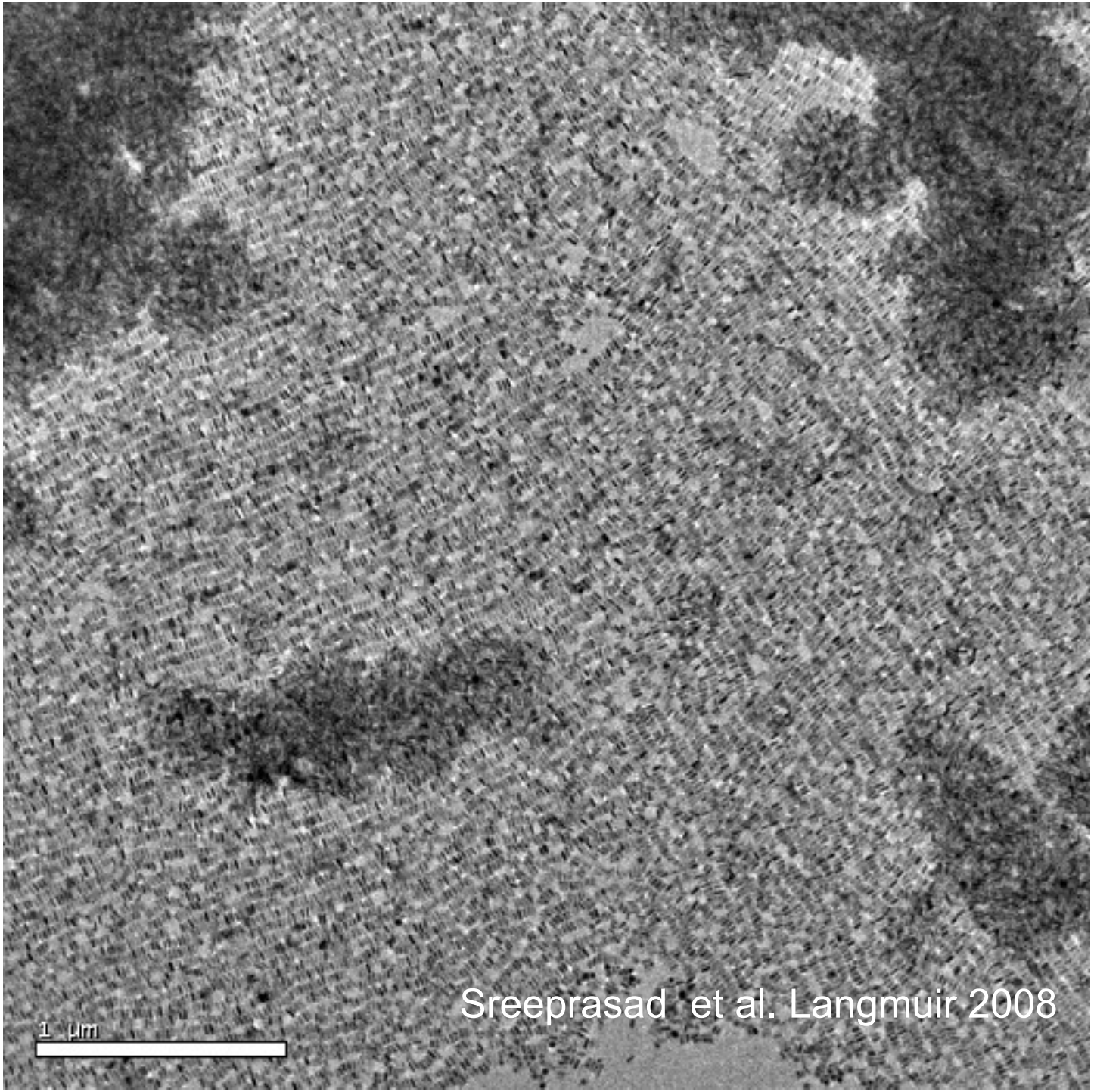

Sreeprasad et al. Langmuir 2007



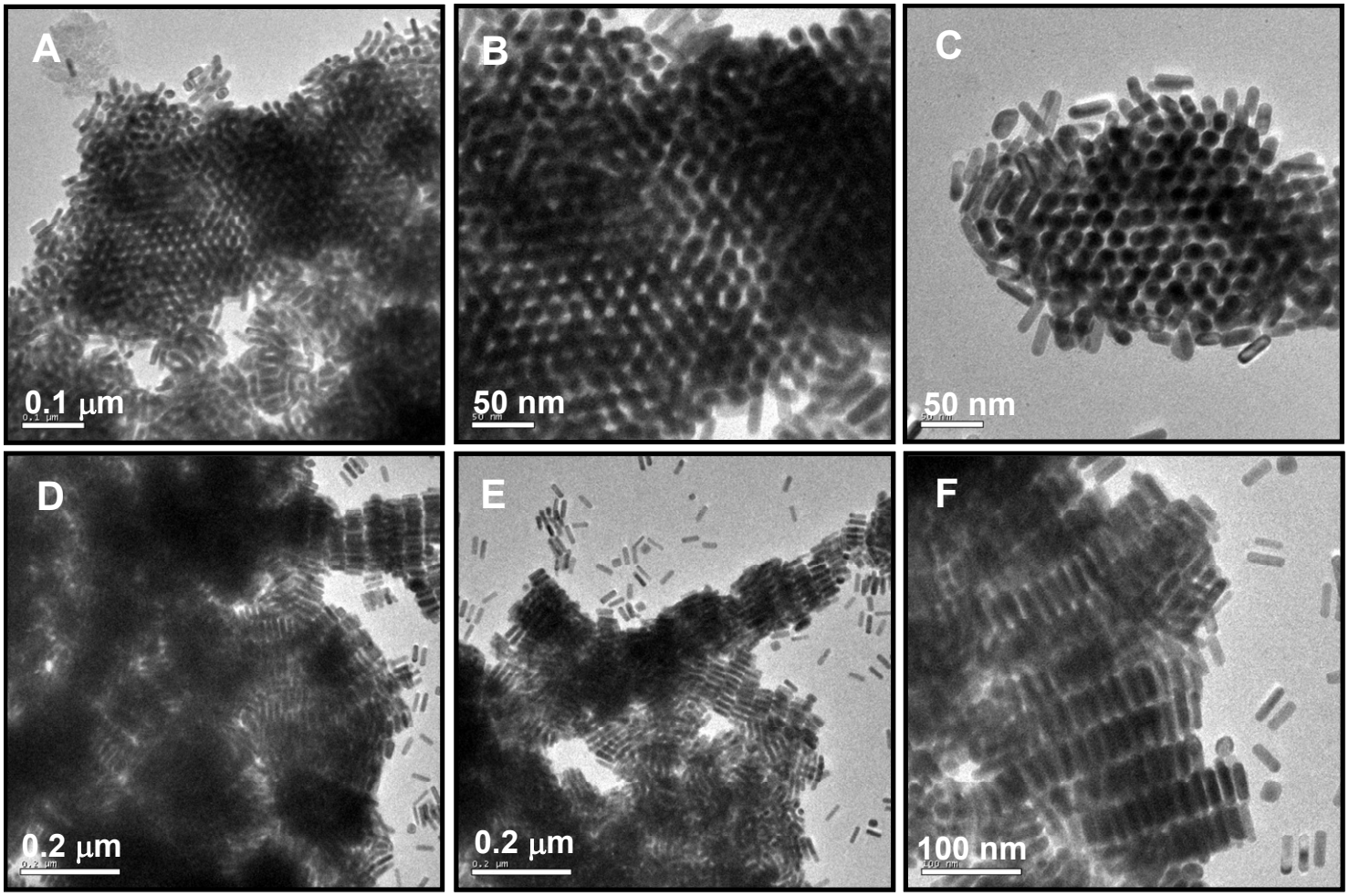



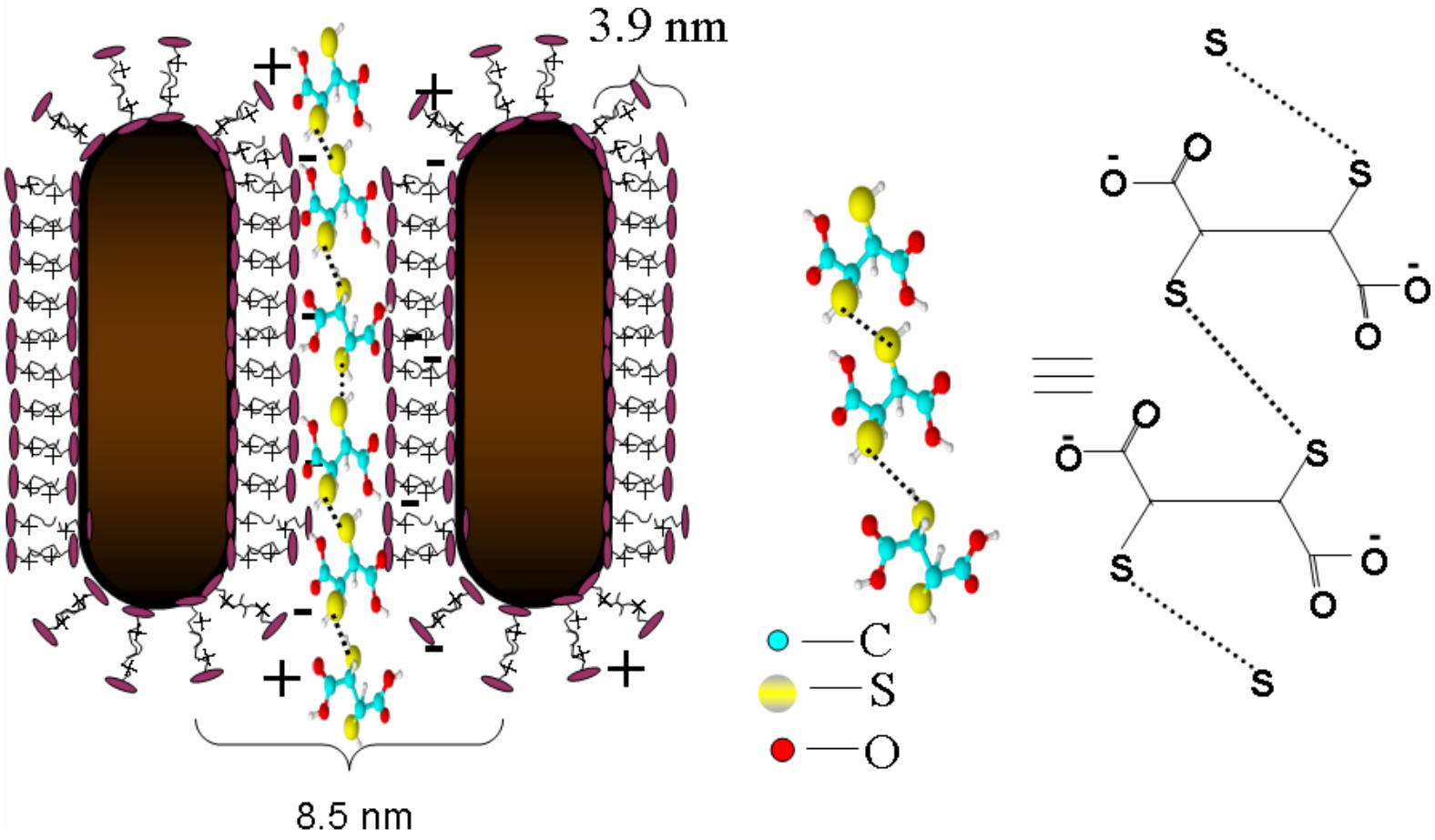

Rajeev Kumar et al. Langmuir 2007

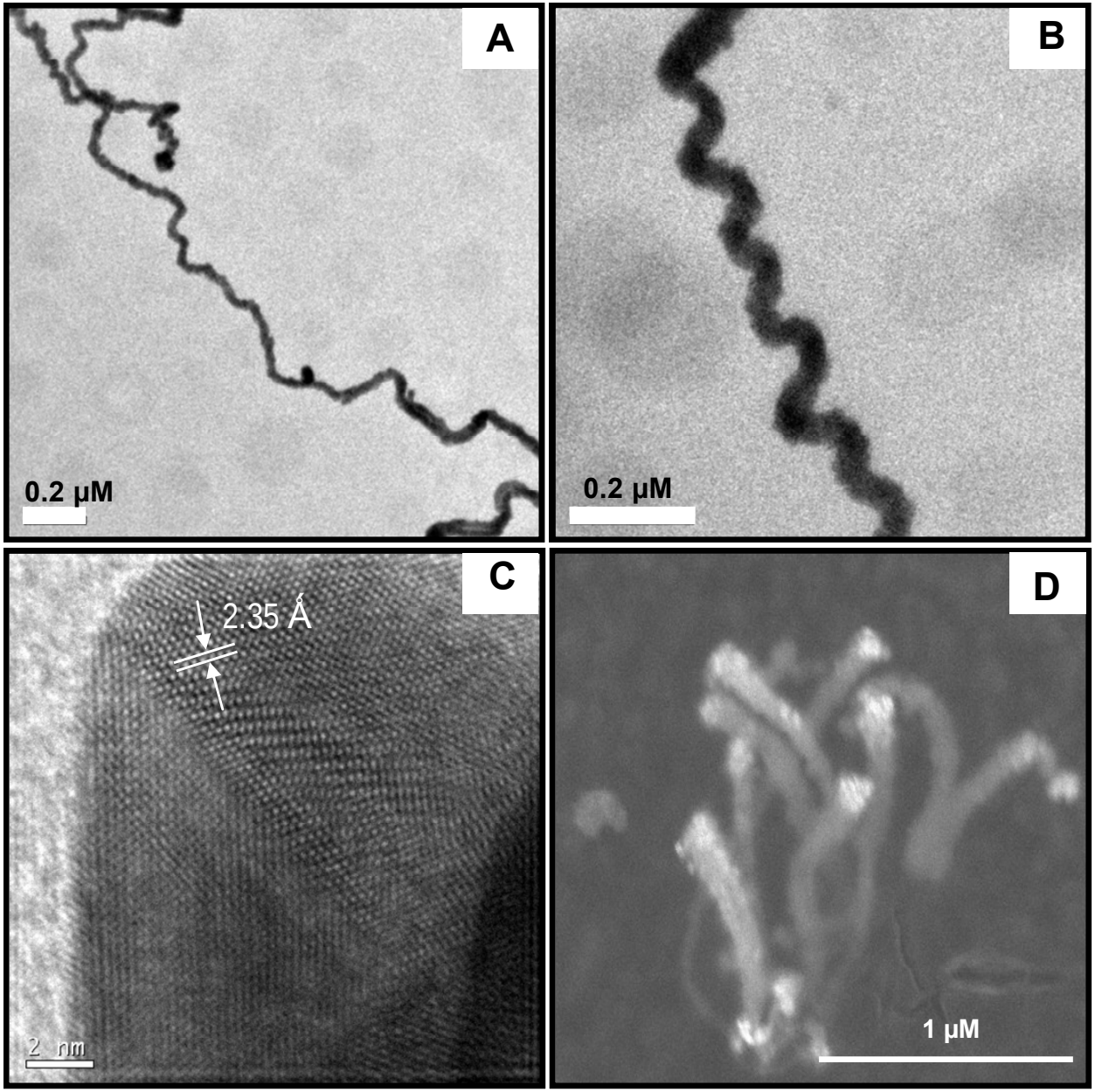

Sheets
3D superstructures of parallel sheets
Tapes
Purified Au nanorods
Perpendicular Sheets
Bended tapes
Globules
3D superstructures of perpendicular sheets




Sreeprasad et al. Langmuir 2008

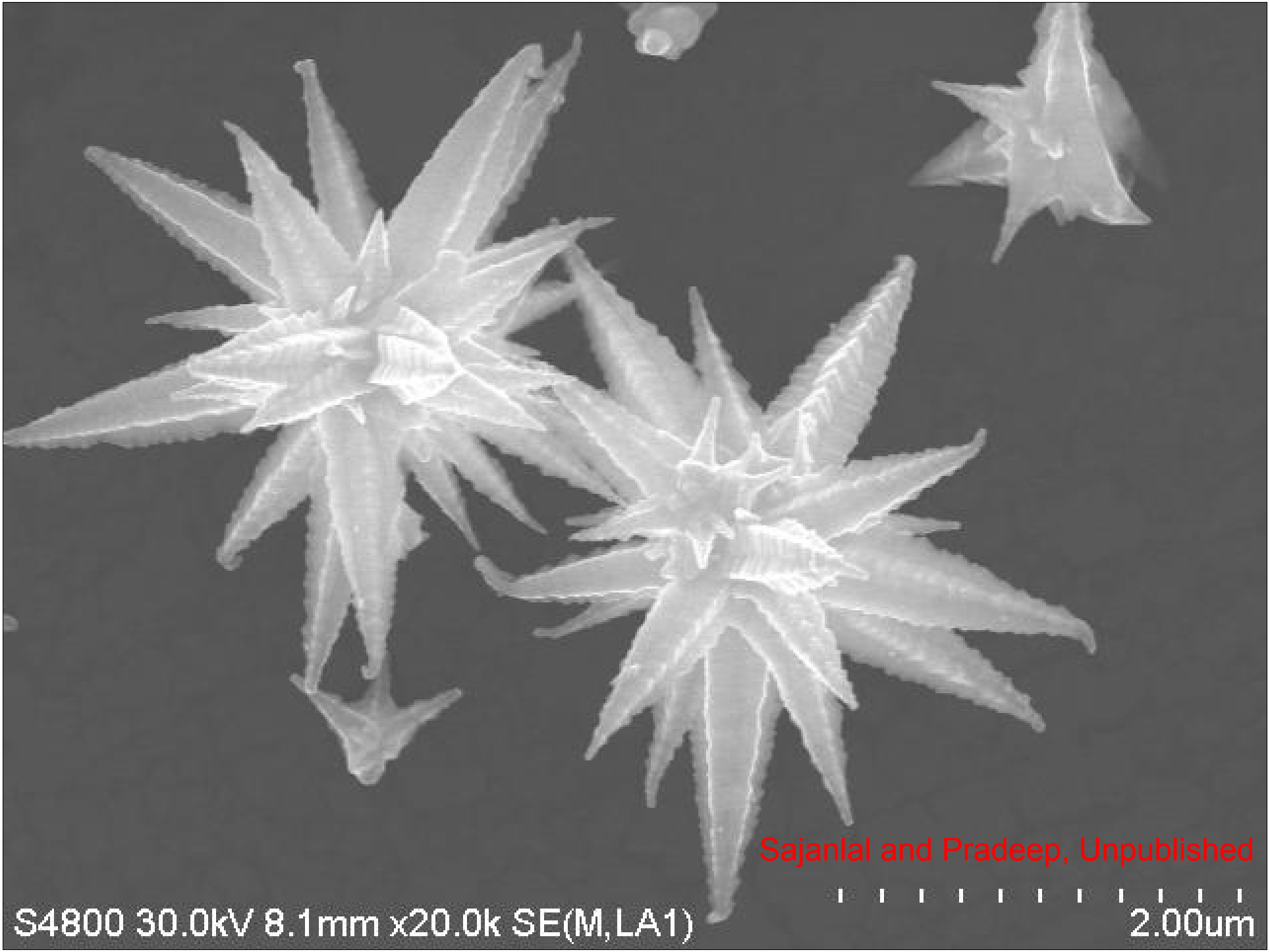

A
0.1 μm
B
50 nm
C
50 nm
D
0.2 μm
E
0.2 μm
F
100 nm


3.9 nm
8.5 nm
C
S
O






Sajanlal et al. Langmuir 2008


Sajanlal and Pradeep, Unpublished
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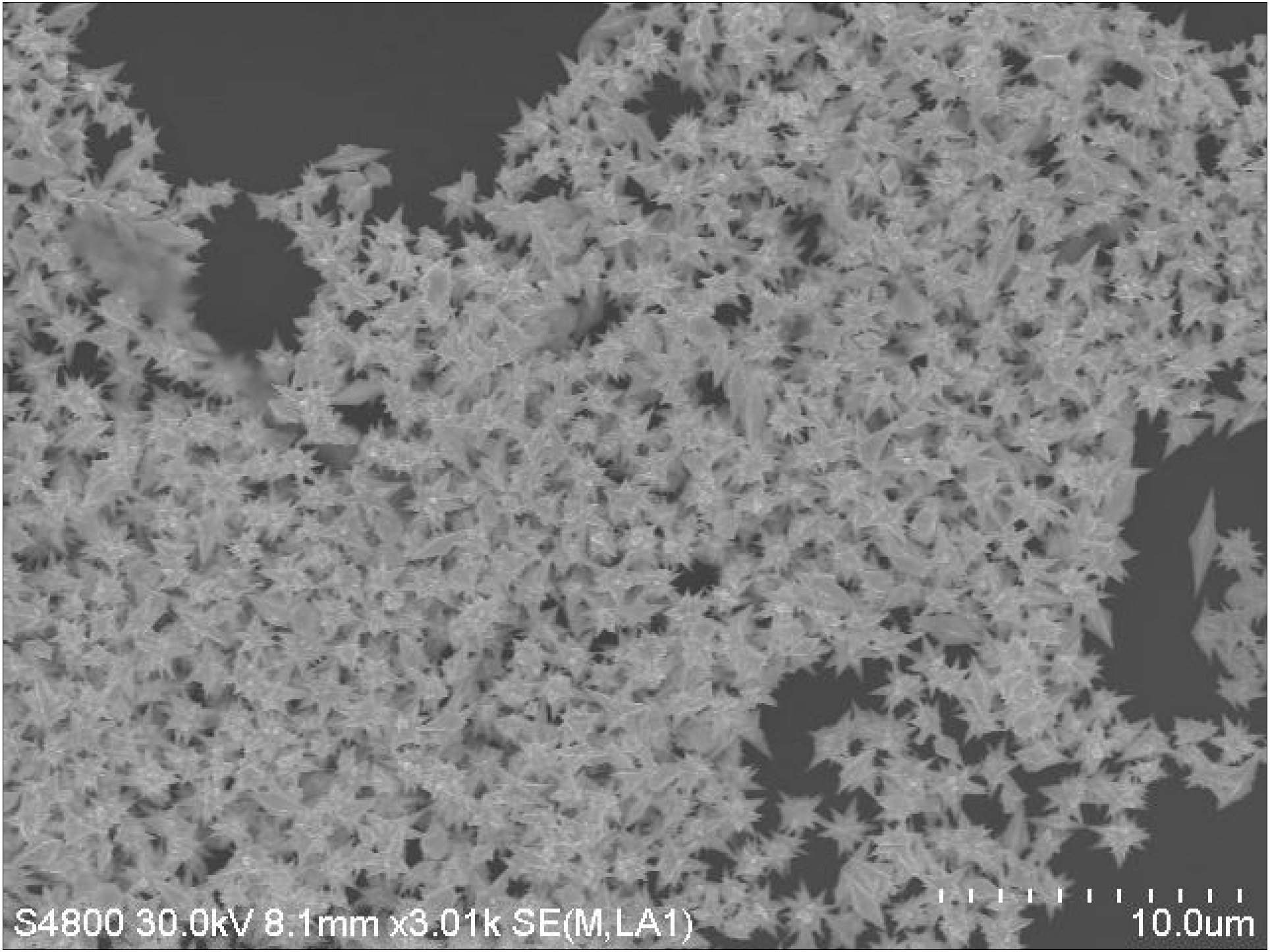
2.00um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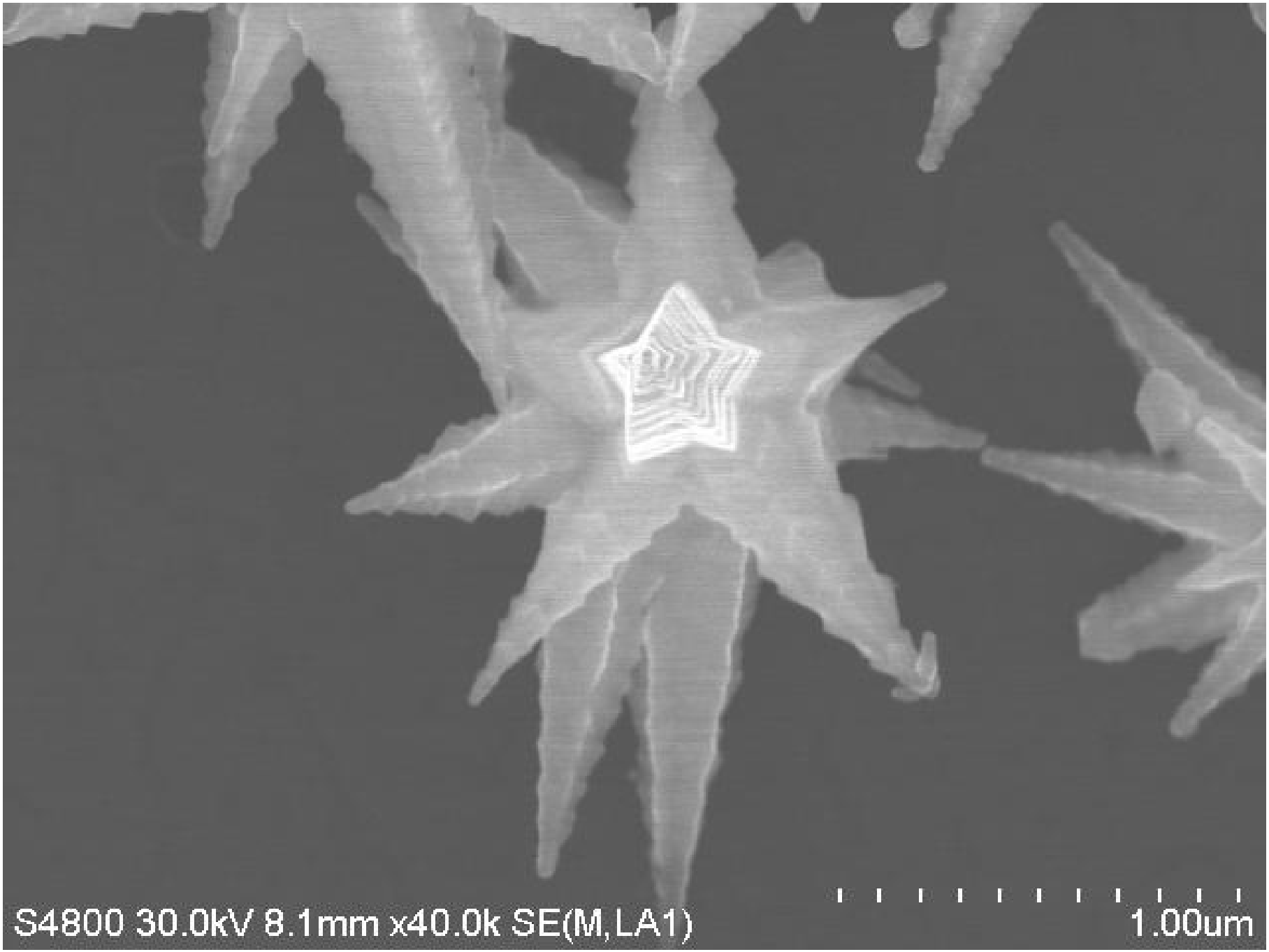
10.0um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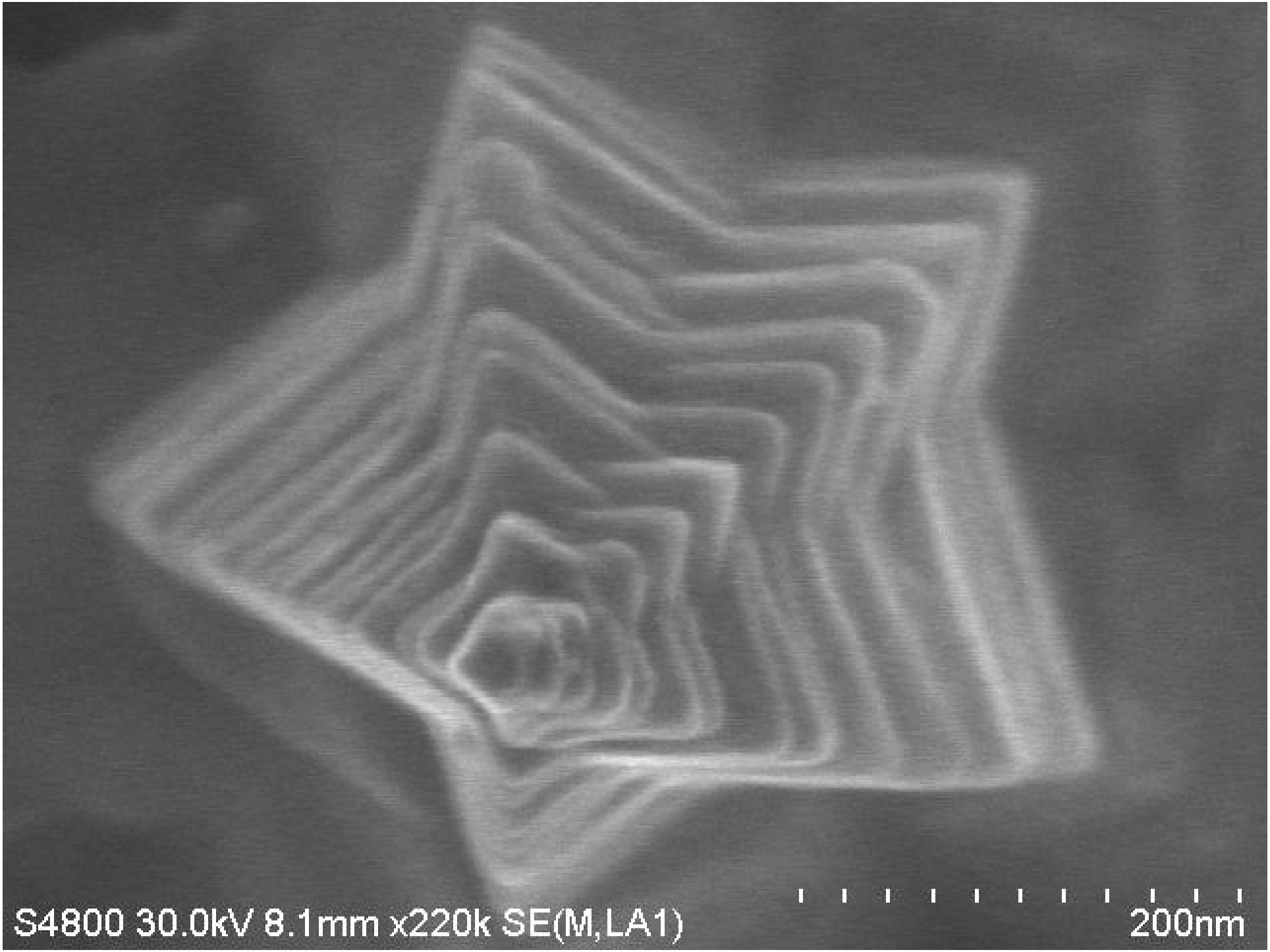
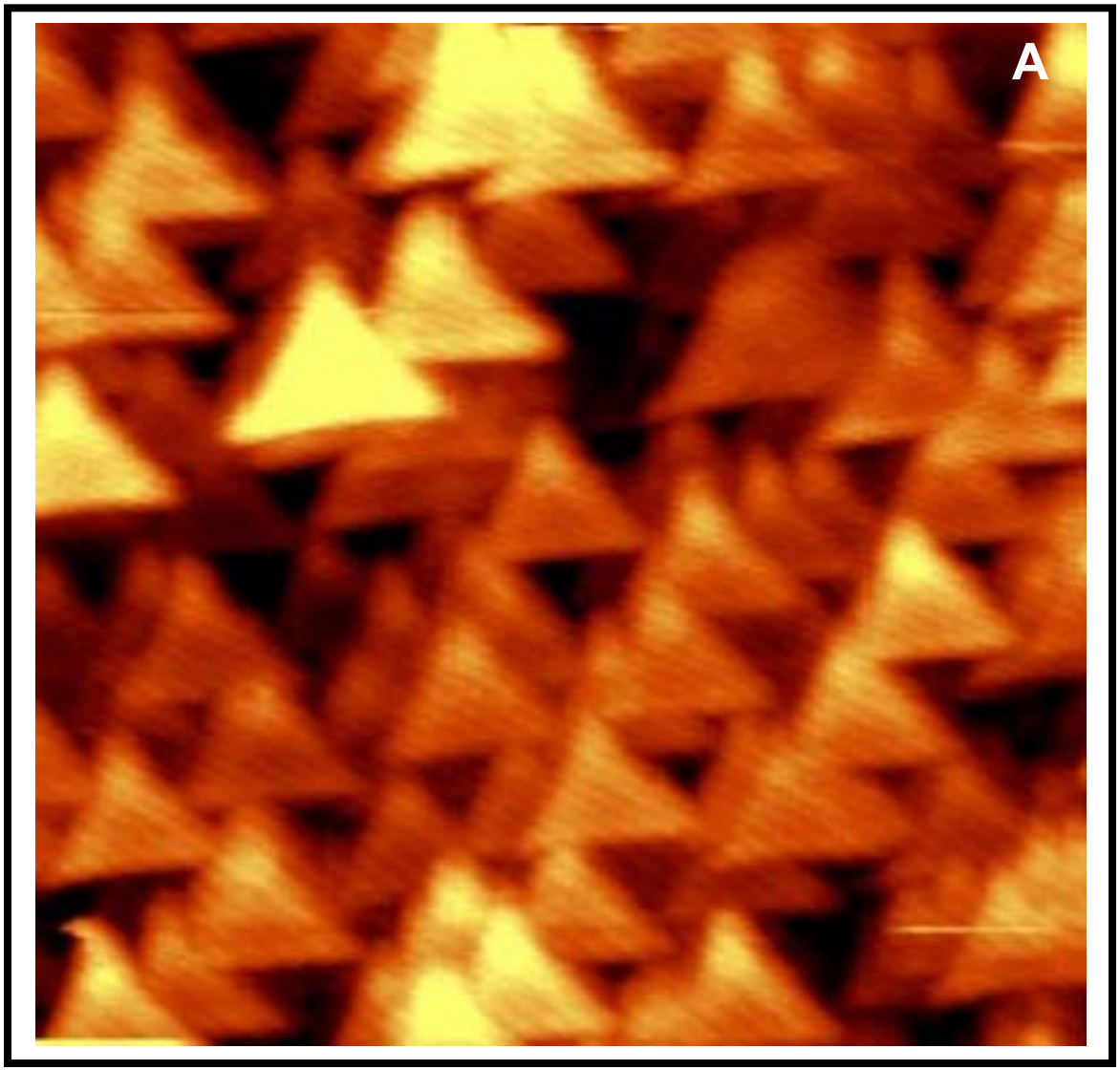
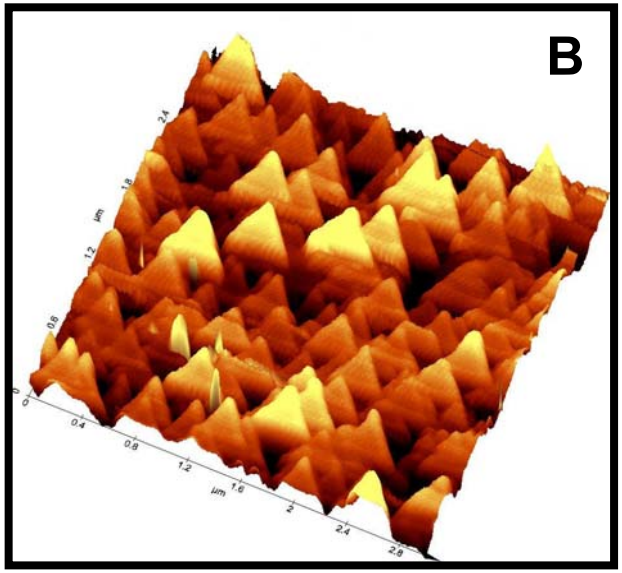
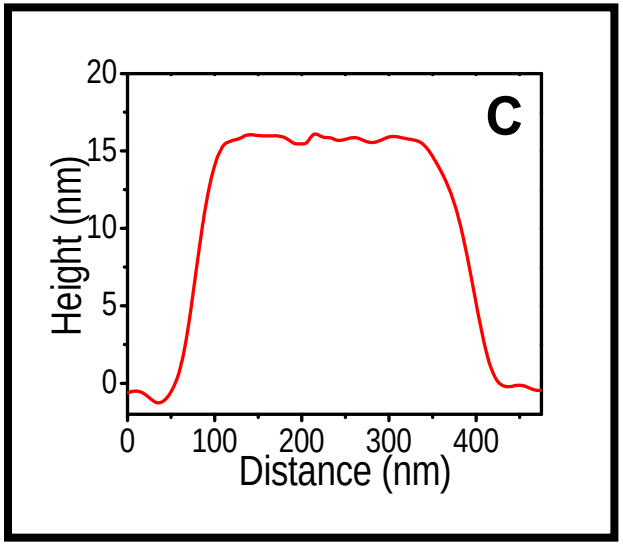
1.00um

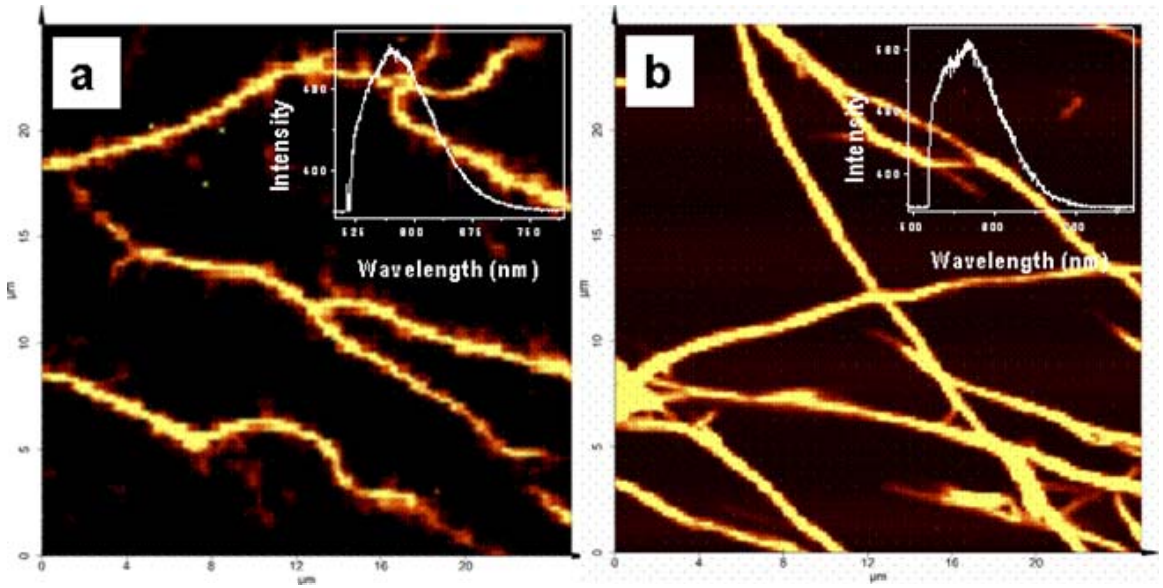

S4800 30.0kV 8.1mm x220k SE(M,LA1)
200nm

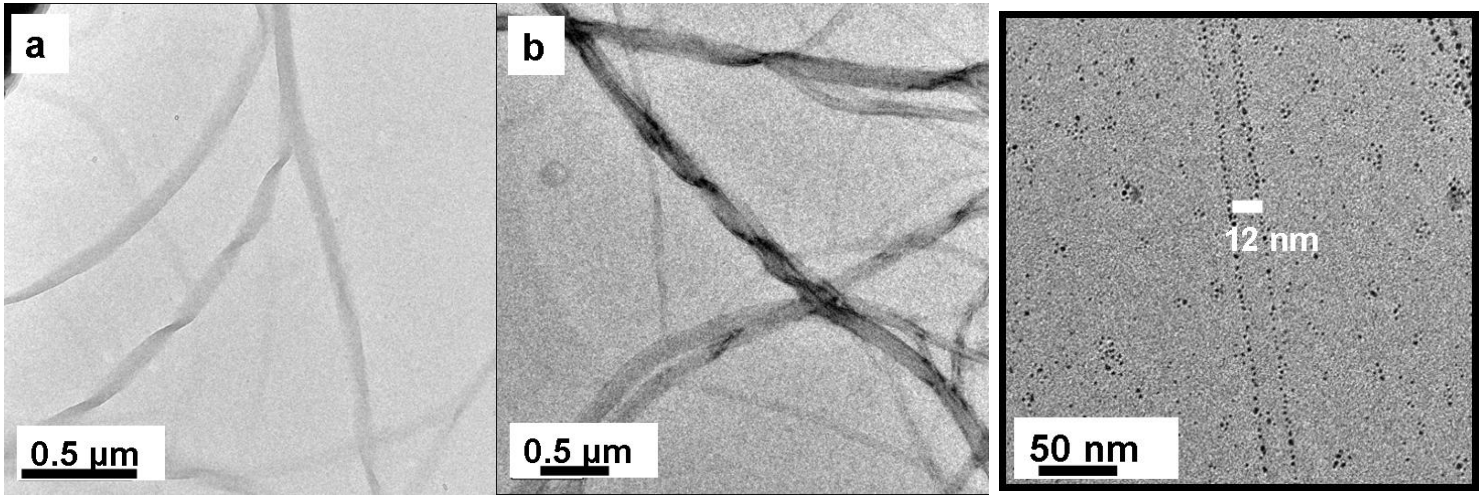


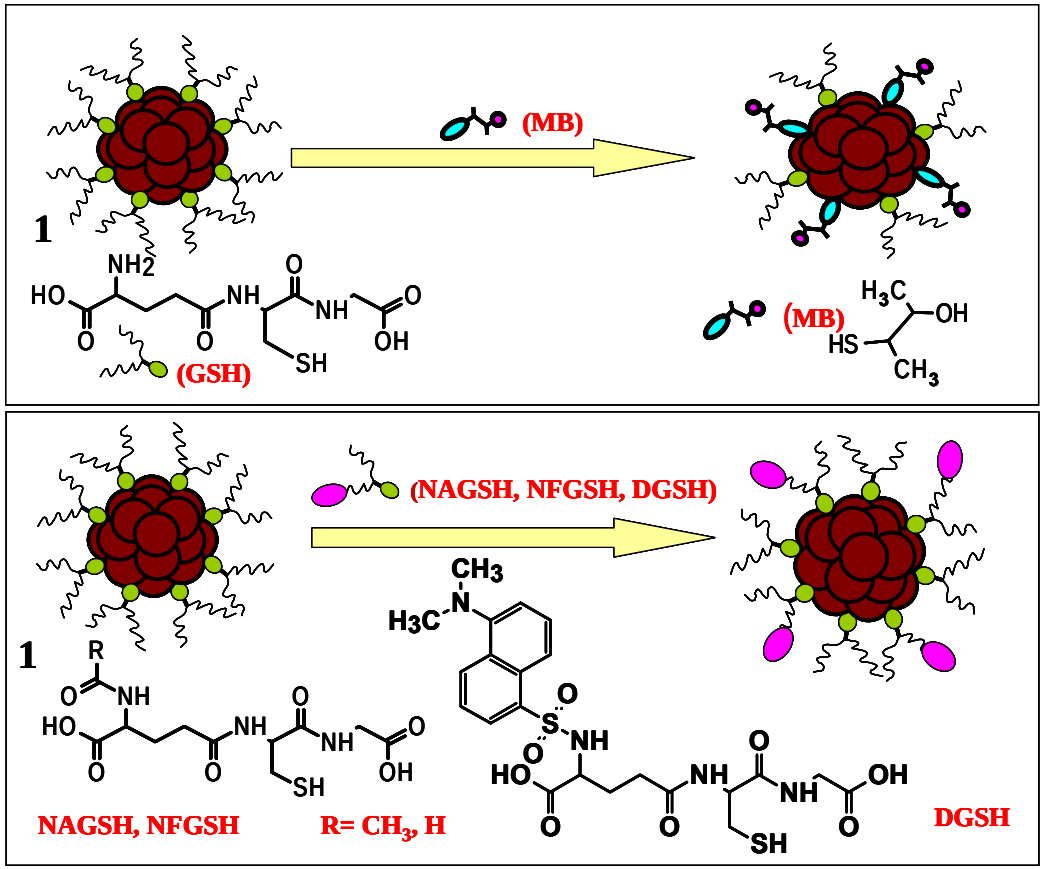



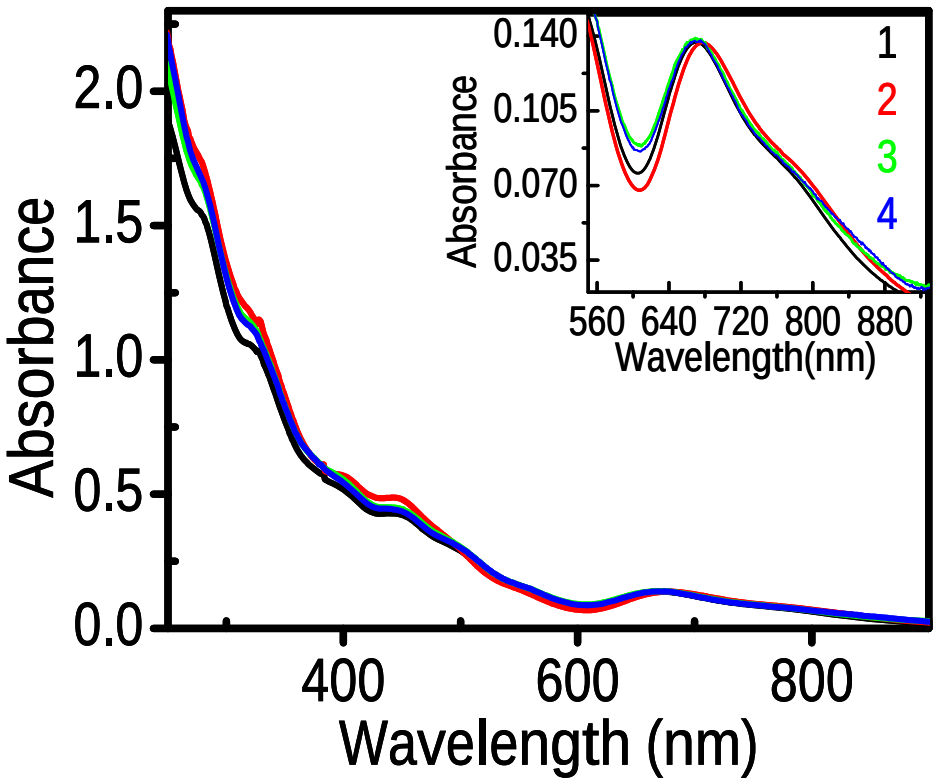

Sajanlal *et al* Adv. Mat. (2008)



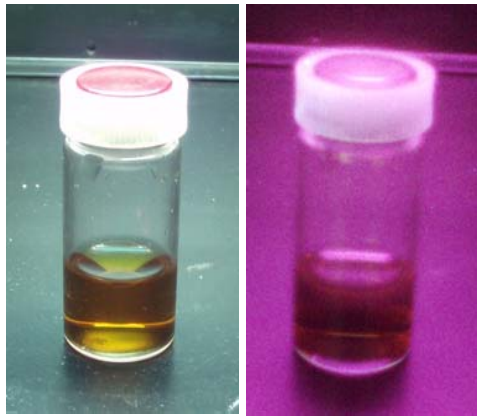




With Ajayaghosh 2008

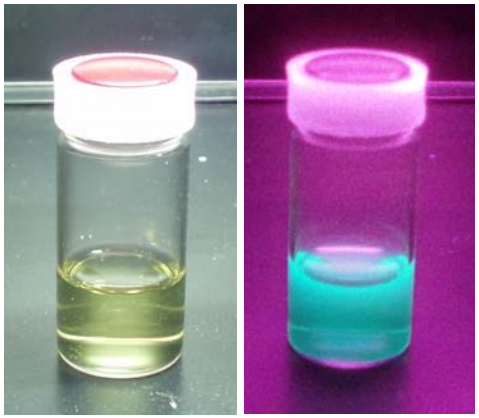

1
(MB)
(GSH)
(MB)
(NAGSH, NFGSH, DGSH)
1
NAGSH, NFGSH
R= CH3, H
DGSH




$Au_{25}$



$Au_8$



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

Habeeb et al. Unpublished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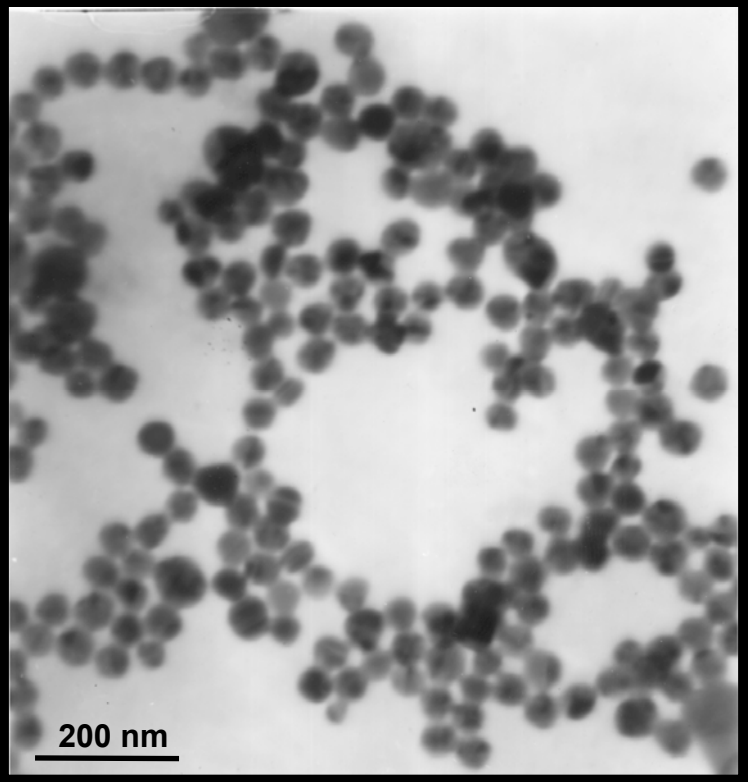
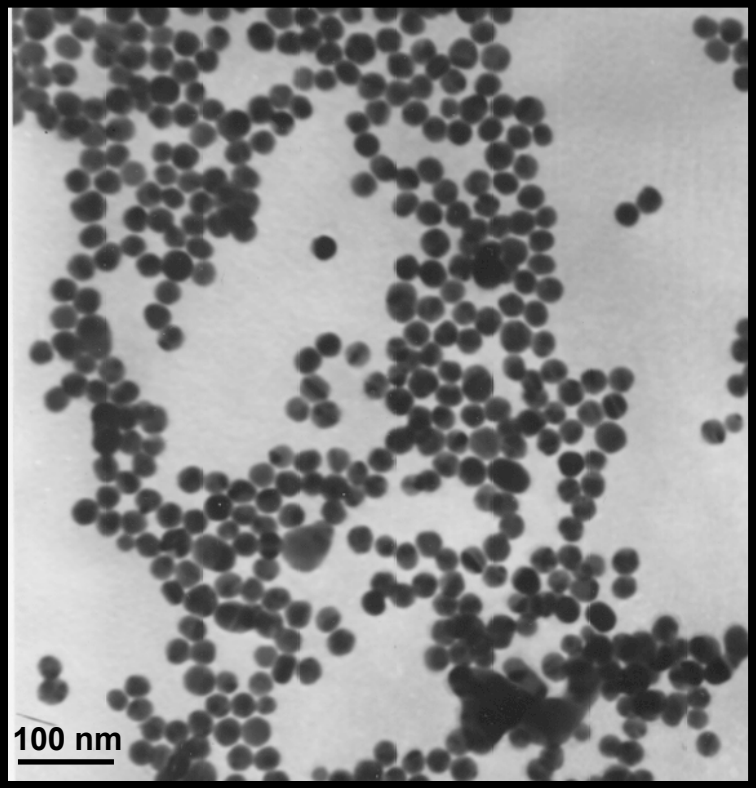
# Reactions with the metal core

Nanoparticles of silver disappear in a chemical reaction.

Nair and Pradeep 2003




Silver nano-particles ~70 nm

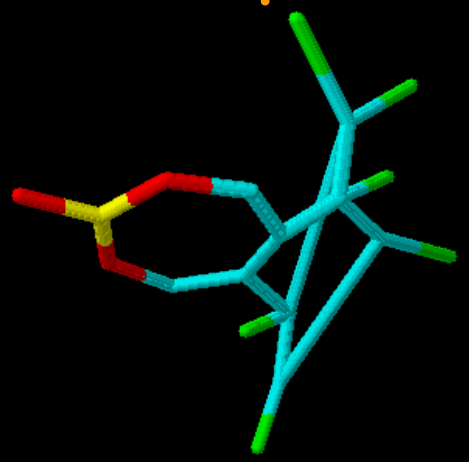



Gold nanoparticles ~15-20 nm

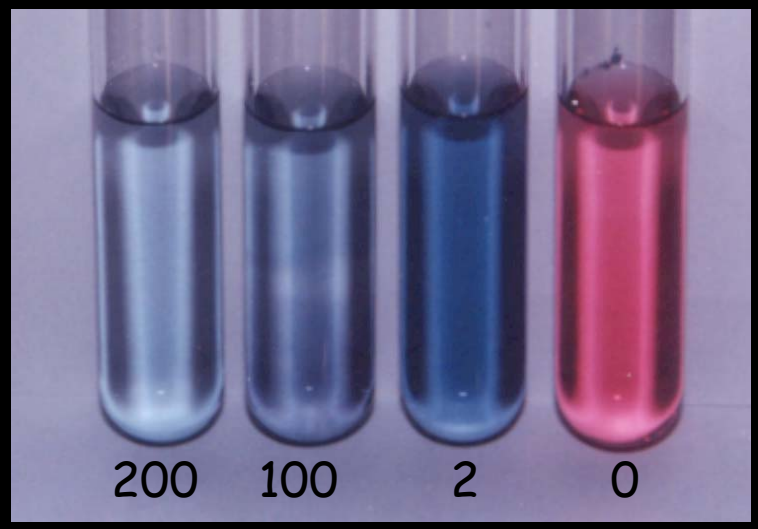
# Reactions with pesticides

Color of gold nanoparticles with endosulfan

**Example**



**Endosulfan**



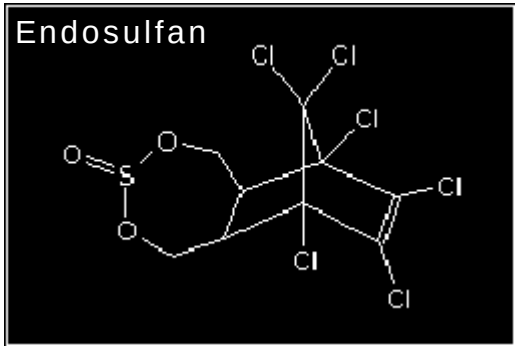

Endosulfan concentration in ppm

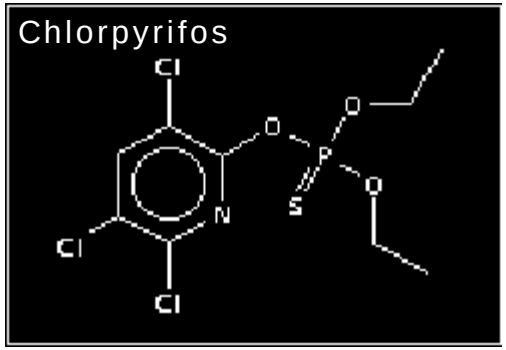
Pesticide removal
Indian Patent granted
International patent filed
Technology commercialized

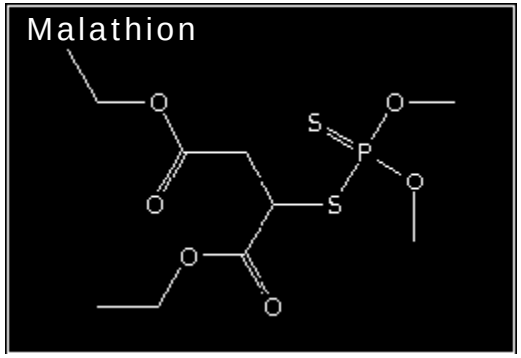
Color changes with pesticide concentration
Good response at lower concentrations
Down to 0.1 ppm
Adsorbed pesticides can be removed from solution

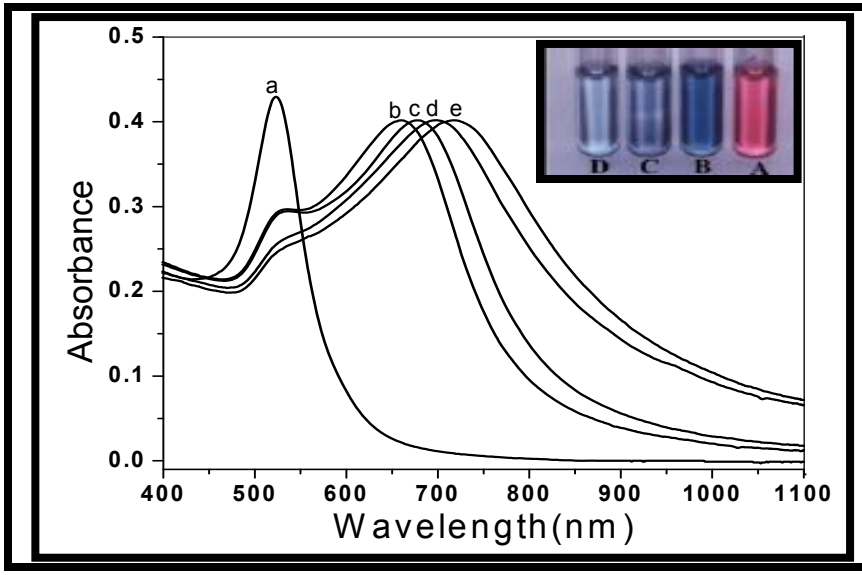
J. Environ. Monitoring. 2003

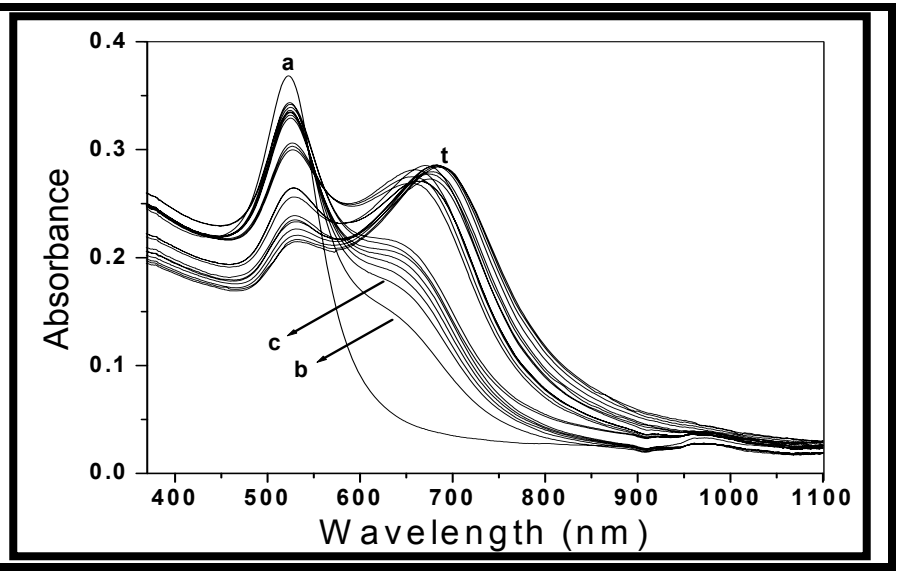
Some of the pesticides contain halocarbons whereas others have P or S, which can bind metal nanoparticles which is used for pesticide detection and extraction.



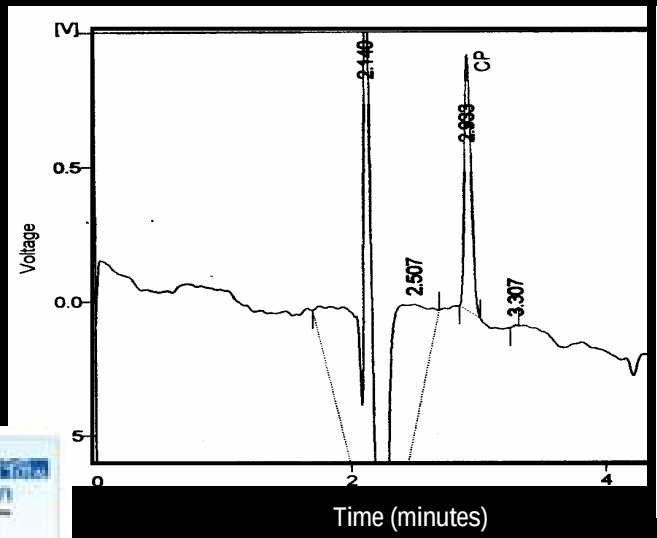



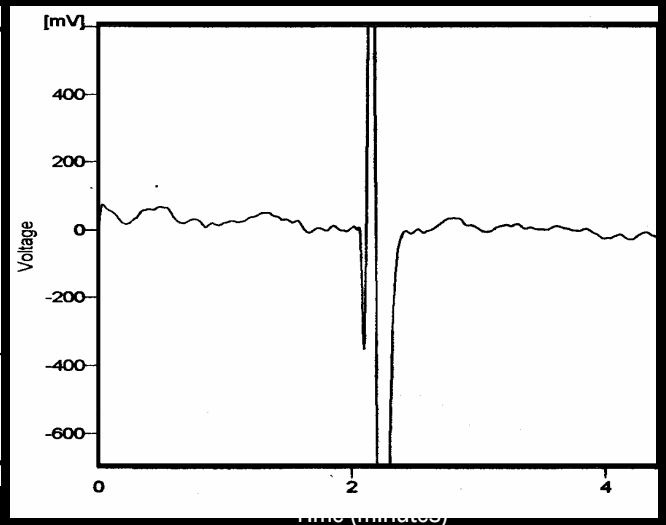

UV-visible spectra of gold nanoparticles showing the detection of endosulfan at different concentrations (b.2, c.10, d.100 and e. 250 ppm). Inset (A-D): Color changes of the solutions corresponding to traces a, b, c and d, respectively.

Time dependent adsorption of endosulfan on gold nanoparticles and the corresponding spectral changes (a-t). The shifts in the plasmon band are due to the binding of the pesticide on the nanoparticle surface.


HEATING VESSEL
2007 1 16

# Pesticide removal from drinking water





Product is marketed now

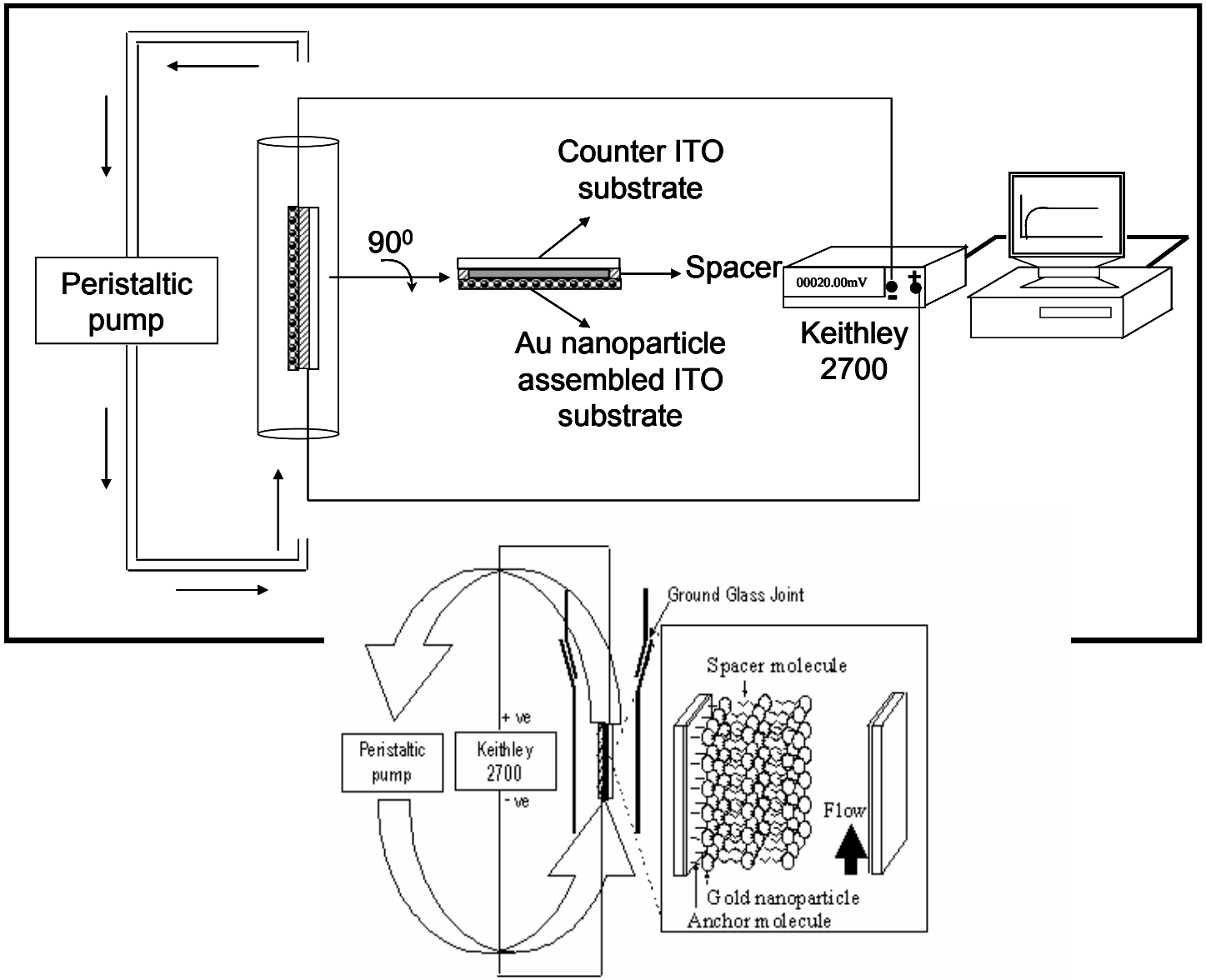
A pesticide test kit has been developed > 25 ppb

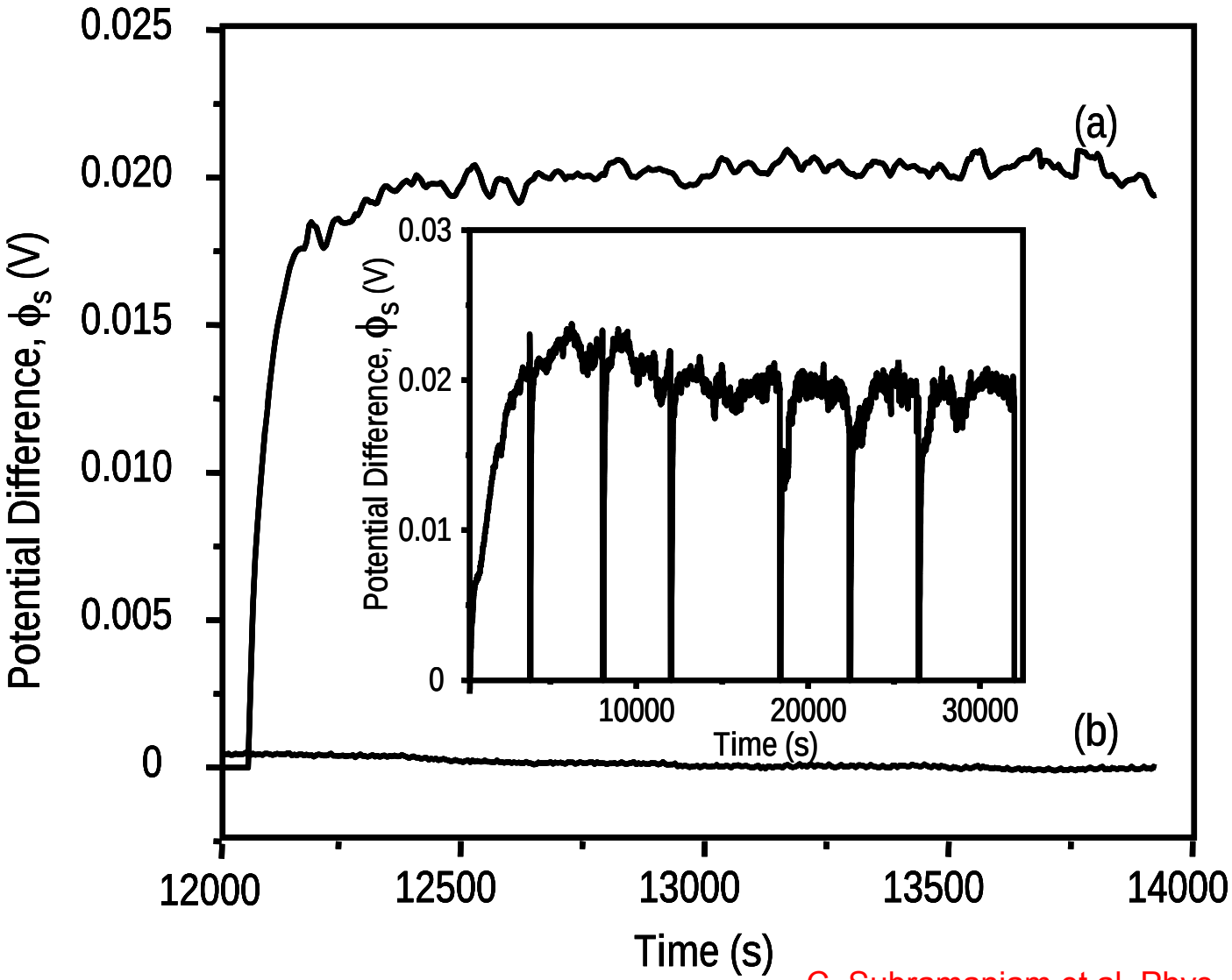
# In this talk…..

Visible emission from single walled carbon nanotubes
Background
Experiment
Control experiments
What next…

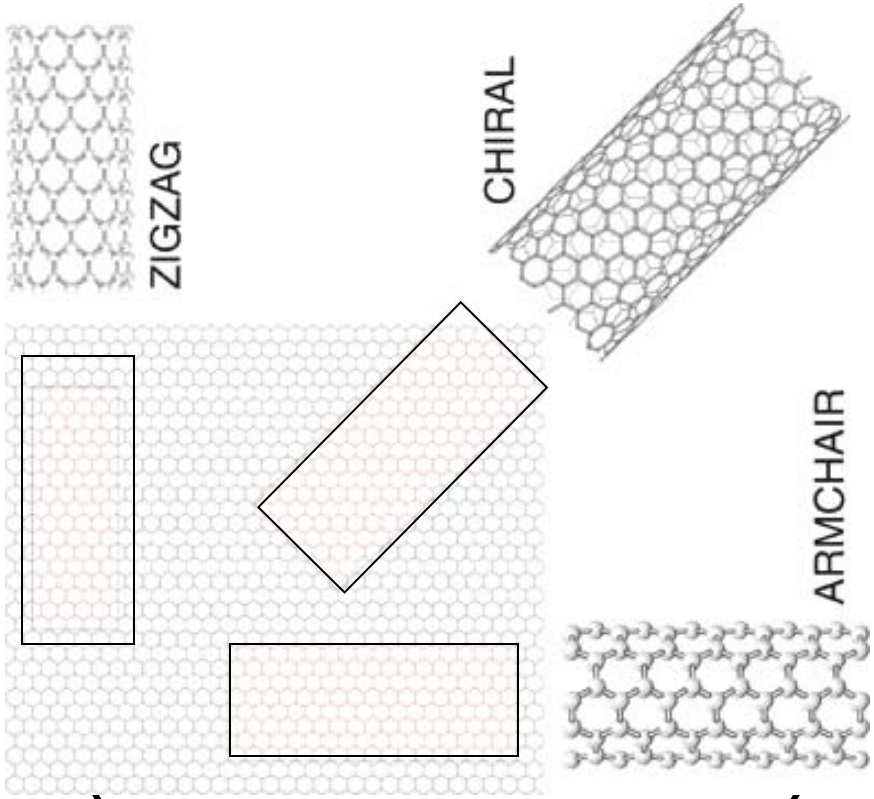
Chemical interactions leading to devices

# Flow induced potential in nanoparticle assemblies






C. Subramaniam et al. Phys. Rev.Lett.2005
J. Phys. Chem. C 2007
Indian Patent application 2005



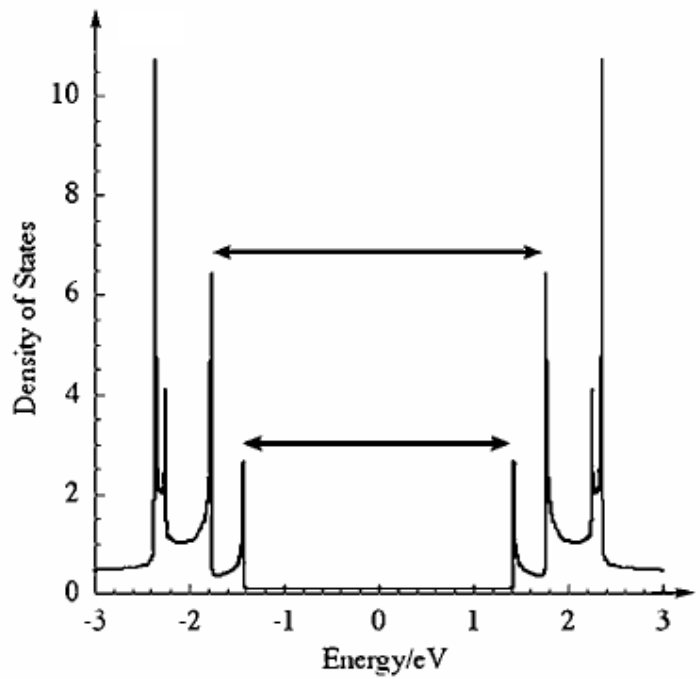

(n,m) indices

Metallic

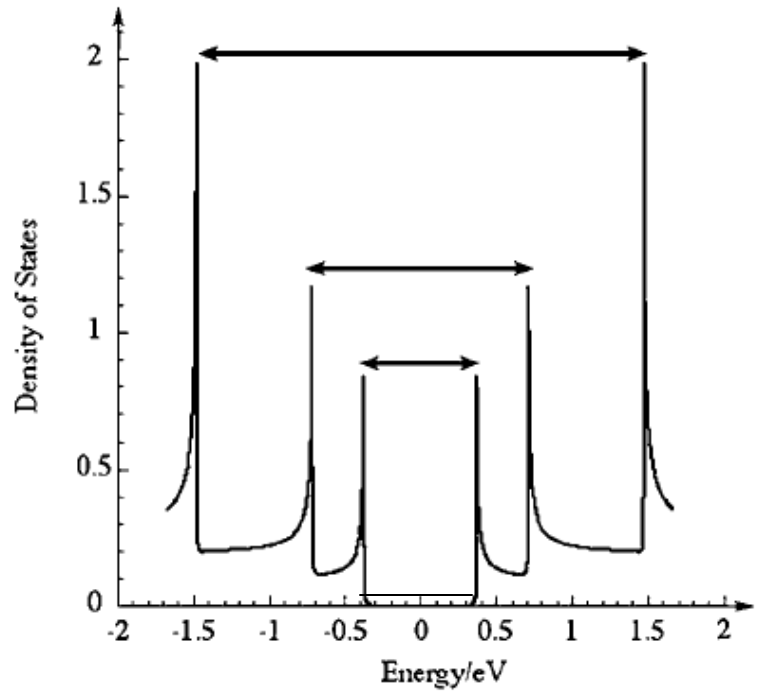
Semiconducting

# 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

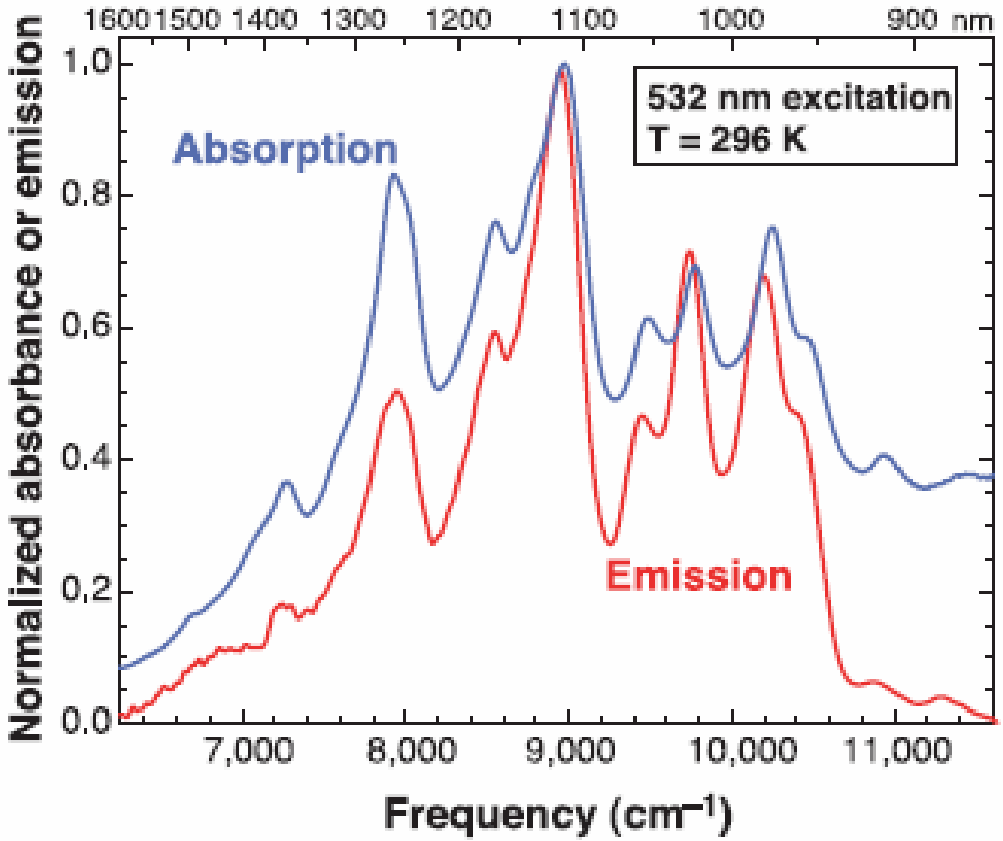



**Semiconducting**




**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.**

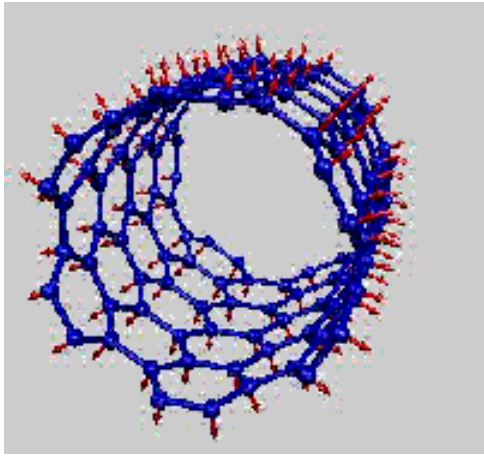
M. J. O'Connell *et al.*, *Science* ***297***, *593 (2002).*

# 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

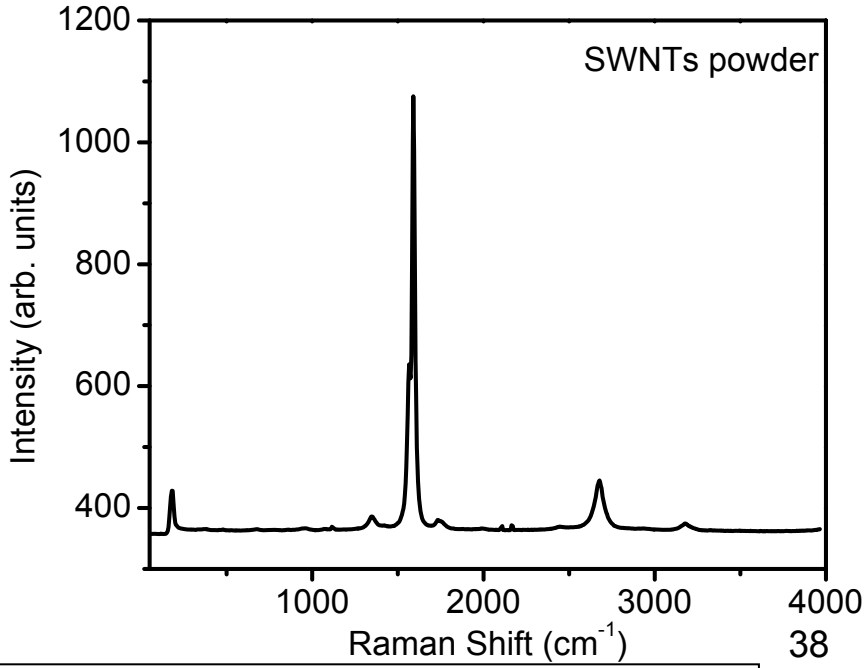
In-plane vibrations

(C) D-band

Defect centered

(D) G` band

Occurs at $2\omega_D$



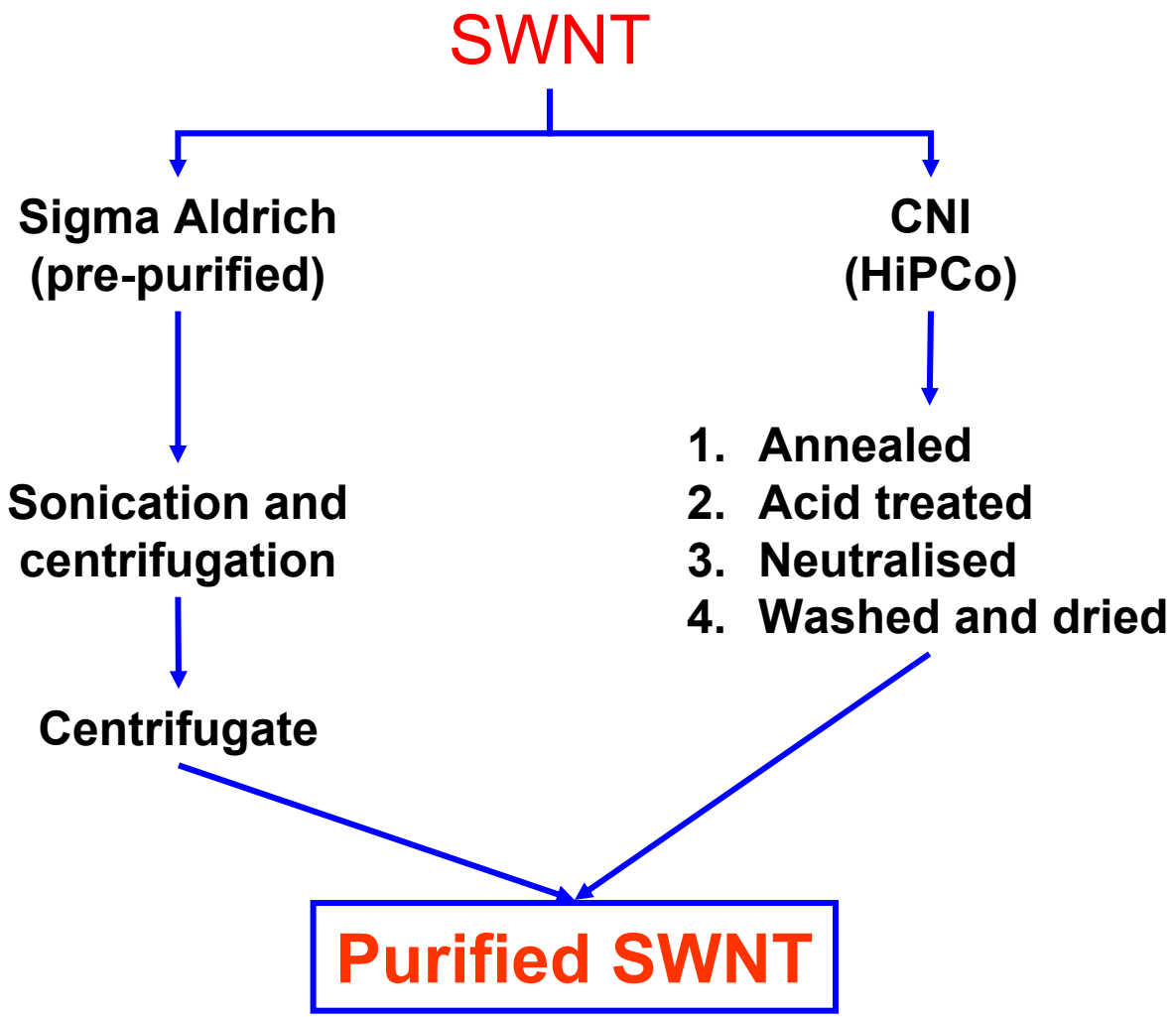



*Science*, **1997**, *275*, 187. & *http://www.photon.t.u-tokyo.ac.jp/~maruyama/*

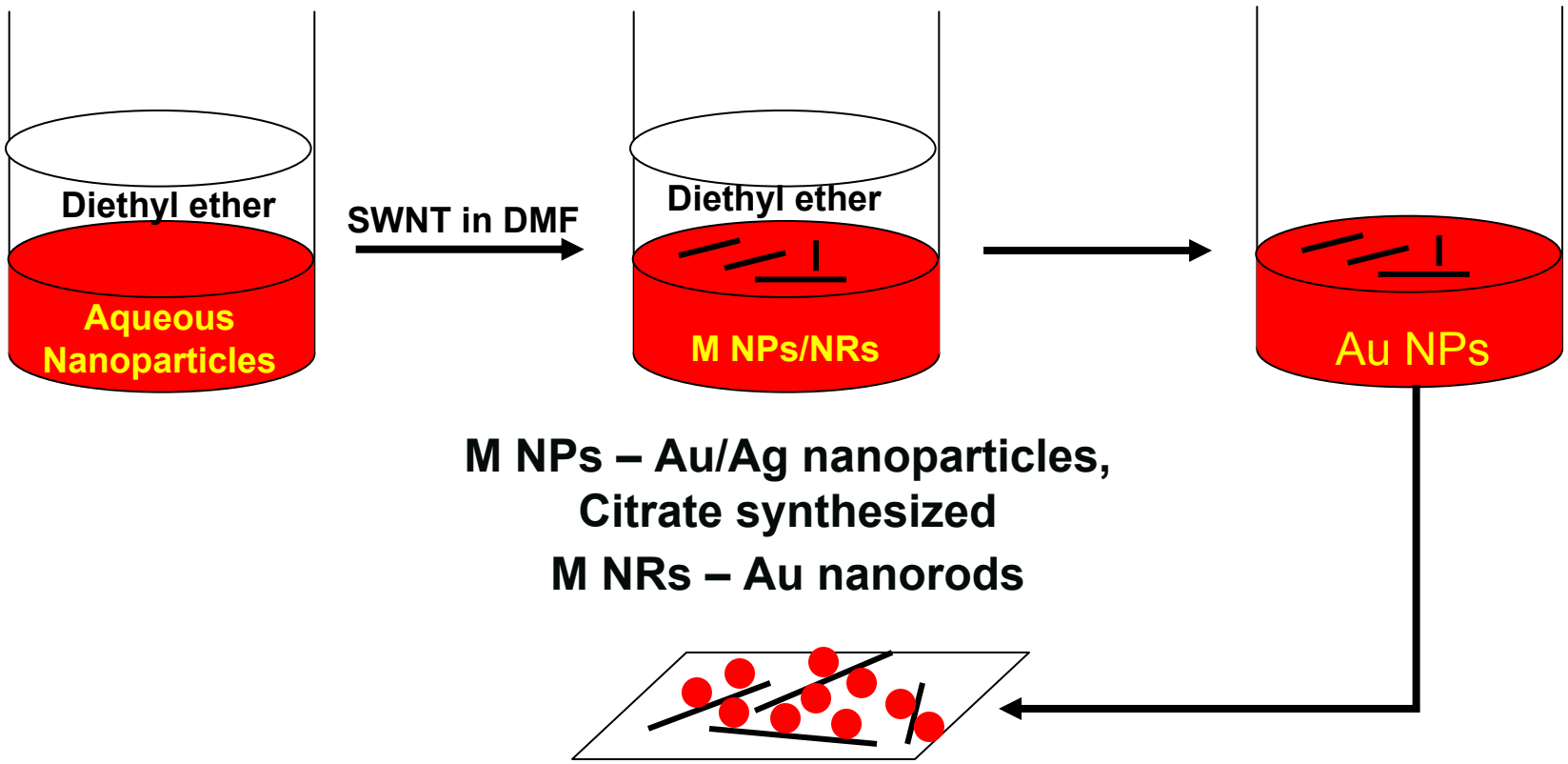
# Vibrational properties of single walled carbon nanotubes (SWNTs)

Experimental methods
Confocal Raman spectral analysis and imaging
Scanning near field optical microscopy (SNOM)
Point-contact current image Atomic force microscopy (PCI-AFM).
Other supporting experiments

# Purification of SWNT



# Preparation of composite




**M NPs – Au/Ag nanoparticles, Citrate synthesized**

**M NRs – Au nanorods**

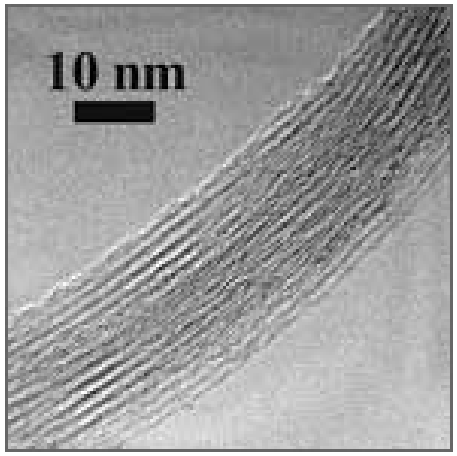
# Types of systems investigated

SWNT

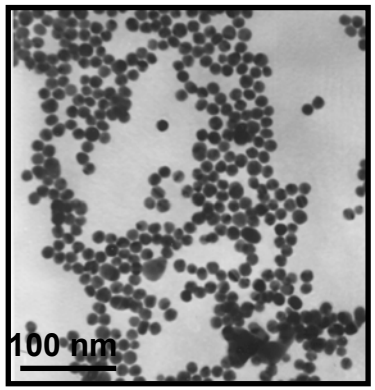
mSWNT

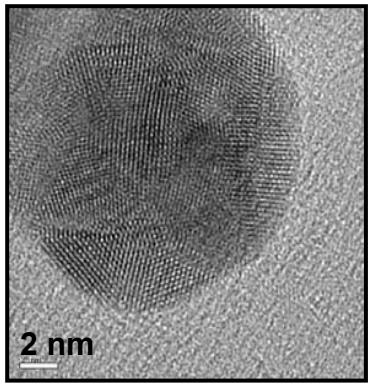
Au nanoparticles
Ag nanoparticles
Au nanorods

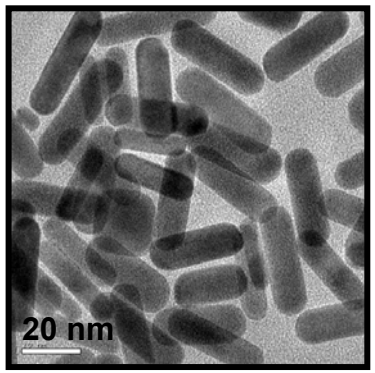
**NP-SWNT**
**NR-mSWNT**

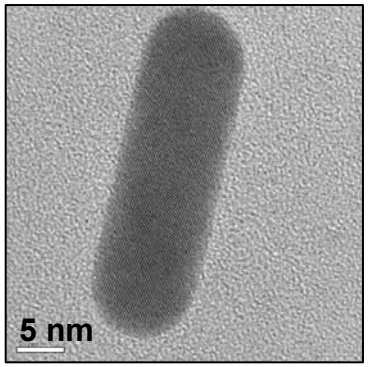



*www1.eere.energy.gov*

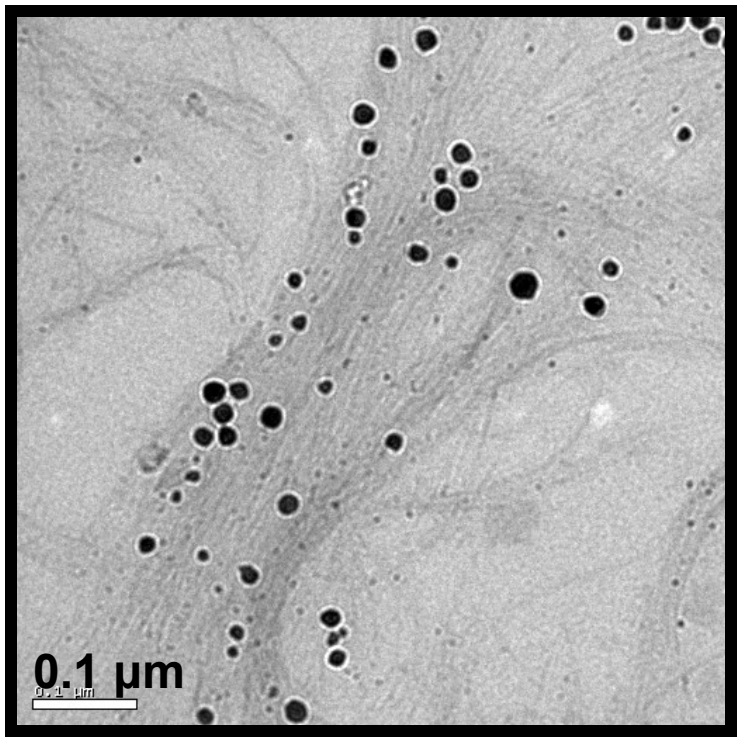


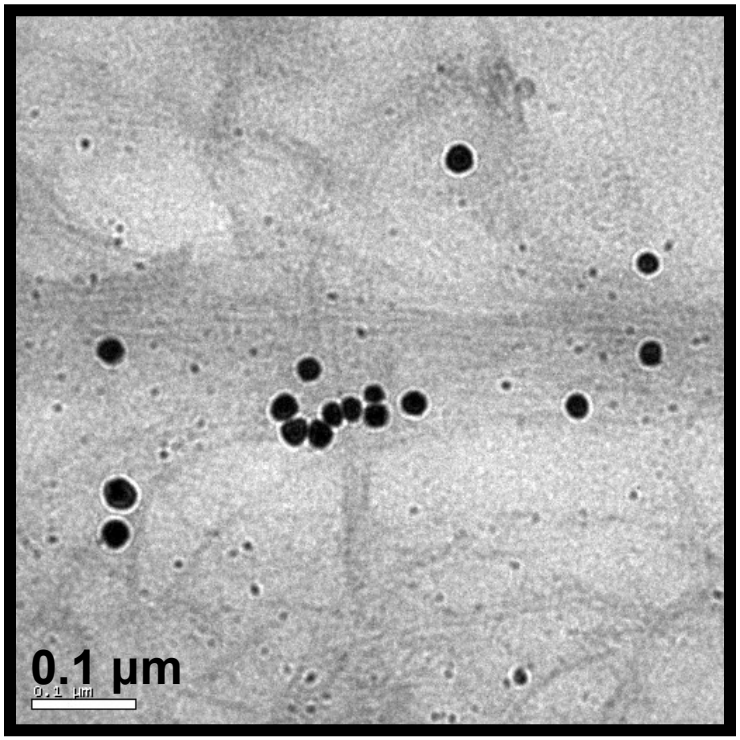



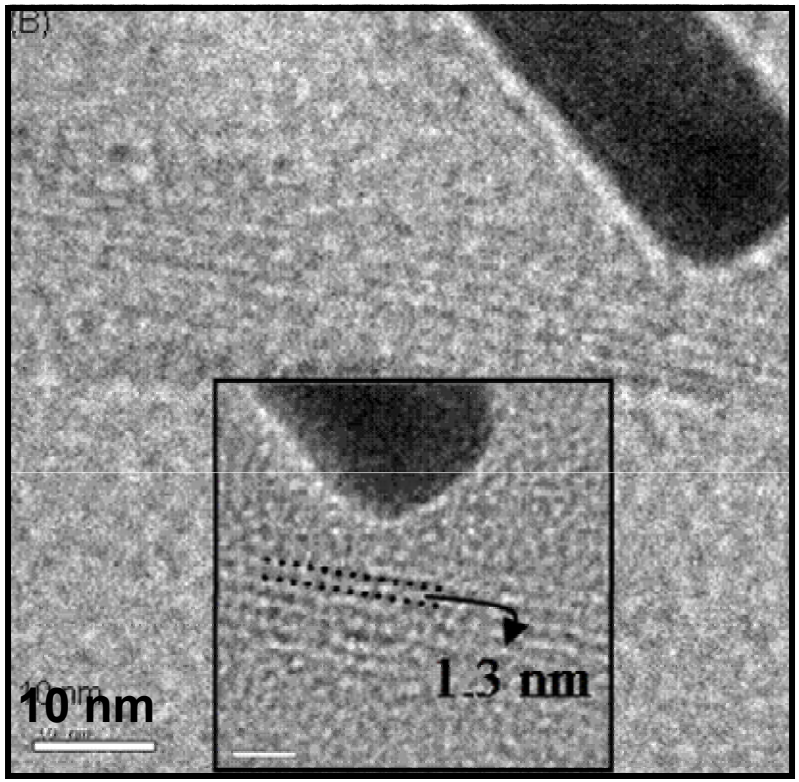



# Transmission Electron Microscopy

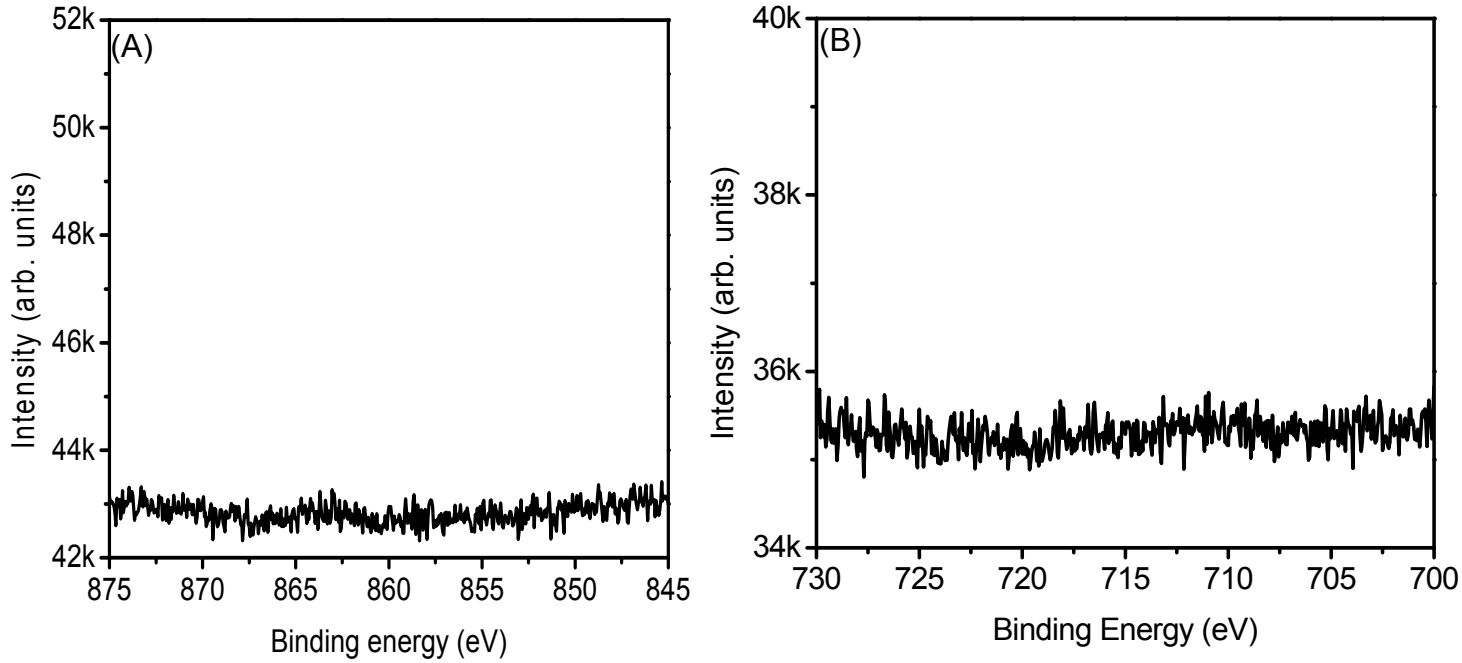



TEM images of Au-SWNTs composite acquired at 100 keV.

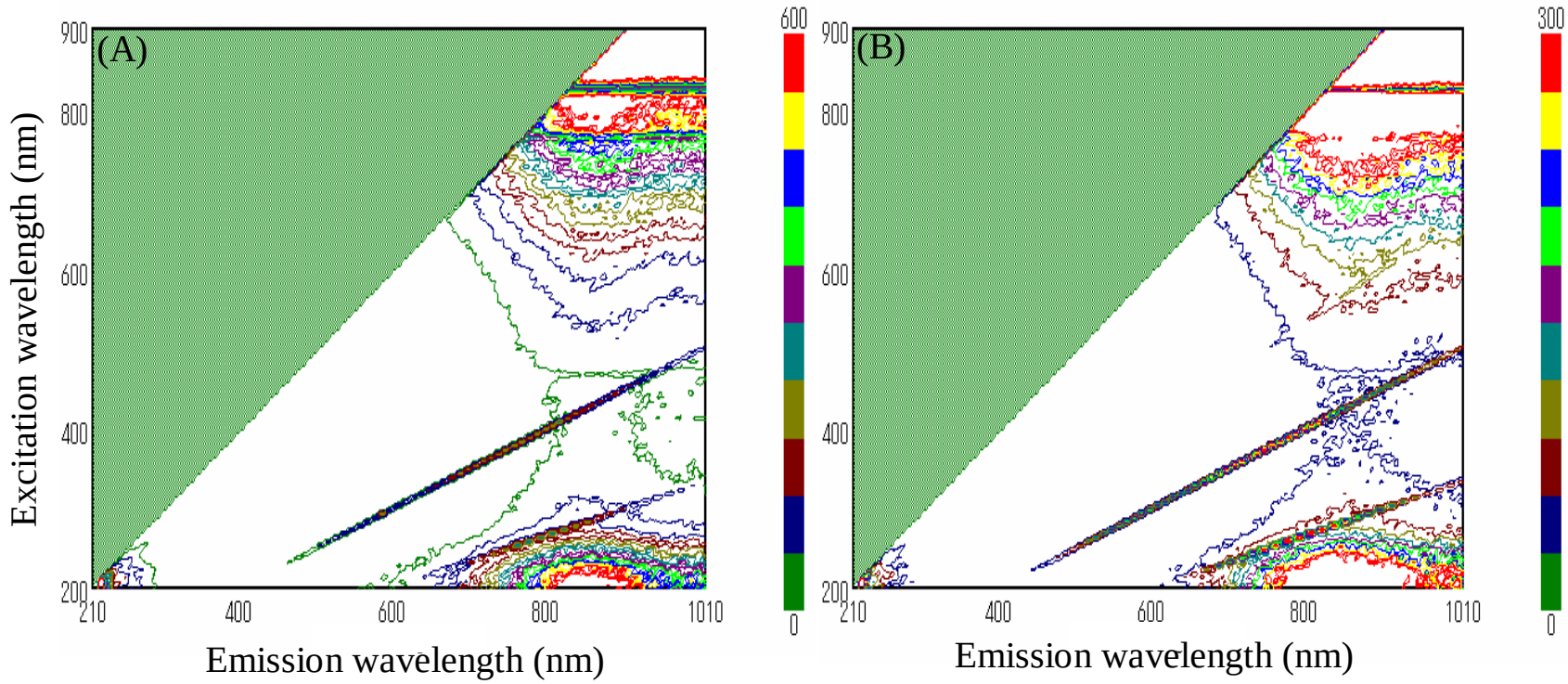



TEM images of (A) AuNRs-SWNTs composite acquired at 300 keV.



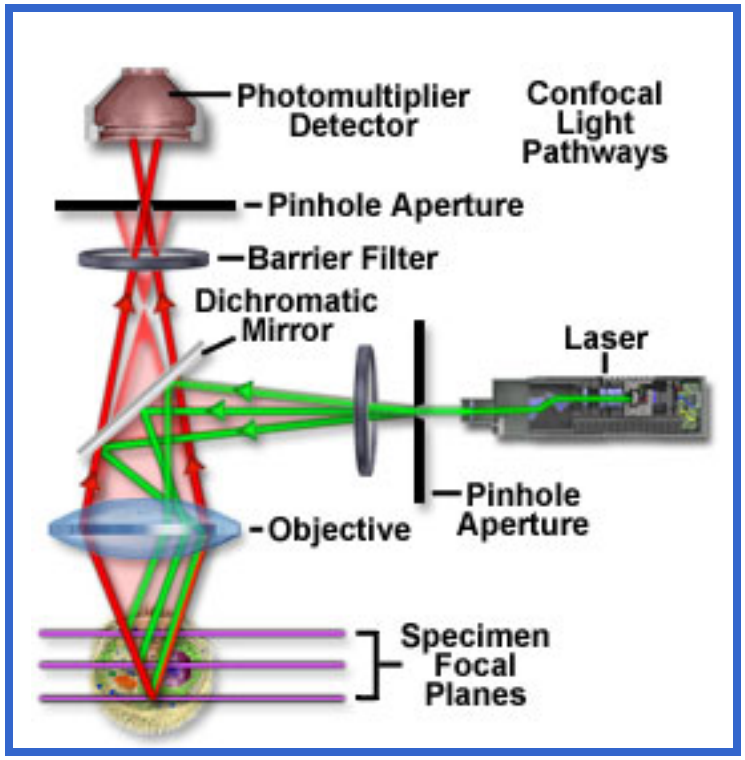

XPS spectra of Au-SWNT composite in the (A) Ni 2p and (B) Fe 2p regions.

ICP - MS

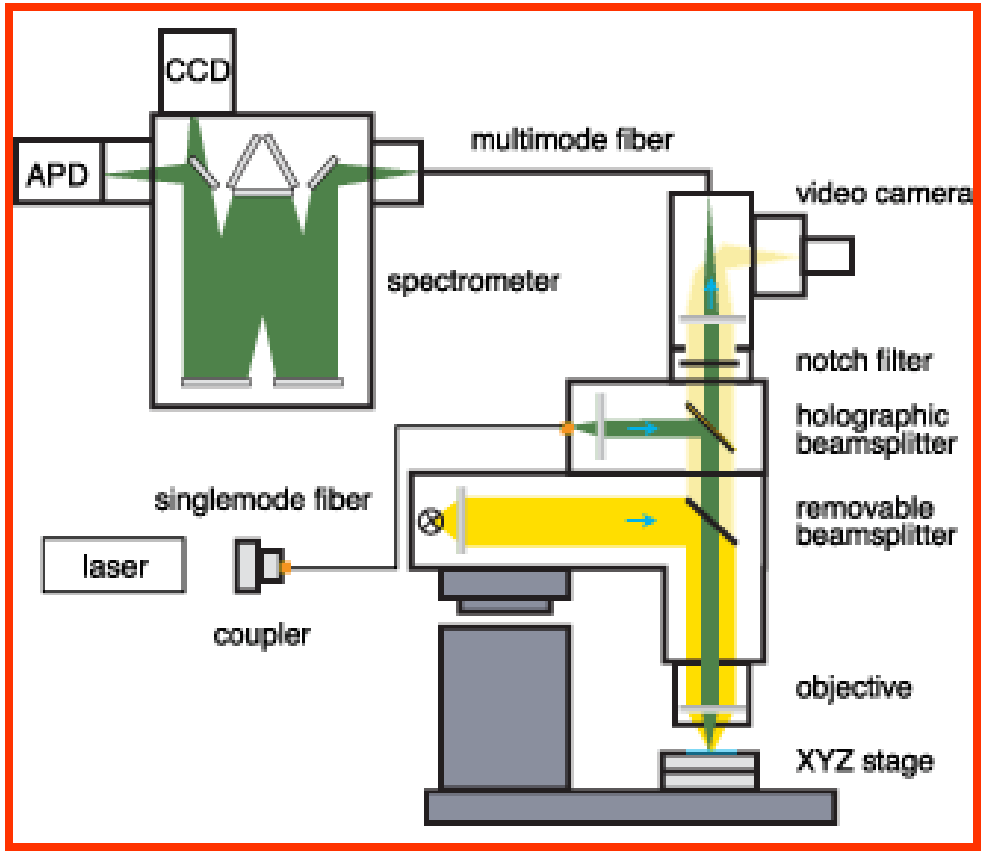



Fluorescence contour plots of (A) supernatant solution and (B) blank water at pH 7.12.

# Instrumentation – Confocal Raman




Concept of confocality




Raman Instrument

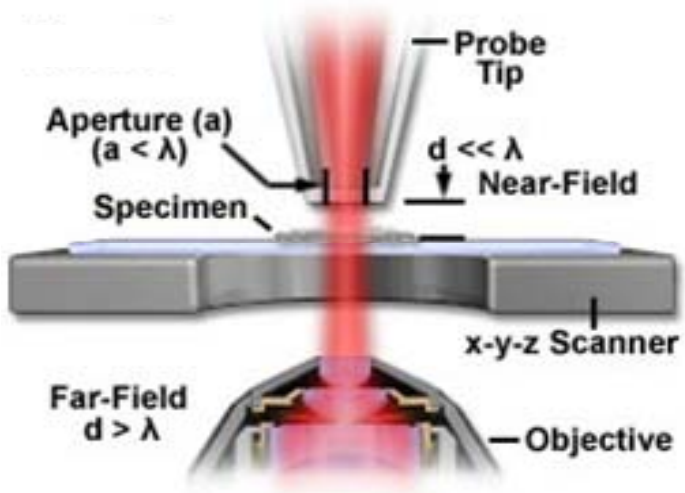
# Key instrument specifications

- Argon Ion laser : 514.5 nm
- Back scattering geometry
- Super notch filter

# Scanning Near-field Optical Microscopy

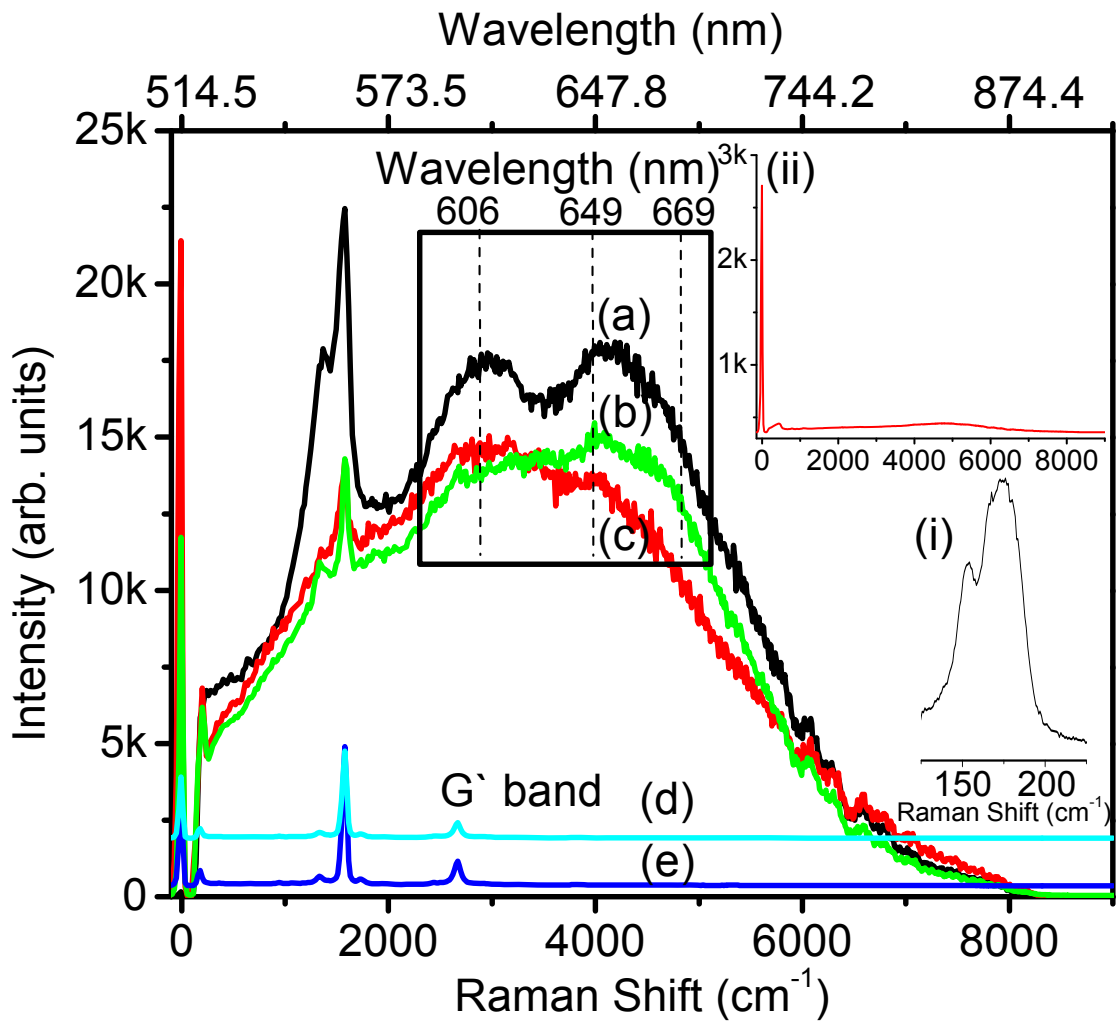
- **Resolution is limited by wavelength of light used.**
- **Near-filed microscopy was first proposed by Synge in 1928.**

***"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]"***



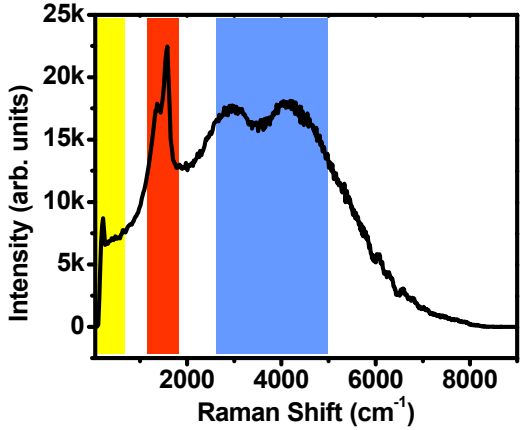


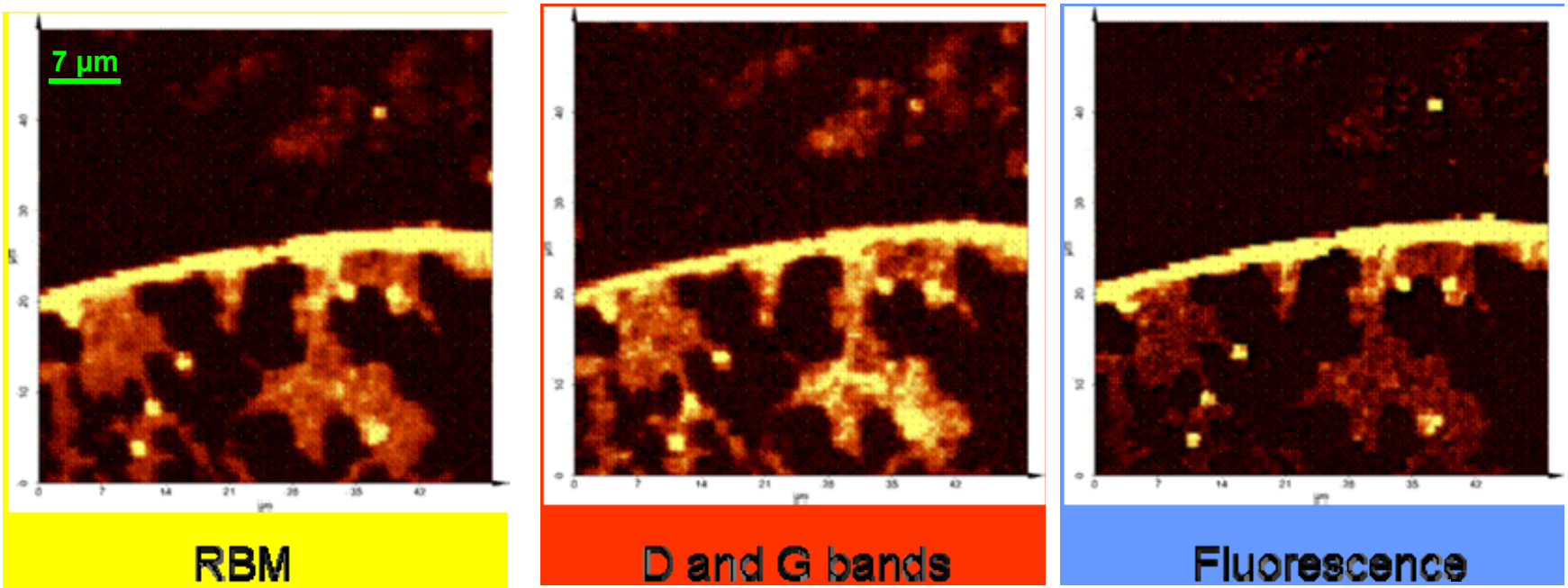
1. *www.olympusmicro.com*
2. E.H. Synge, *Phil.Mag.* **6**, 356 (1928)



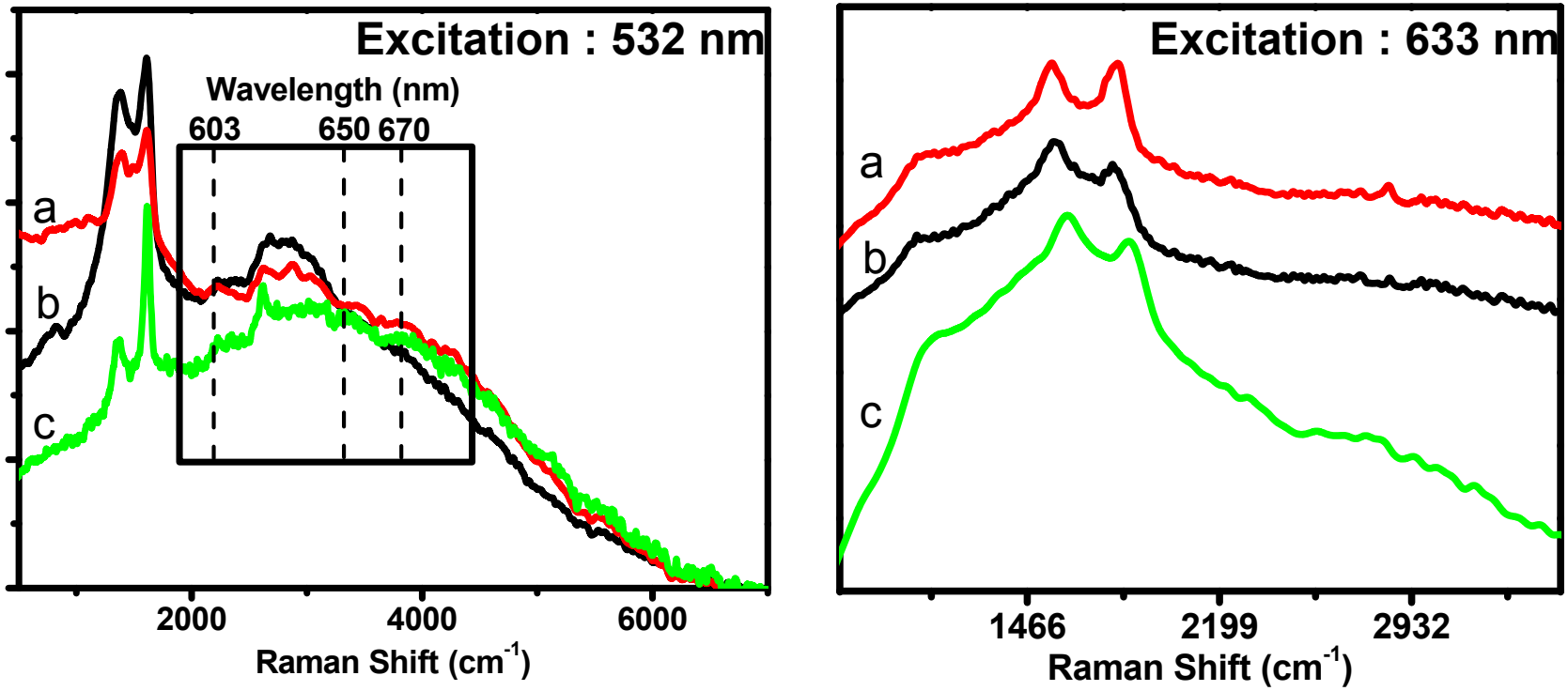

Raman Spectra of (a) Ag-SWNTs composite, (b) Au-SWNTs composite, (c) AuNR-SWNTs composite, (d) pristine SWNTs, (e) Pristine SWNTs treated with trisodium citrate and (f) Au nanorods.

# Raman Spectral imaging

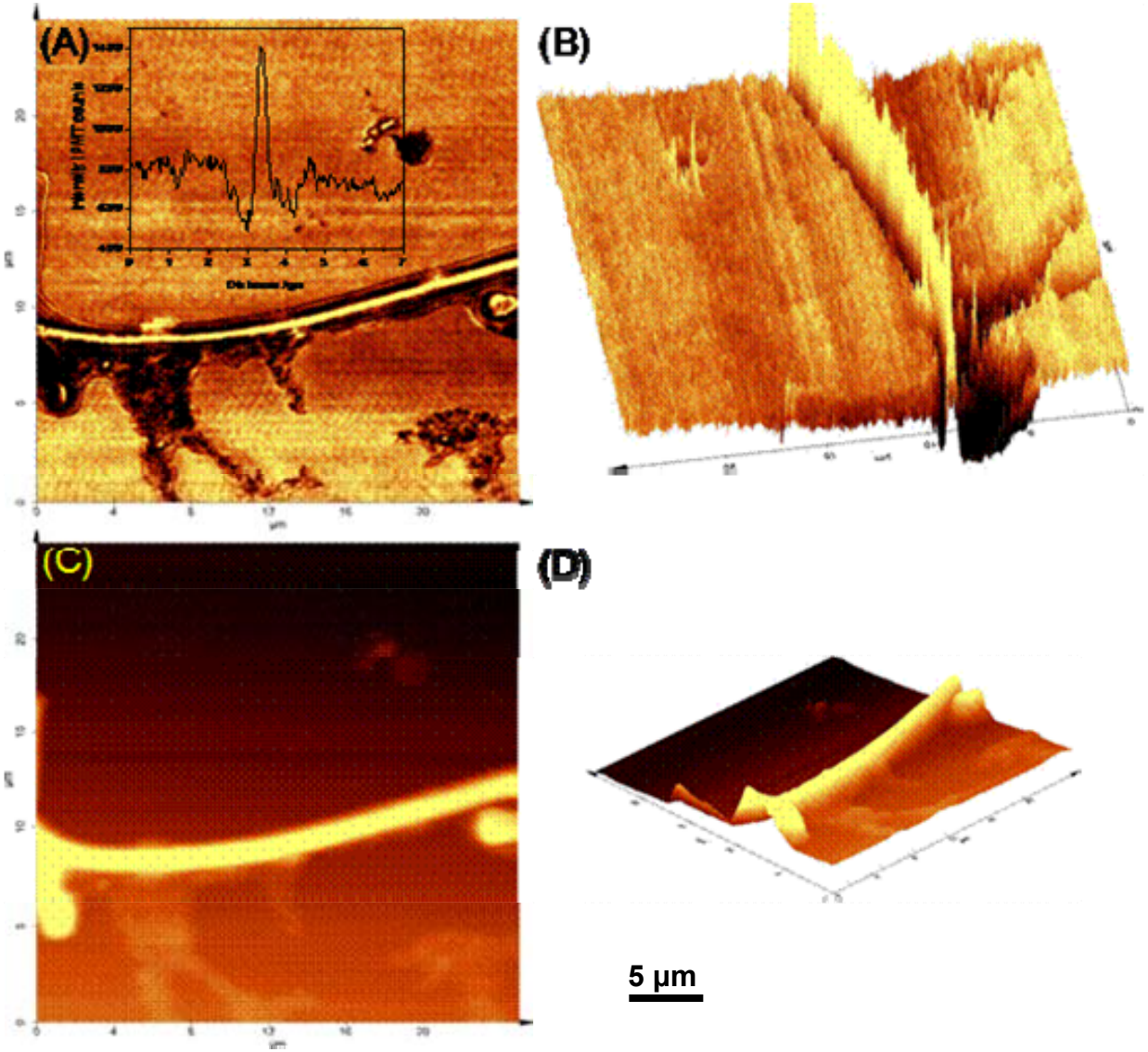


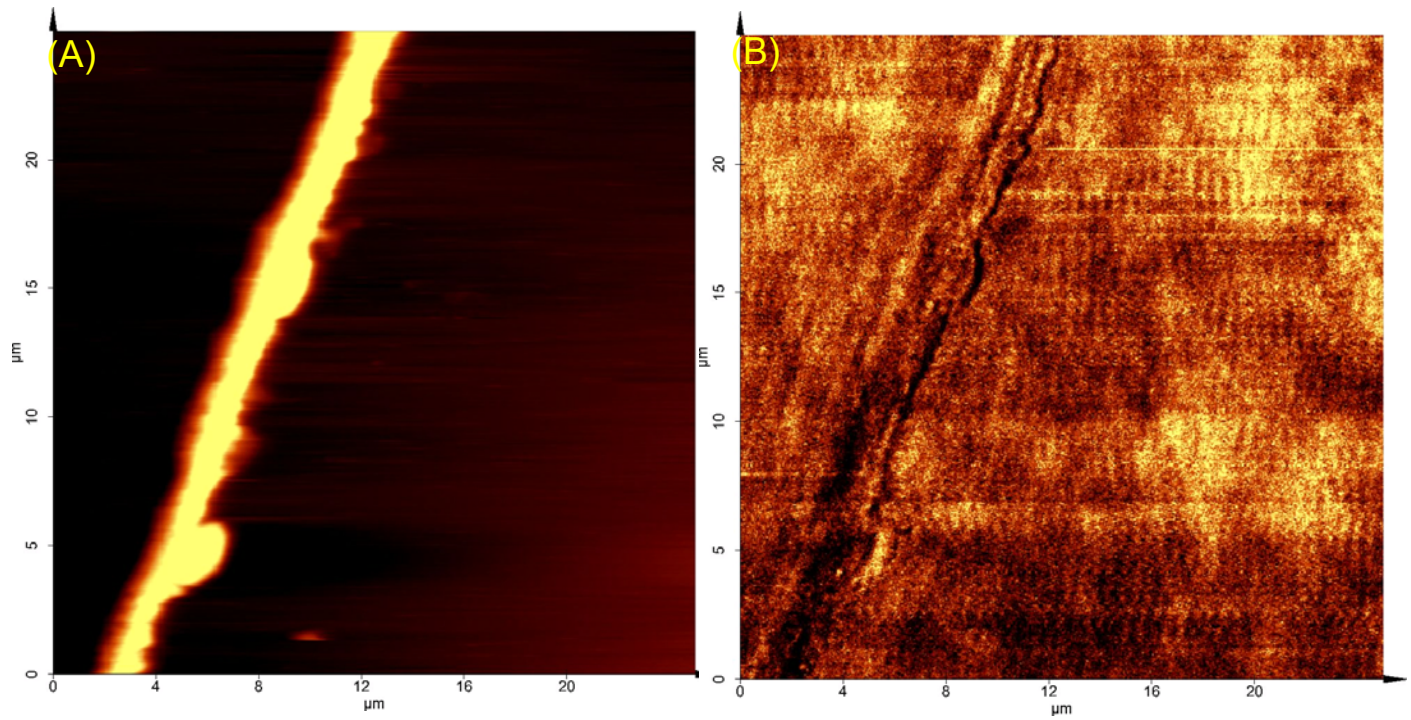
# Varying excitation sources




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.

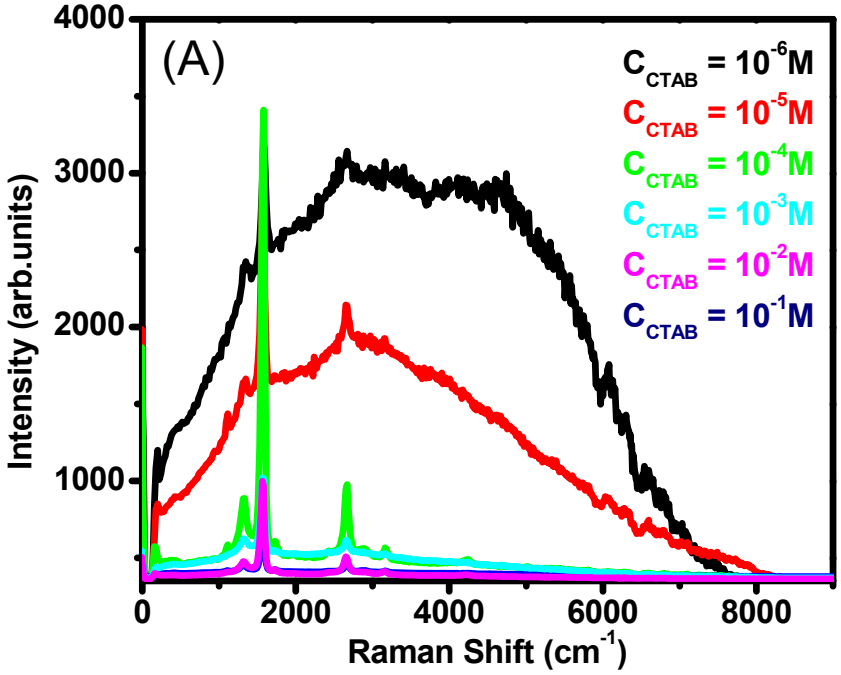


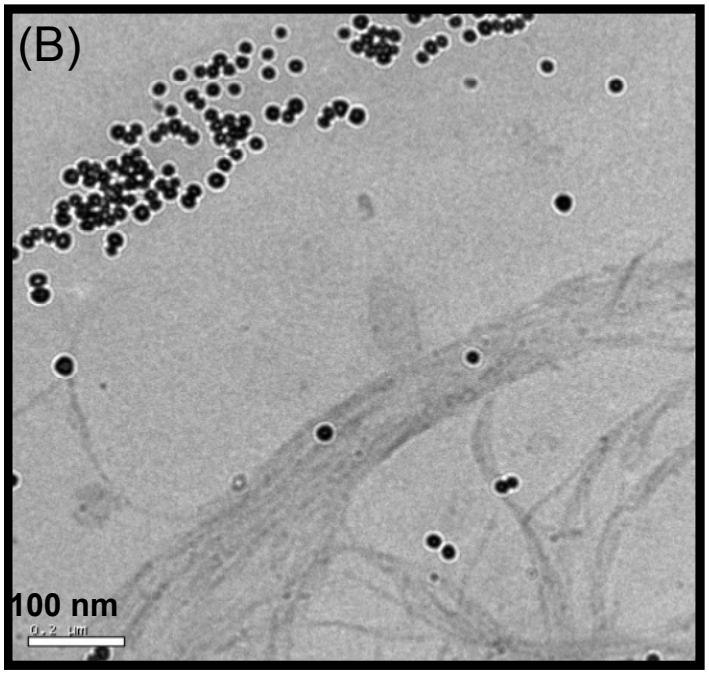

(A) SNOM images of Au-SWNT composite along with the (C) topography. (B) and (D) are their three dimensional representations.



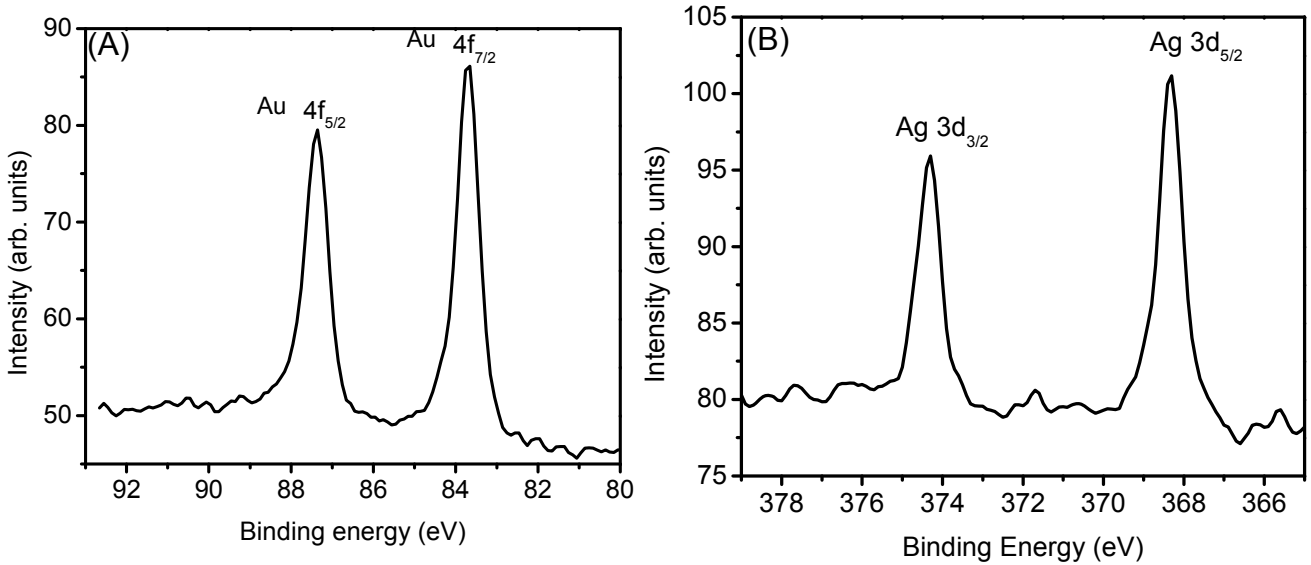

Transmission SNOM images of pristine SWNT based on (A) topography and (B) light intensity.

# Supporting experiments

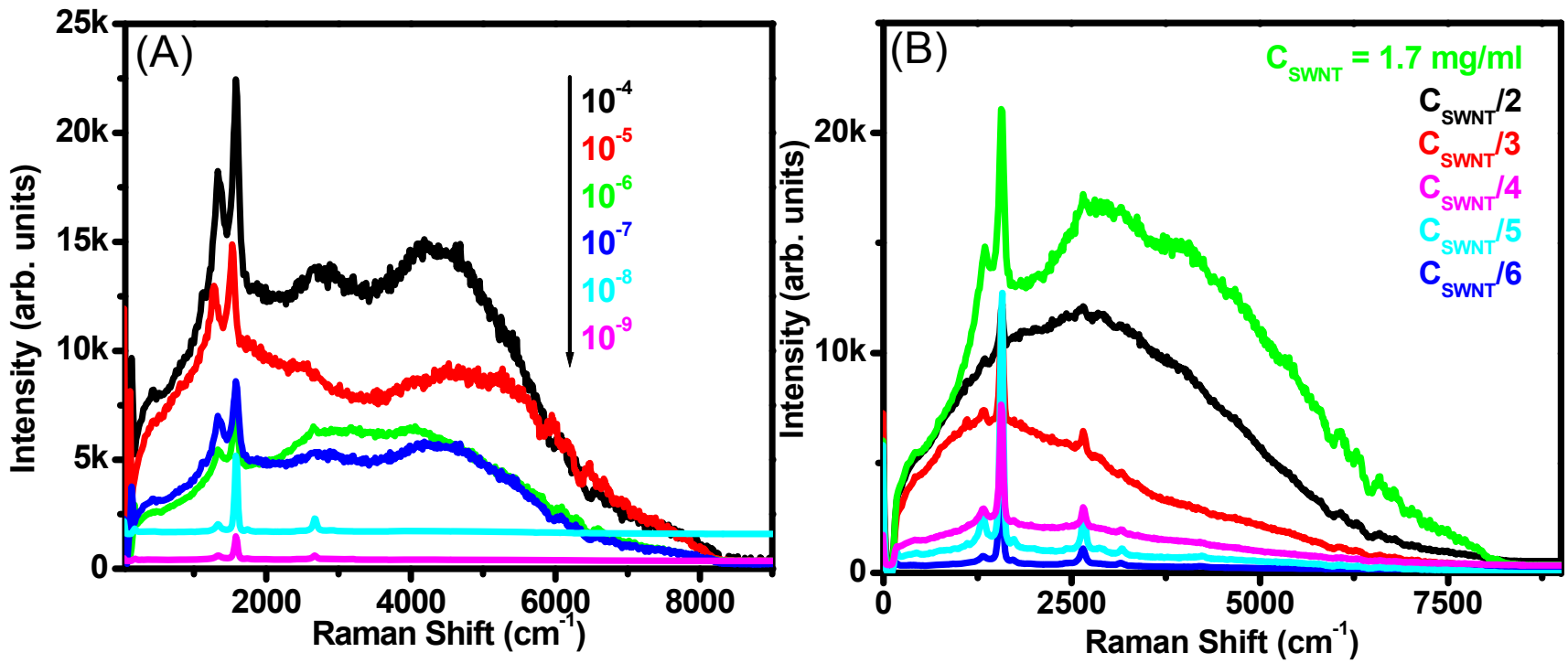



(A) Raman spectra of Ag-SWNT composite measured as a function of CTAB concentration. (B) TEM image of Au-CTAB-SWNT at $C_{CTAB} = 10^{-4}$M




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




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

# (*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 | |

## What we know so far

✓ Visible fluorescence from SWNTs is demonstrated.

✓ Raman spectral mapping is done to ascertain the origin of fluorescence.

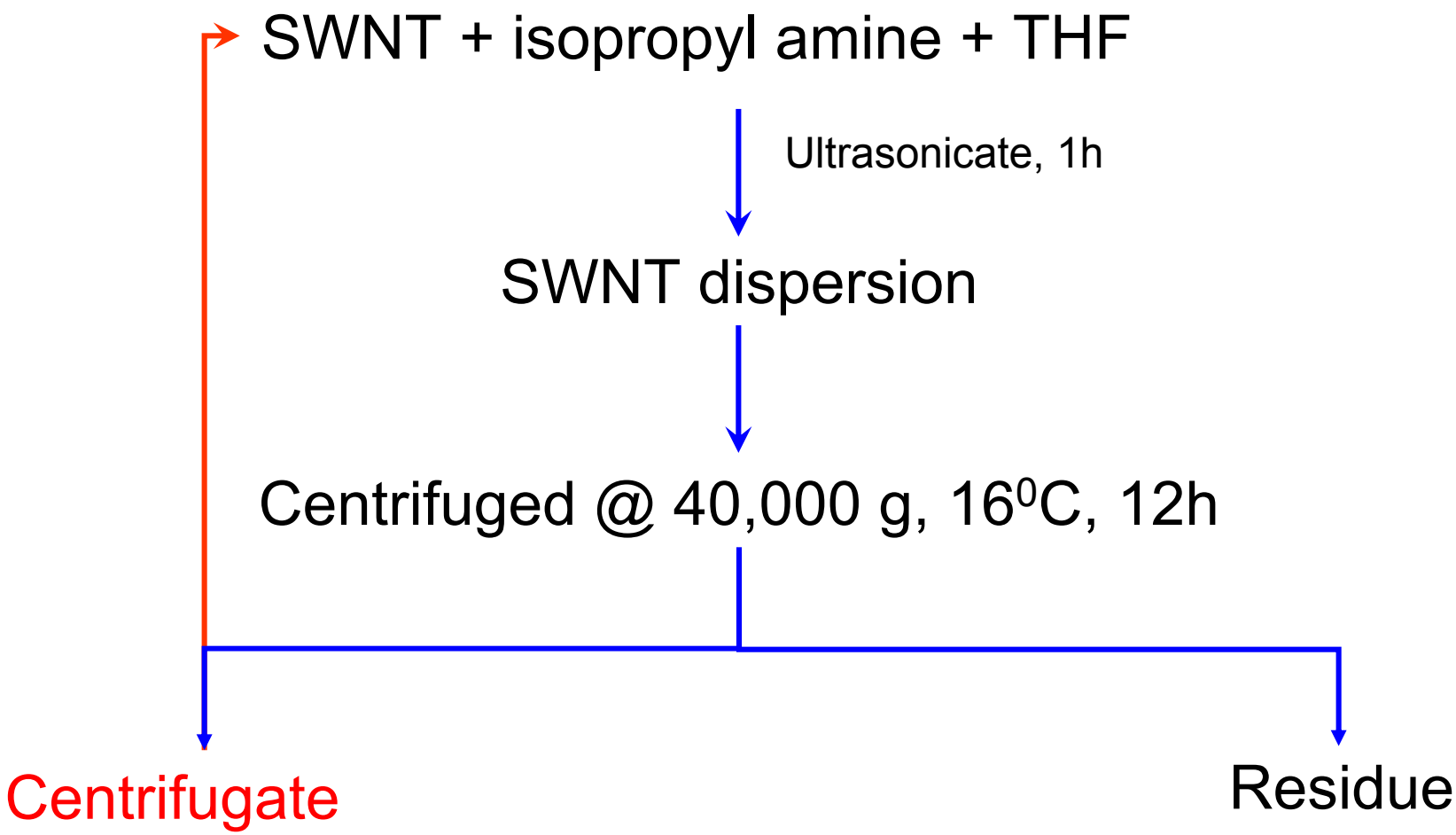
✓ SNOM of SWNT structures is done using this fluorescence.

## Origin of visible fluorescence

- Near-infrared fluorescence in isolated SWNT is known.
- This is not observed in bundles and metallic SWNTs.
- Metallic SWNTs offer non-radiative decay channels.

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

# Separation protocol

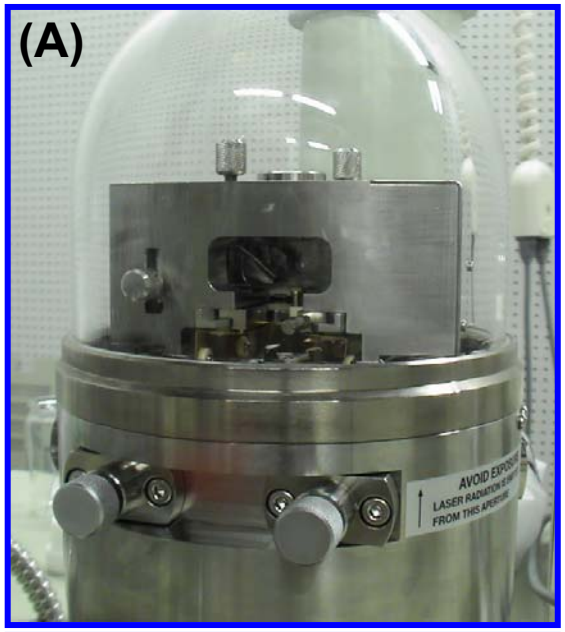


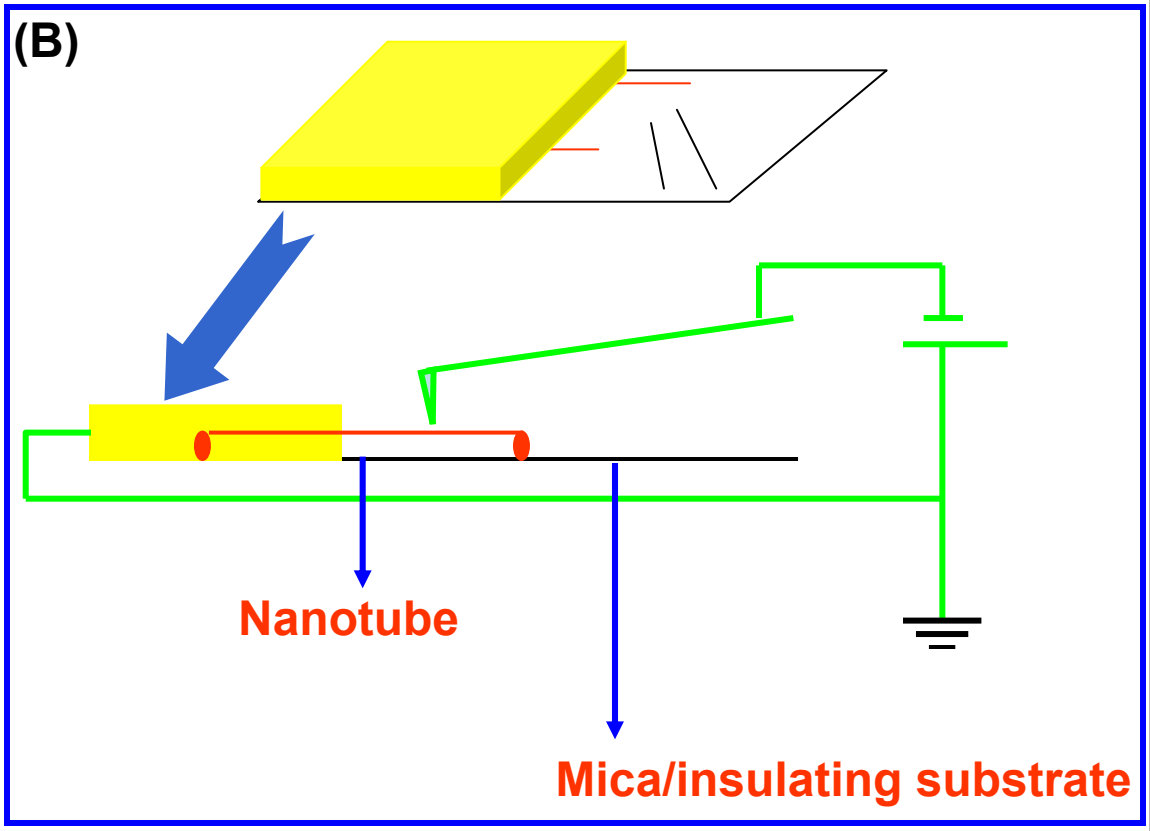

Alkyl amines stabilize metallic SWNT

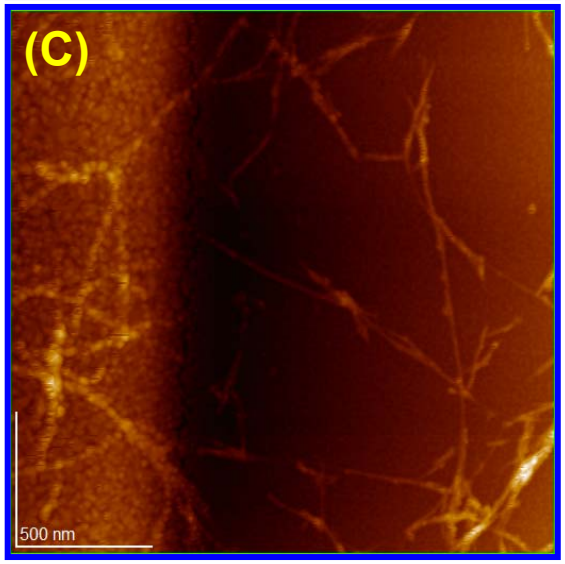


Maeda, S., *et al J. Am. Chem. Soc.*, **2005**, *127*, 10287.

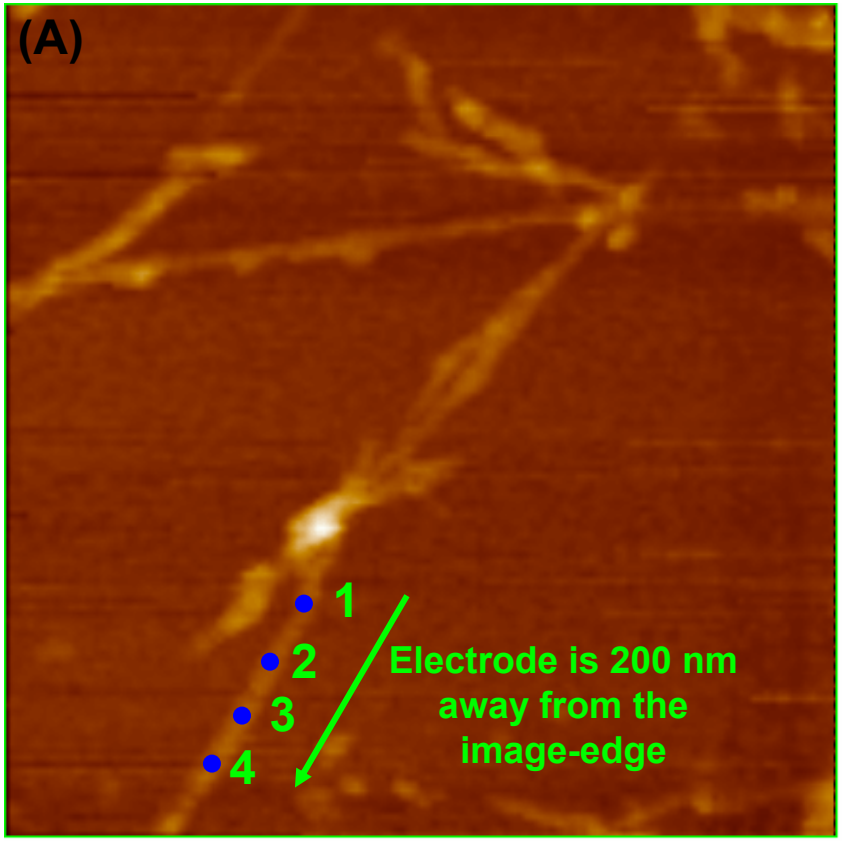
# Measurement geometry

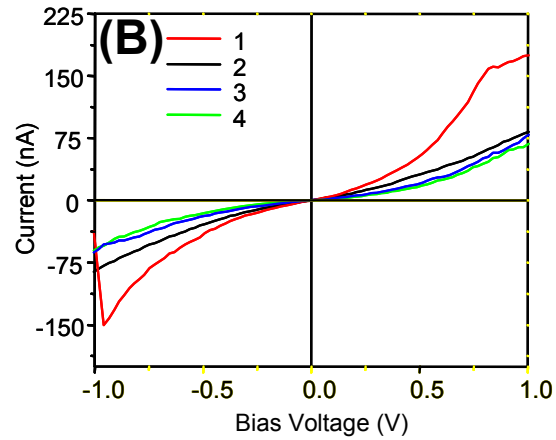


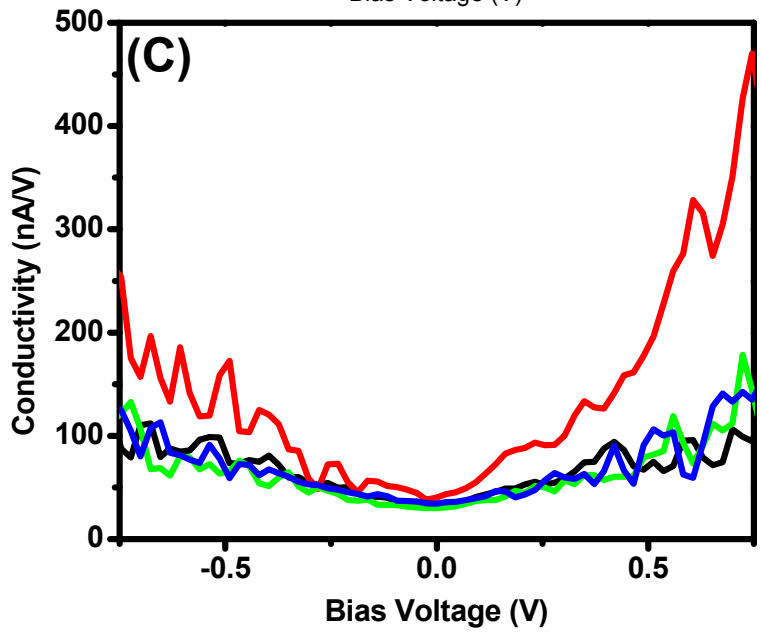



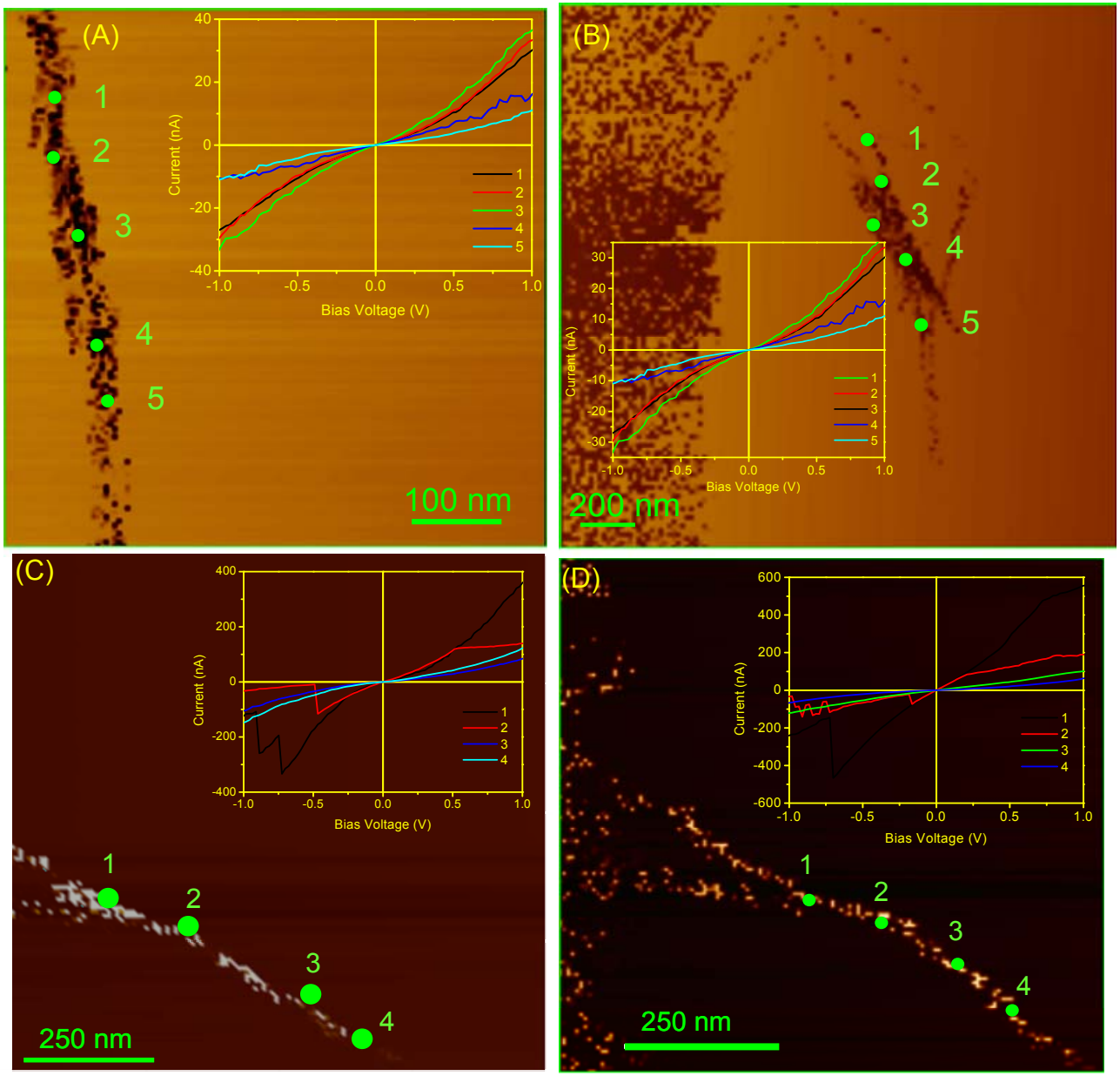

(A) Photograph of the scanning head, (B) schematic of the PCI-AFM measurement and (C) representative AFM image of pristine SWNTs

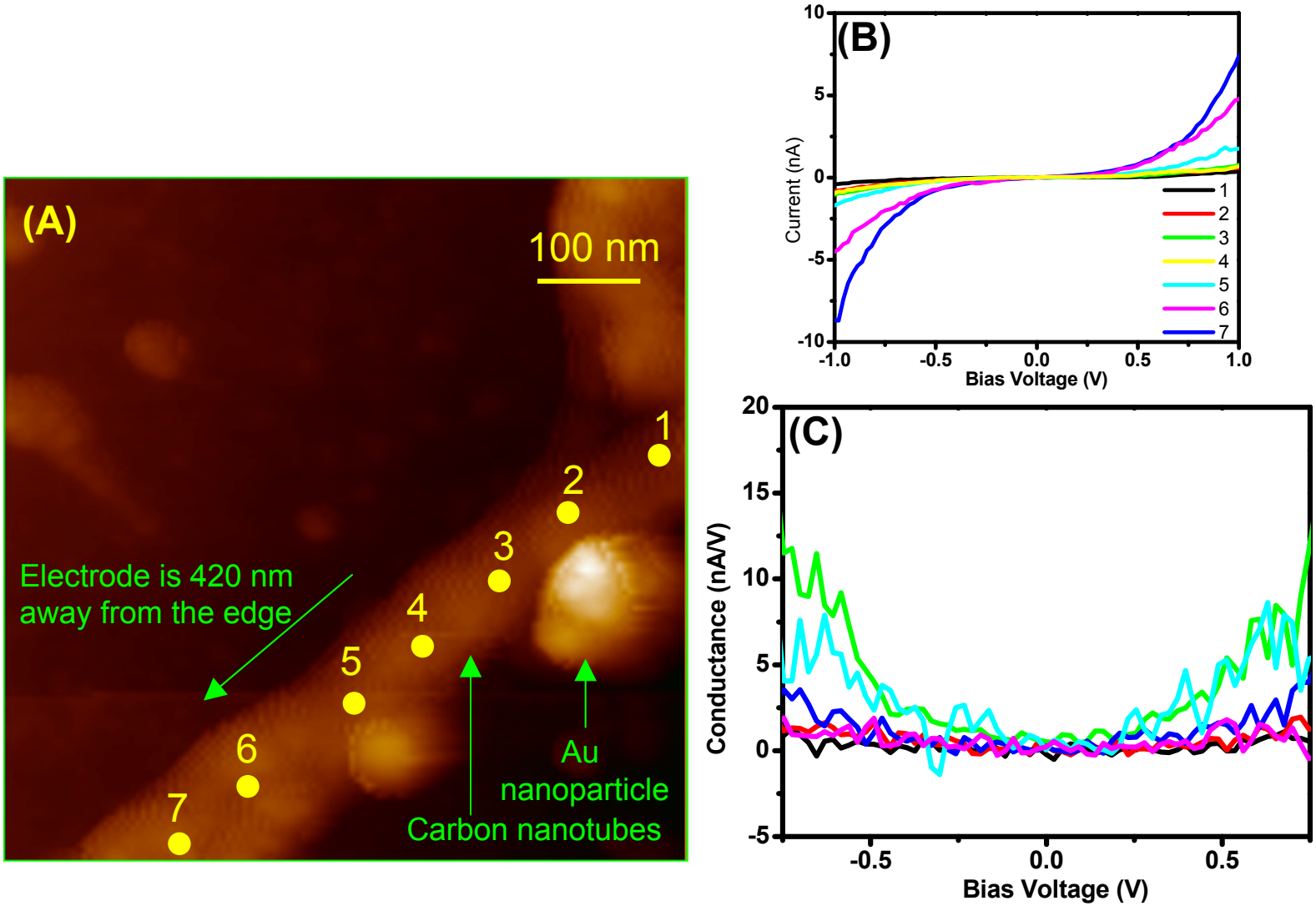


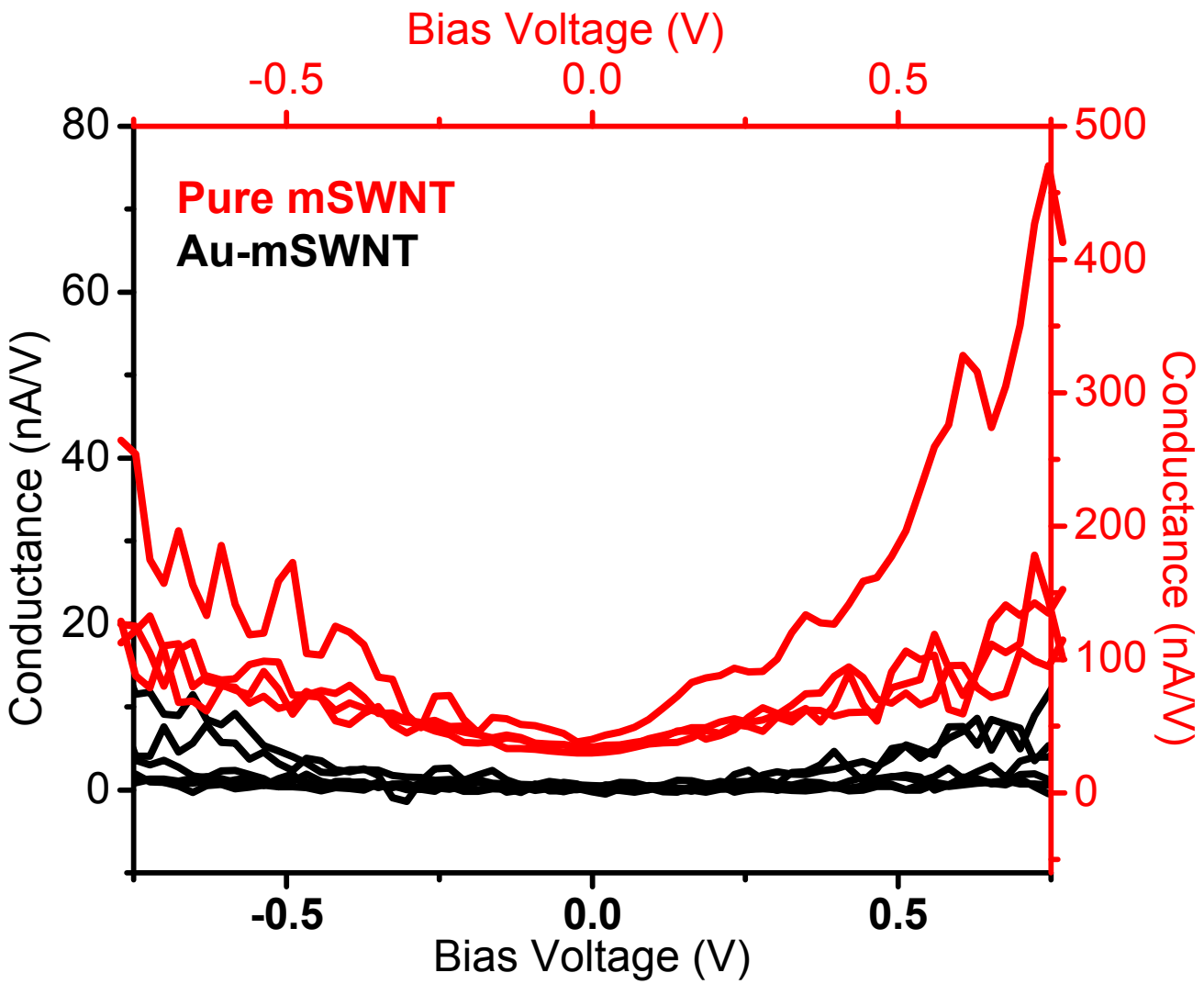




(A) PCI-AFM images of pure mSWNT with (B) I-V curves and (C) plot of conductance versus bias voltage.


(A)
1
2
3
4
5
100 nm
Current (nA)
Bias Voltage (V)
(B)
200 nm
(C)
250 nm
(D)
250 nm

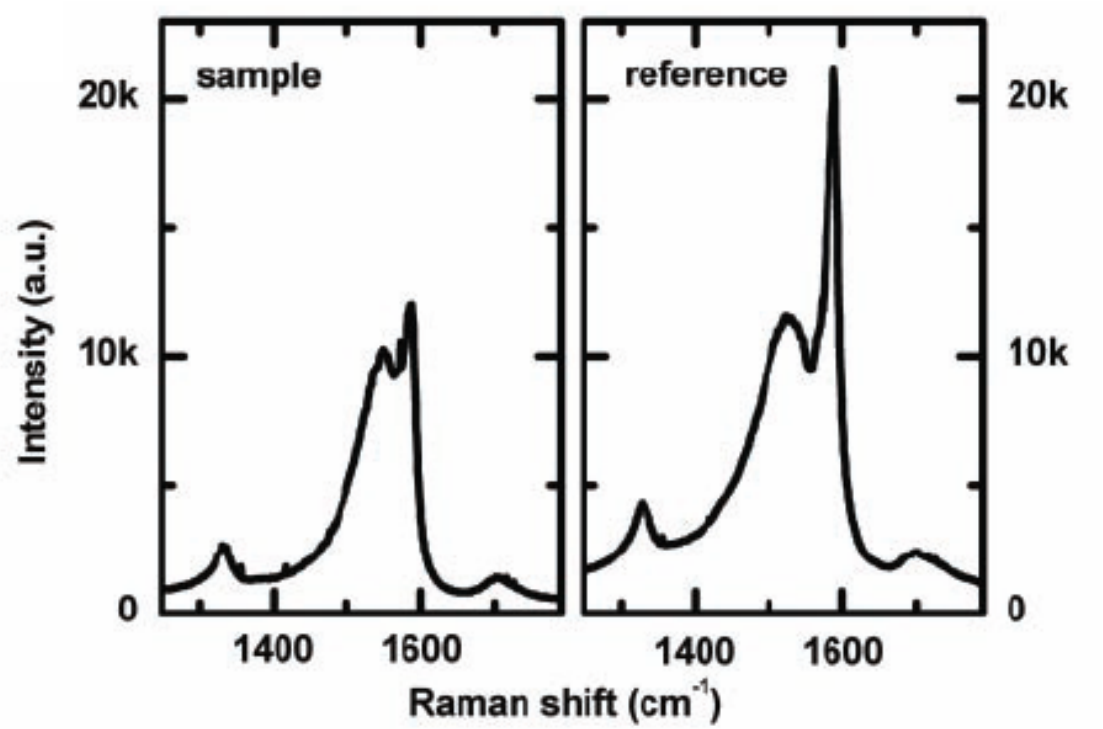



(A) PCI-AFM image of Au-mSWNT with (B) the corresponding I-V curves and (C) Plot of conductance versus bias voltage.




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

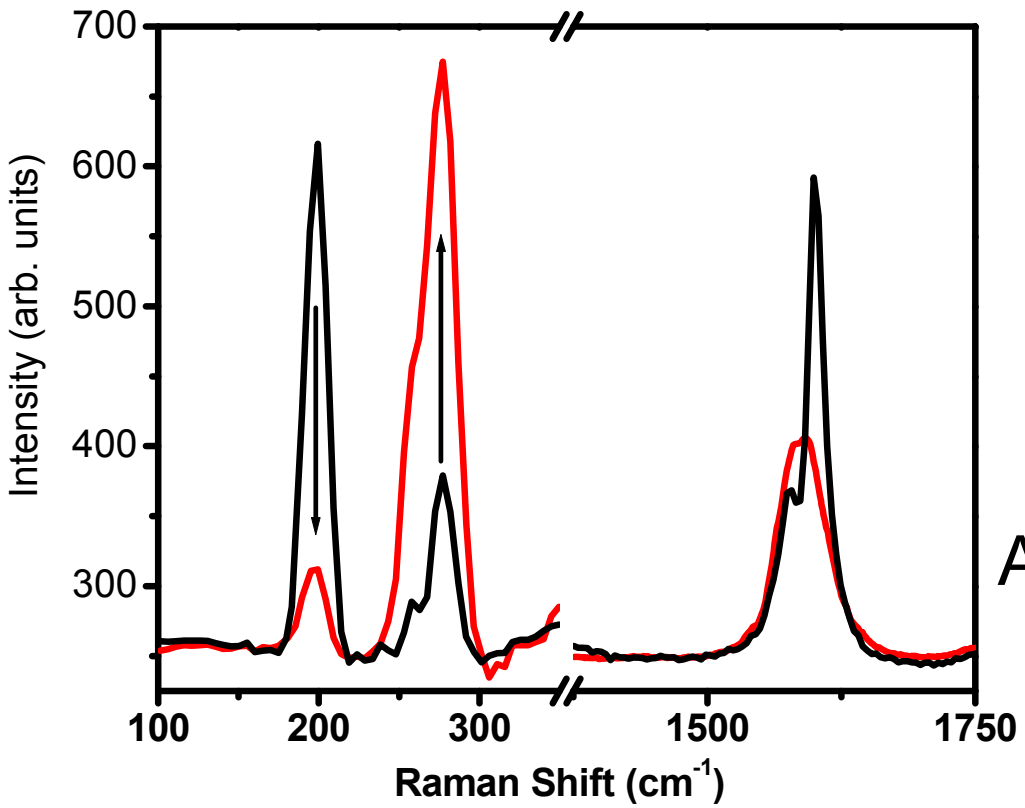
# G-band line shapes of metallic and semiconducting SWNT




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

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

# Confocal Raman investigations



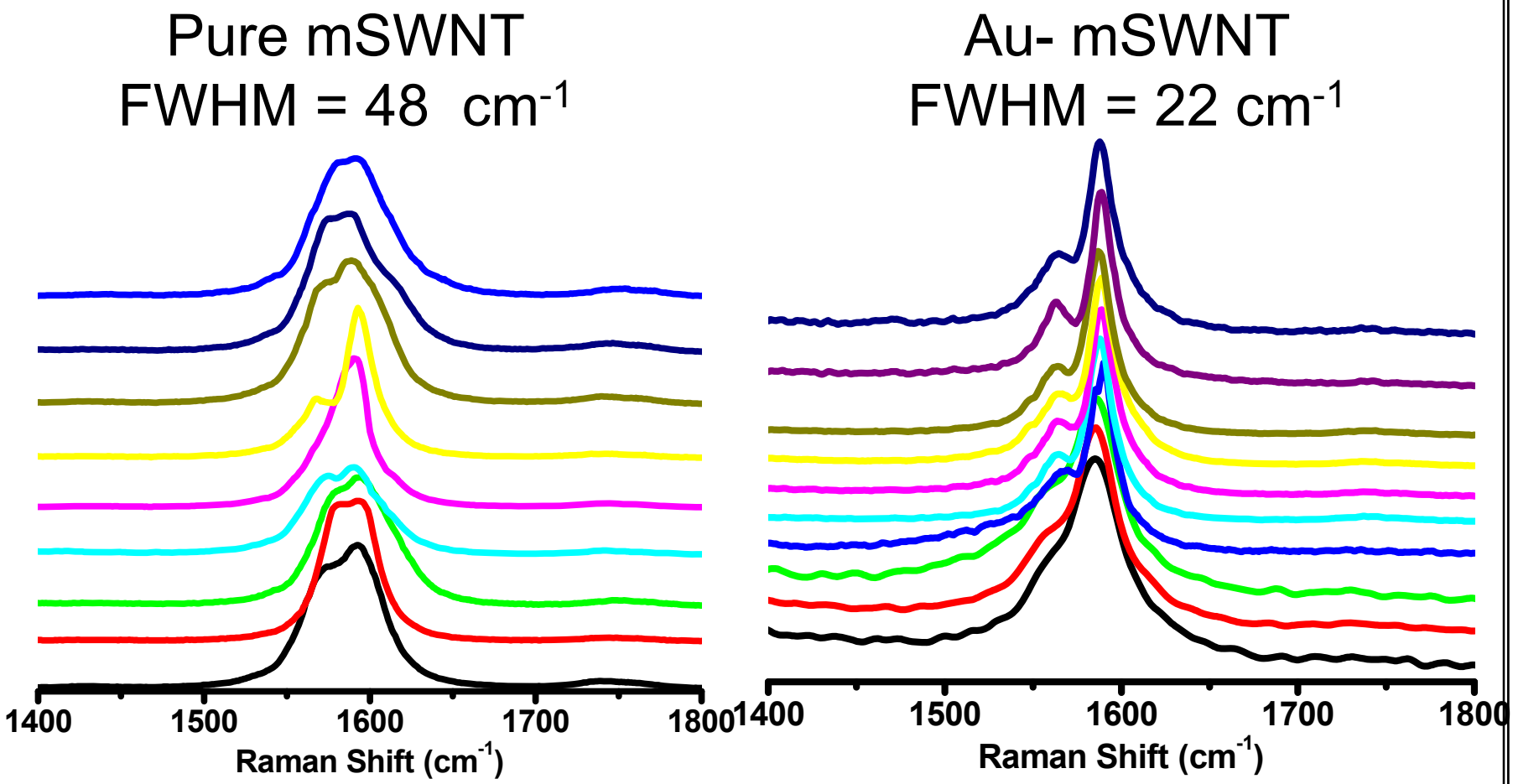

$A_s/A_m = 65.0$

$A_s/A_m = 0.14$

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.

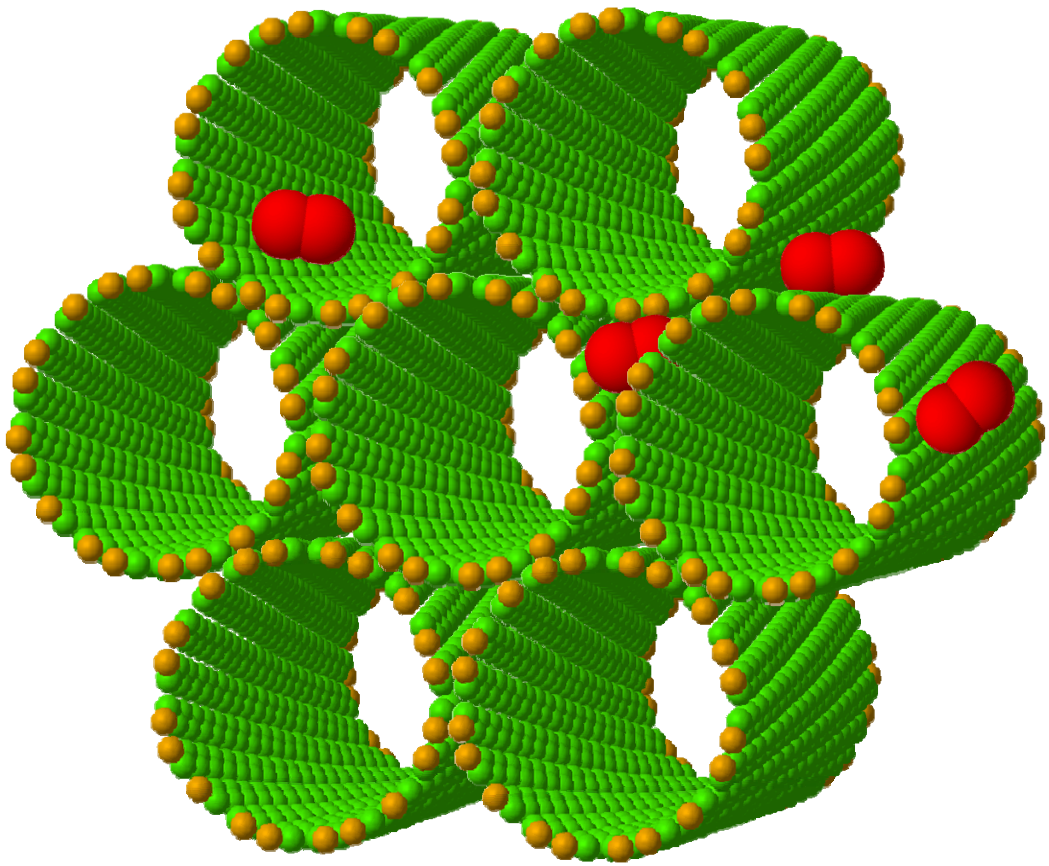
M-S transition has far reaching implication in nanoelectronics and design of nanodevices.

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

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

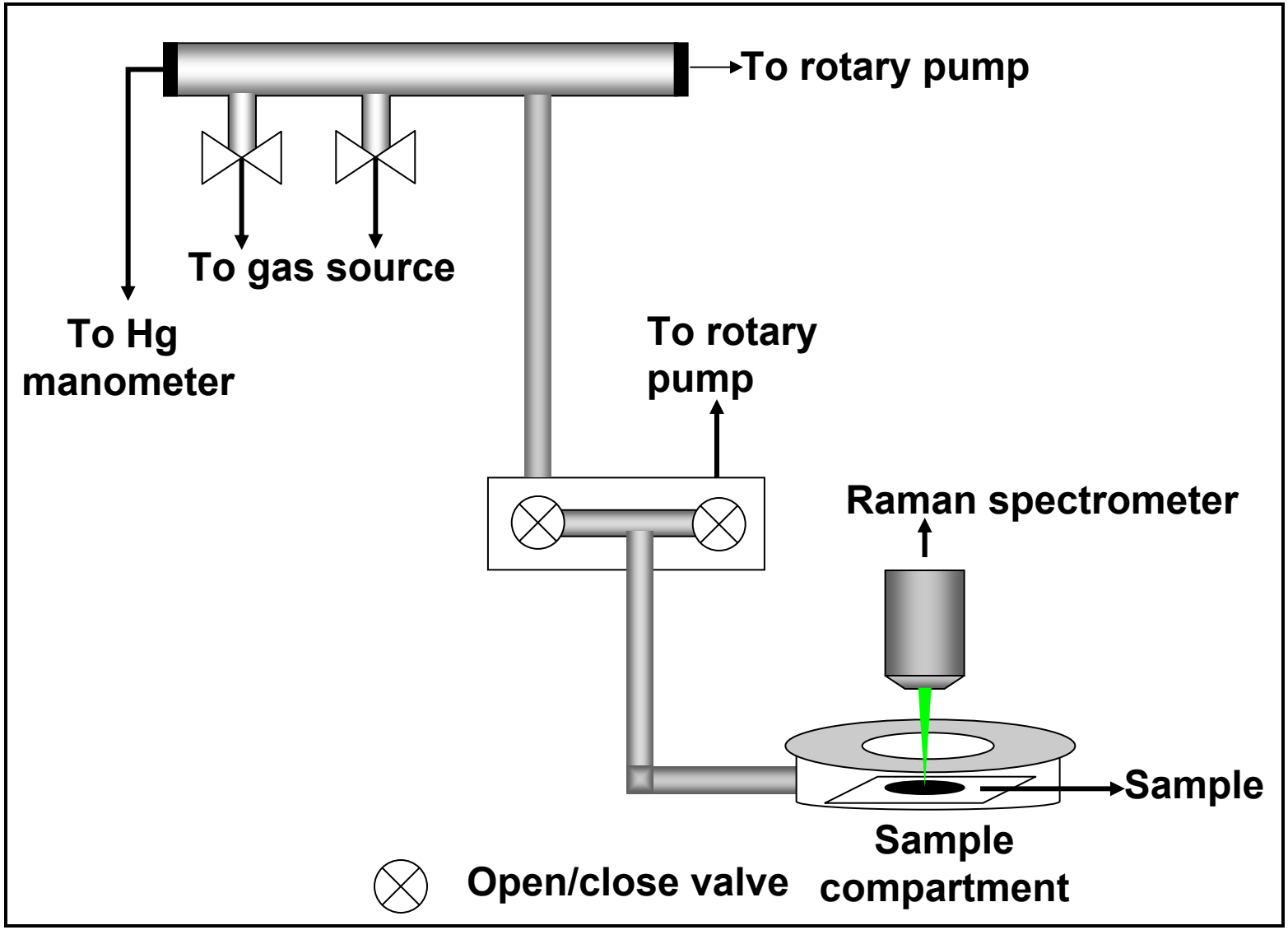
# *Nanotube gas sensors using fluorescence*

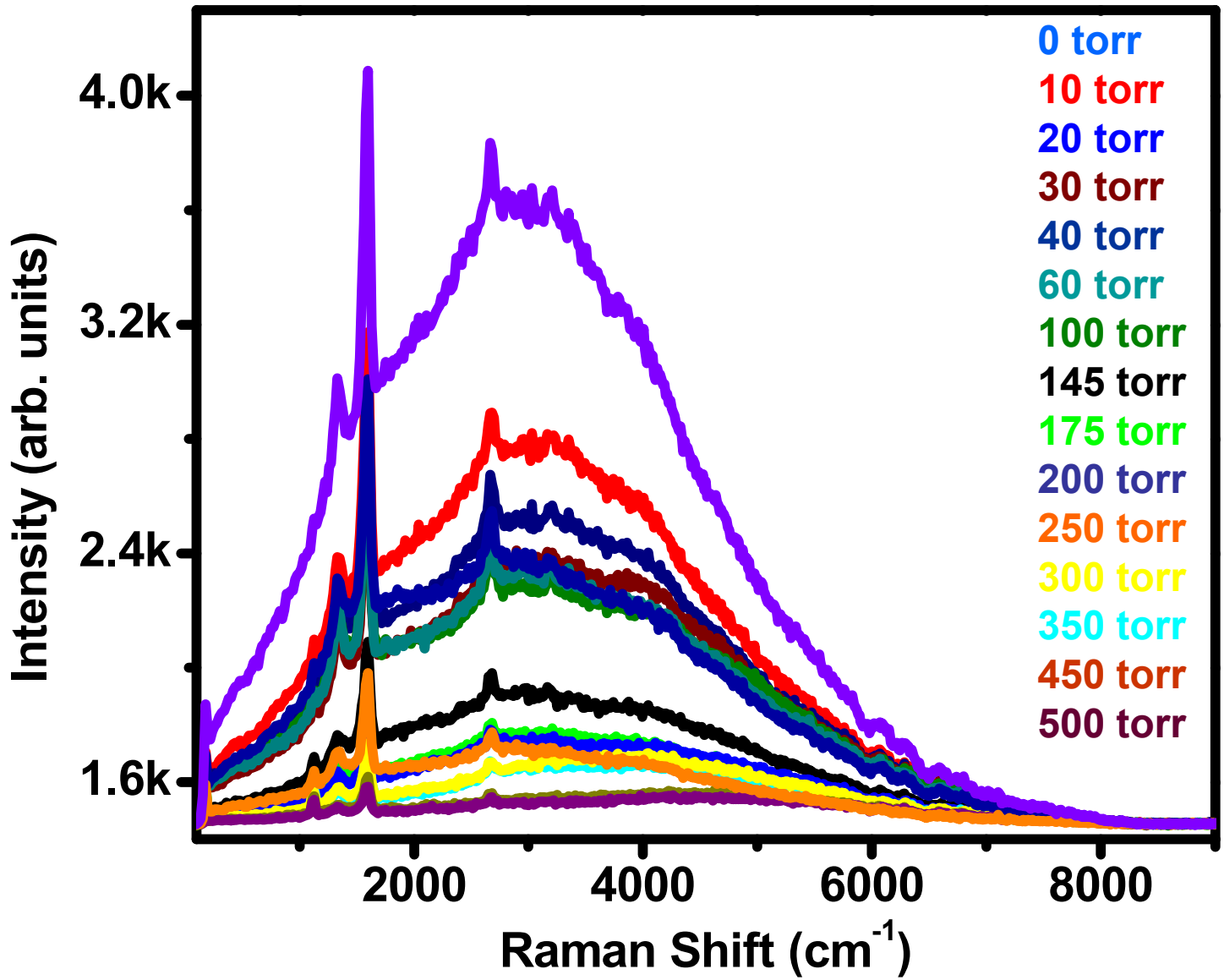
# Fluorescence as a probe for studying gas-adsorption behavior



- Endohedral
- Interstitial
- Groove
- External

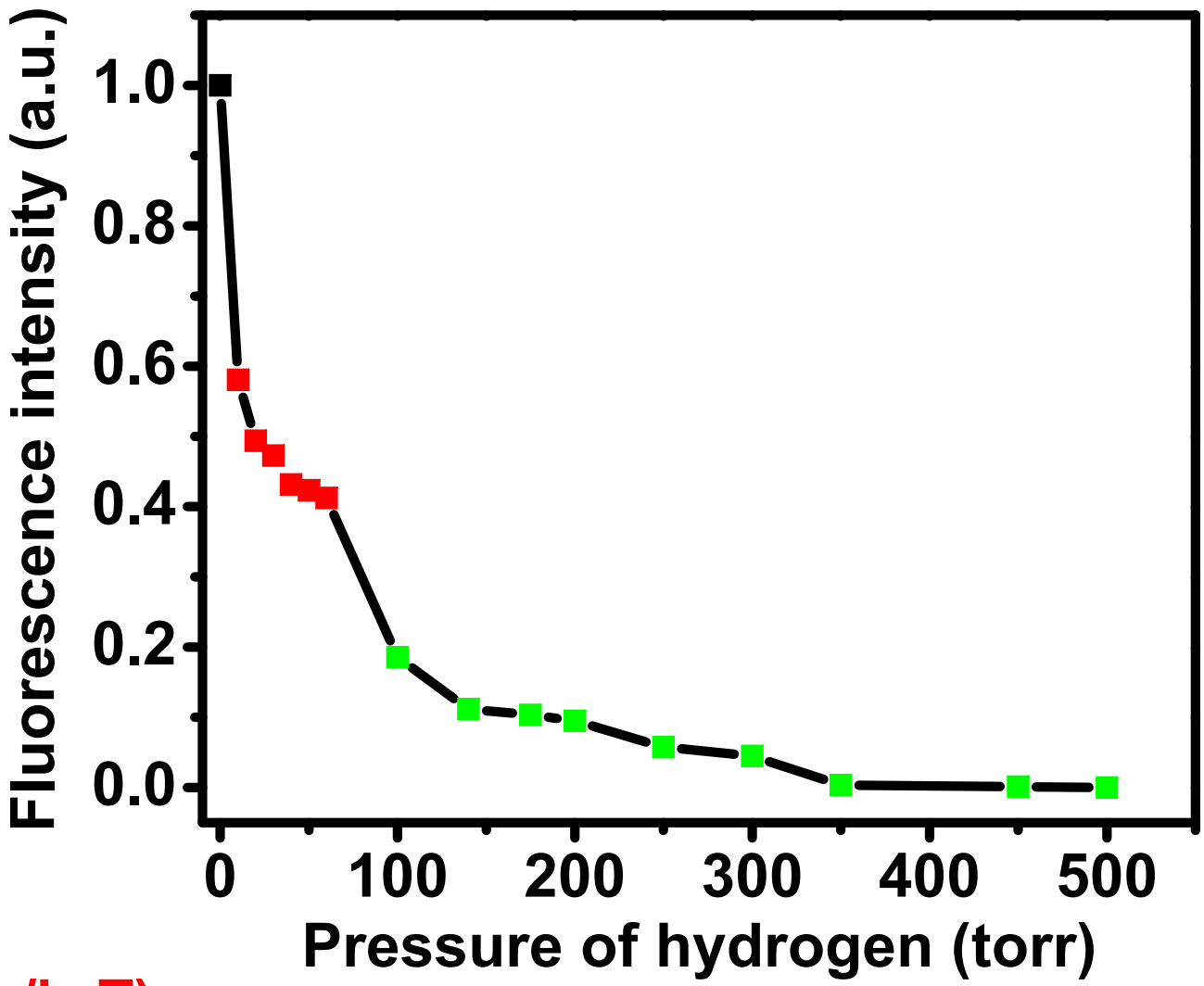
# Instrumentation – Schematic of the gas-setup






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

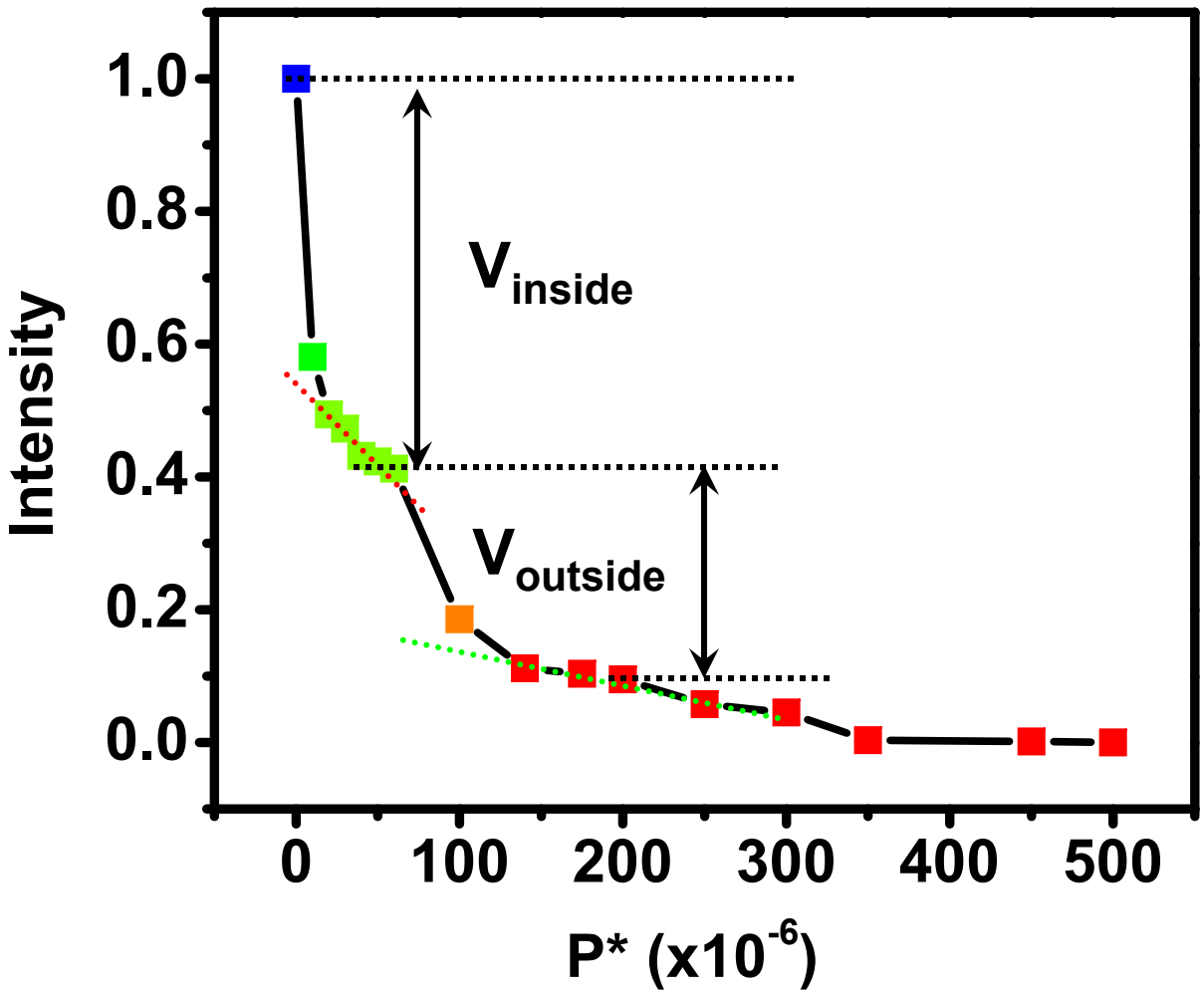
% occupancy ~




$I = P_0 \exp(-E_a/k_B T)$

Slope, $m \sim E_a(\Delta H)$

Bulk pressure

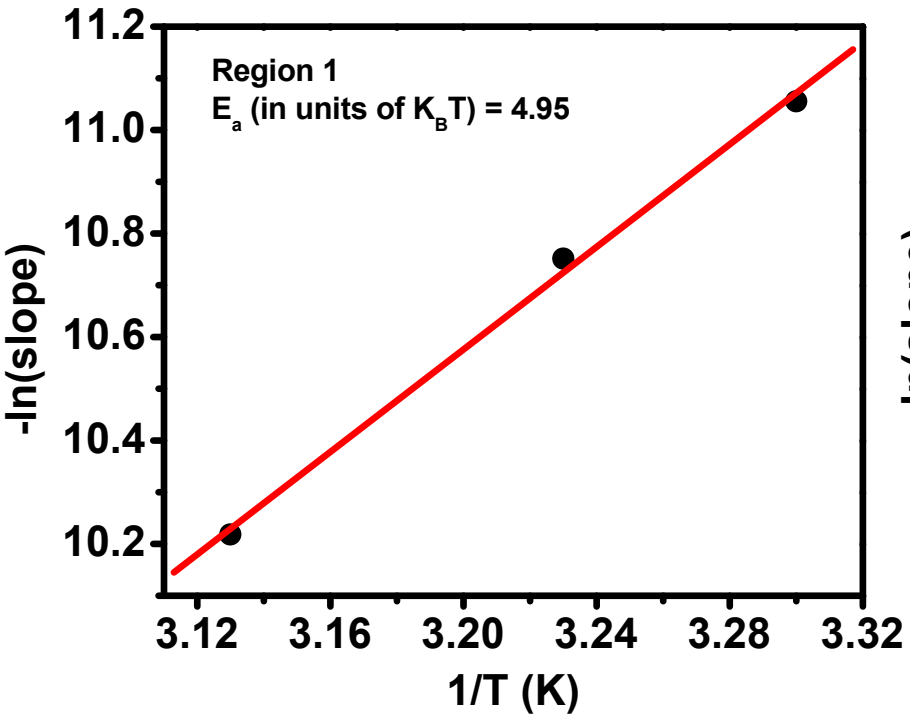


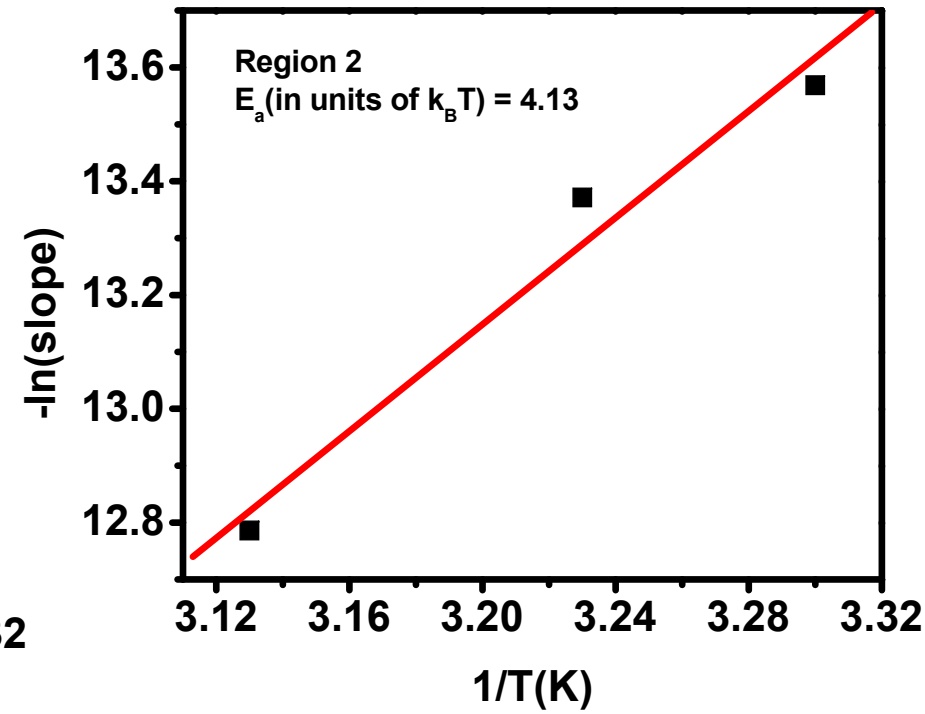

$V_{inside}$ = 59 % (60%)

$V_{outside}$ = 32 % (40%)

$m_{inside}$ = 8.6 (3.0)

$m_{outside}$ = 6.9 (2.0)



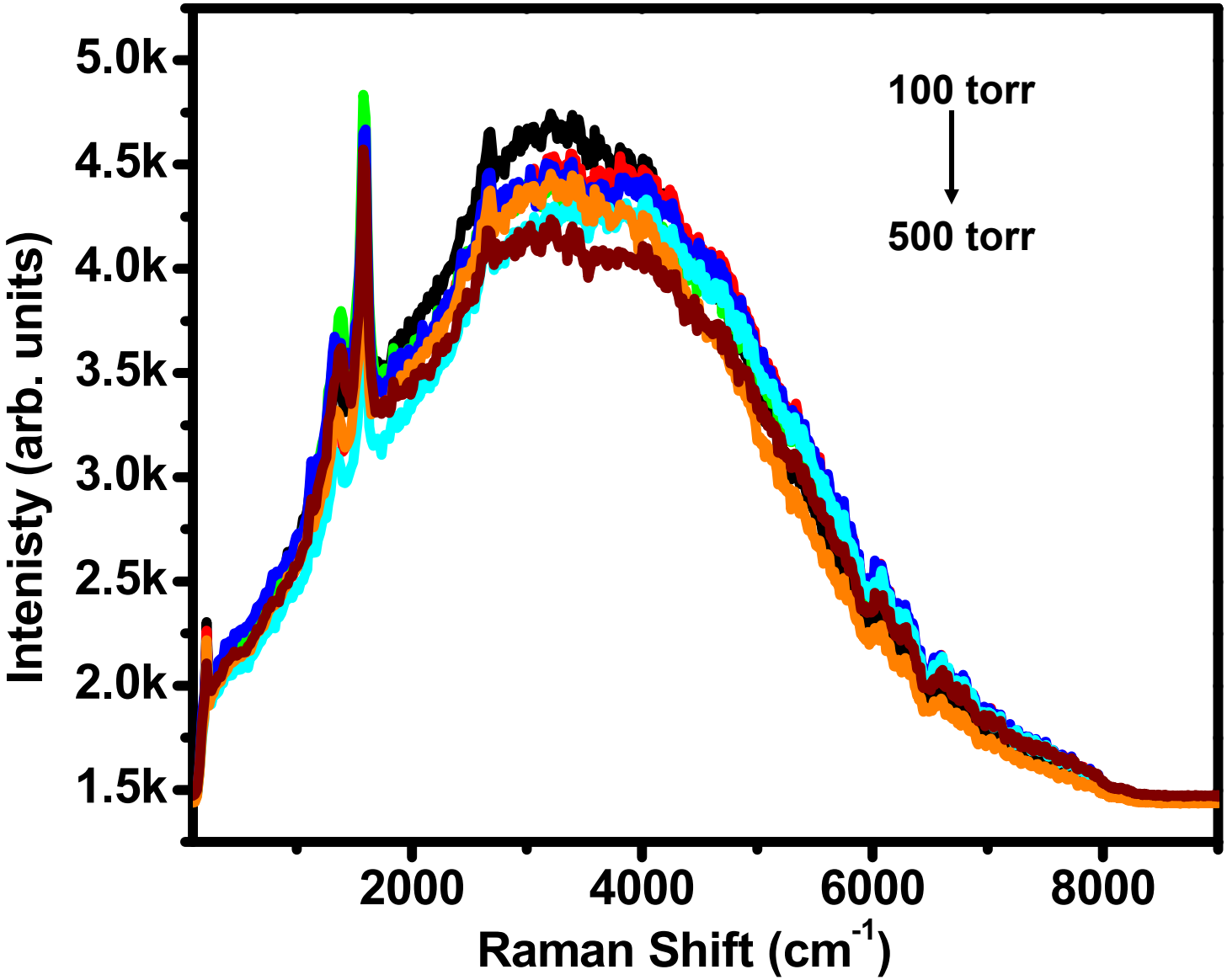




**Arrhenius plot of -log(k) versus 1/T for two different regions where,**

**Region 1 : Interstitial and endohedral sites**

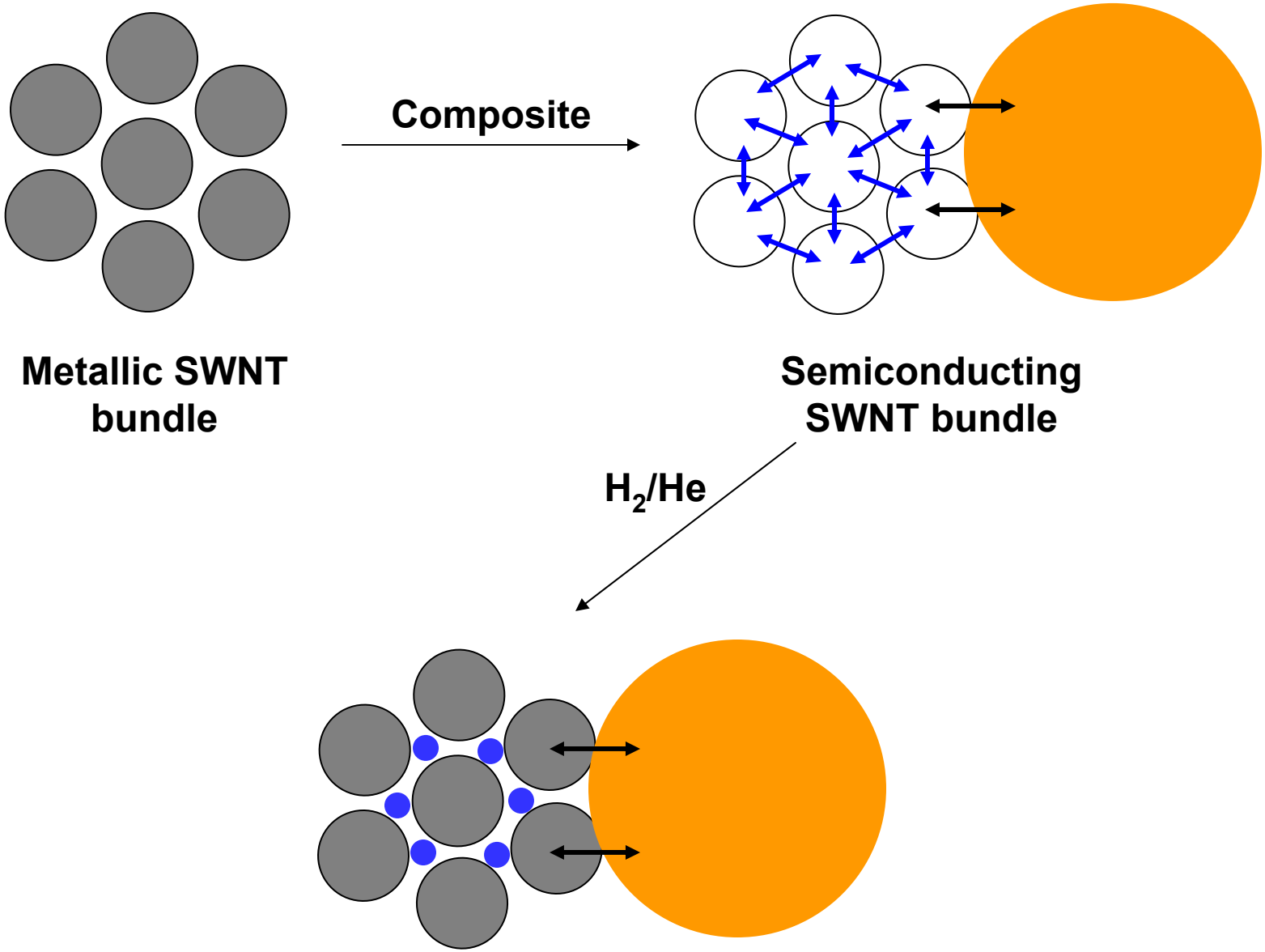
**Region 2 : Groove and external sites**

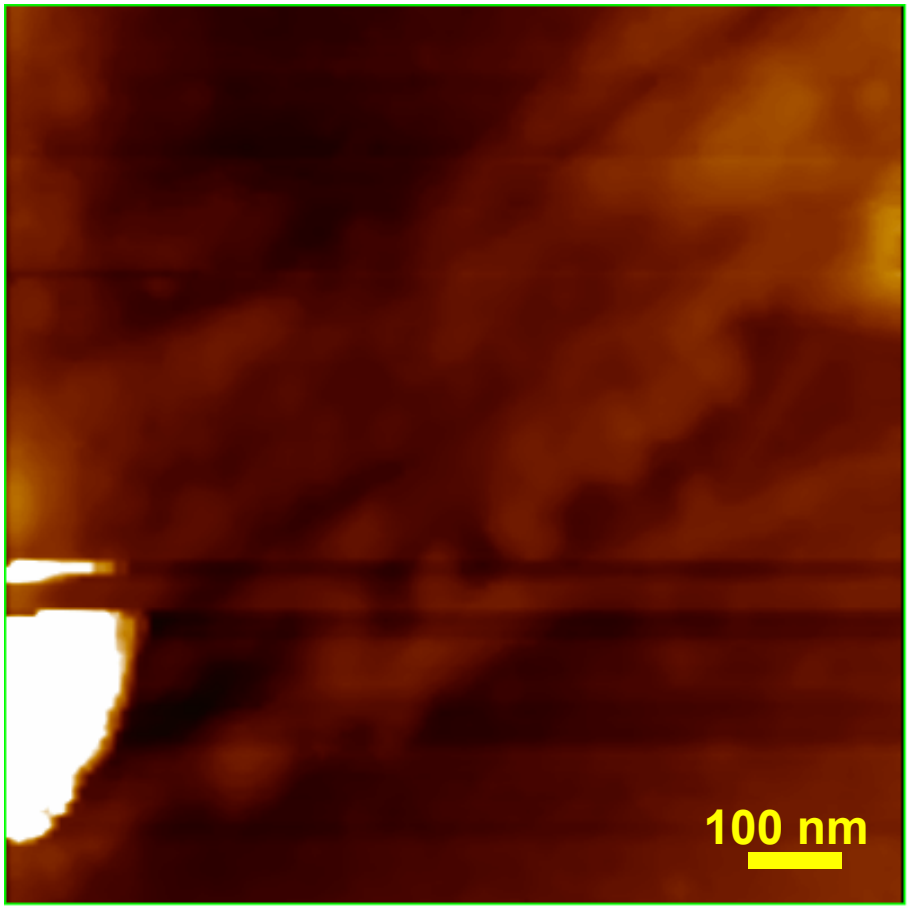
**The slope, giving the value of $E_a$ is given in the inset.**

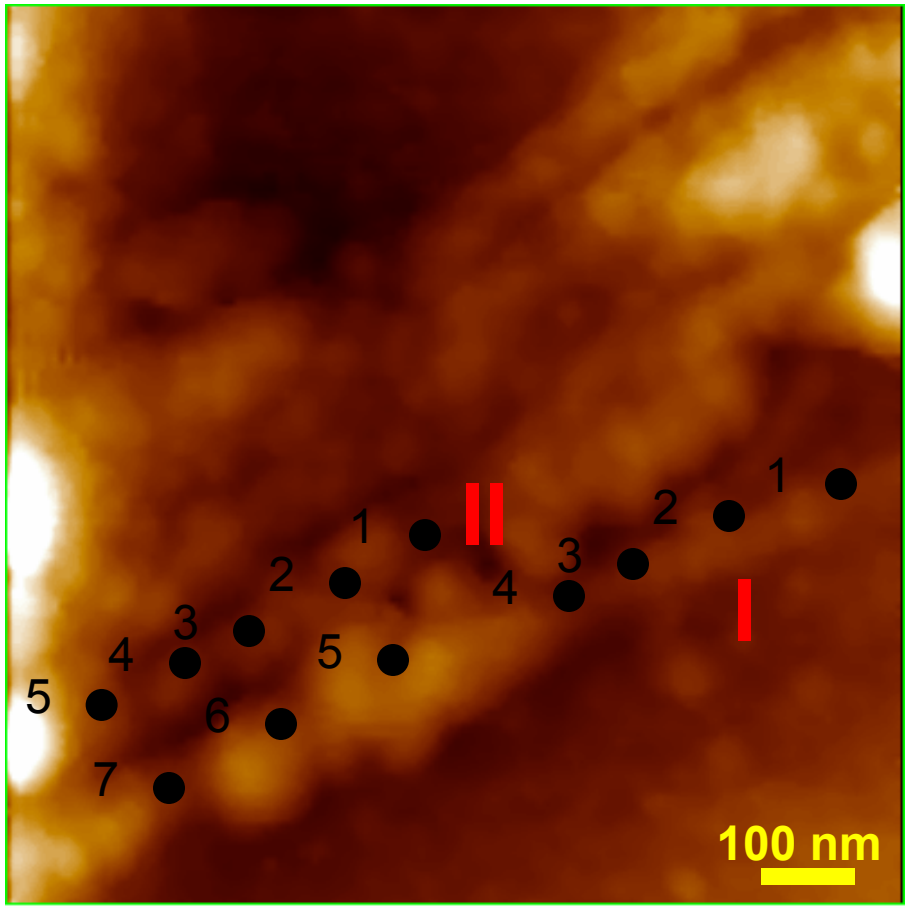



**Au-SWNTs exposed to $N_2$ gas at various partial pressures.**

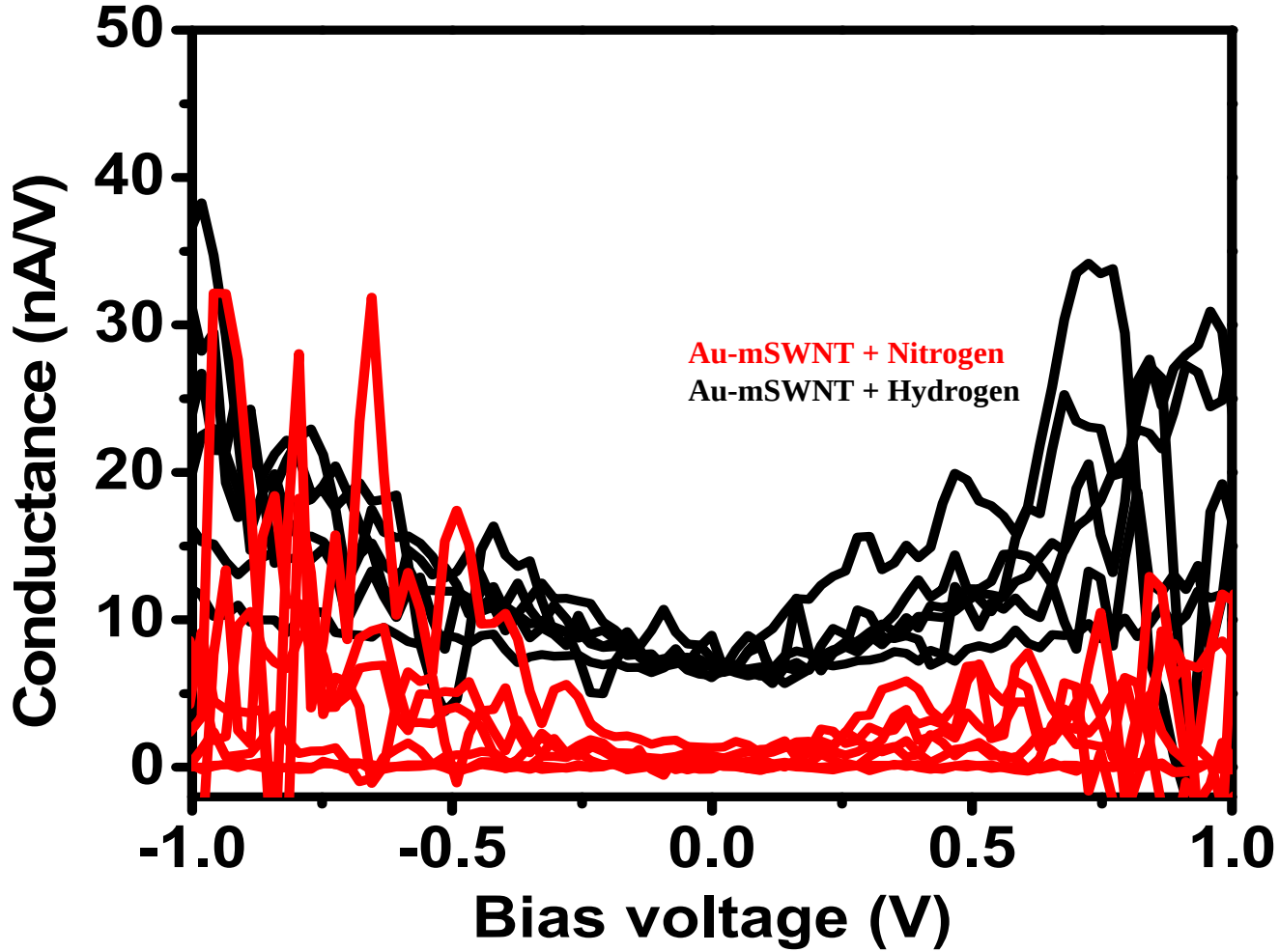
## Suggested mechanism



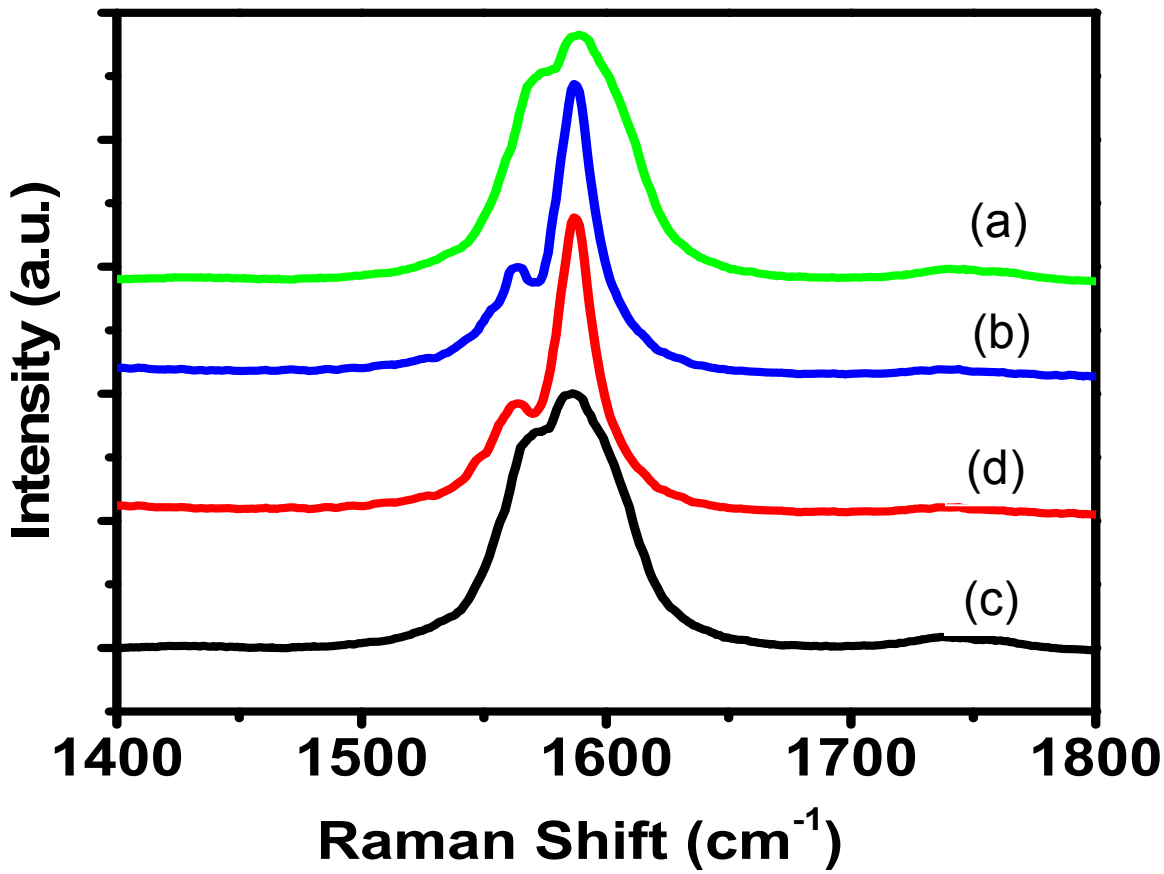



**PCI-AFM images of Au-mSWNT composite. The points on the bundles considered for I-V characteristics have been marked, although all other bundles are also characterized.**




**Plot of conductance versus bias voltage constructed at various point of Figure 1A, under an atmosphere of nitrogen (red traces) and hydrogen (black traces).**




**Raman spectra of (a) purified mSWNTs, (b) Au-mSWNT composite, (c) Au-mSWNT upon exposure to 500 torr $H_2$ and (d) Au-mSWNT composite after pumping out $H_2$ exposed in (c). Spectra (a) to (d) are recorded at the same point on the composite sample.**

## Conclusions and future directions

**Gas adsorption inside SWNT was studied using visible fluorescence from Au-SWNTs composite**

**Behavior was similar in case of Ag-SWNT and AuNR-SWNT composites.**

**In-situ gas storage detection**

**Observation of different adsorption sites**

**Gas separation**

**Understanding gas storage inside SWNTs**

**Probing electronic structure variation upon gas adsorption**

**Possibilities of isomer separation**

*C. Subramaniam and T. Pradeep Patent application 2008*

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Thank you all