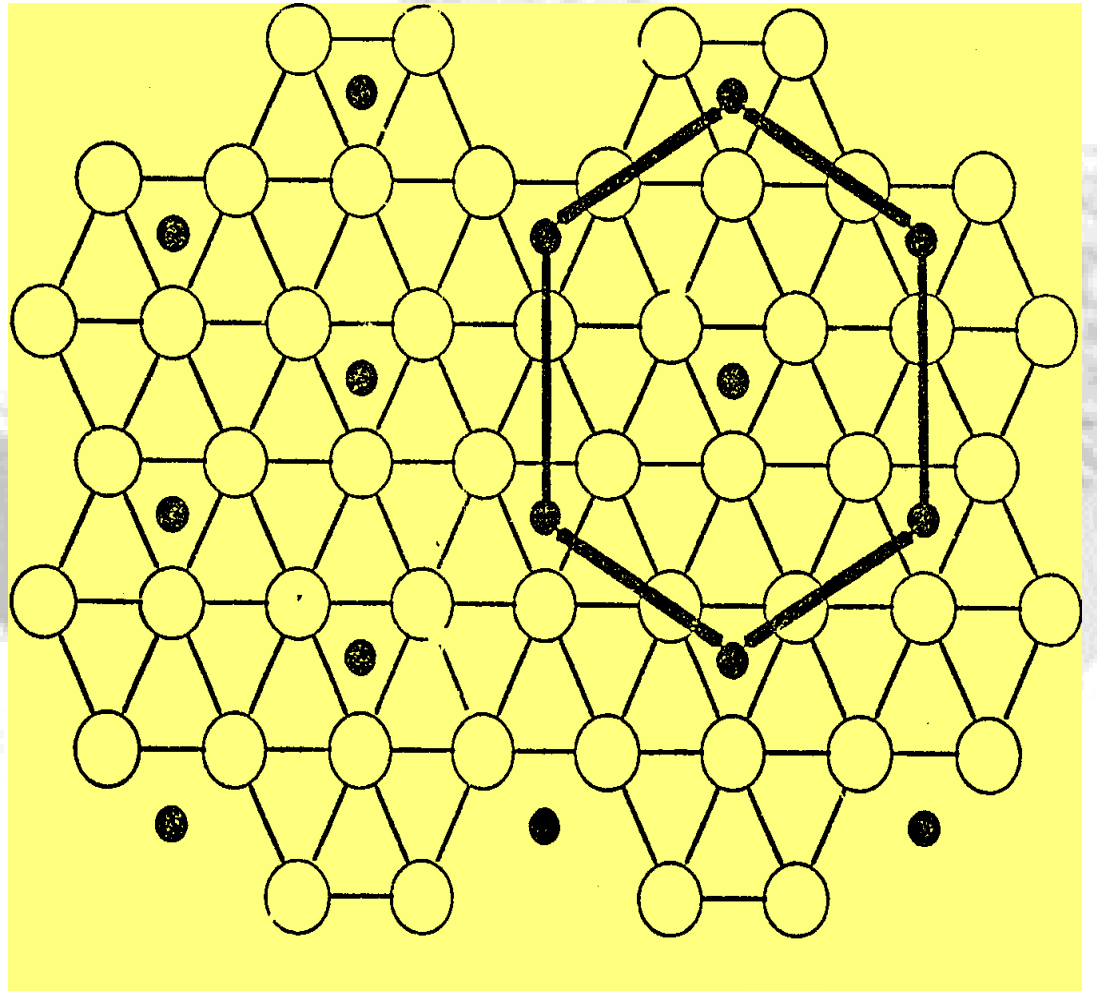
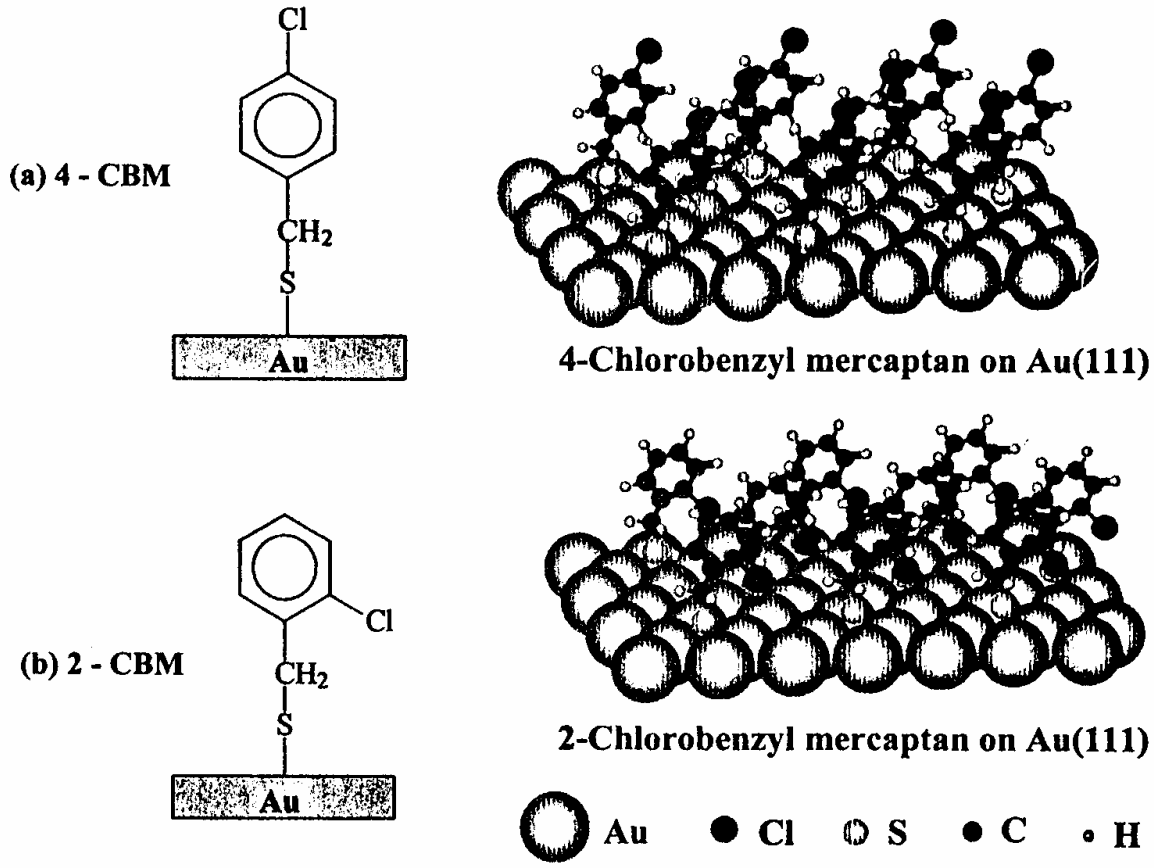
From Molecular Surfaces to Nanomaterials

T. Pradeep
pradeep@iitm.ac.in

1. Introduction to molecular surfaces
2. Materials through monolayers
3. New approaches for nanomaterials





T. Pradeep et al. Anal. Chem. 1999

Research programmes with monolayers

Monolayer structure (SERS)

Reactivity

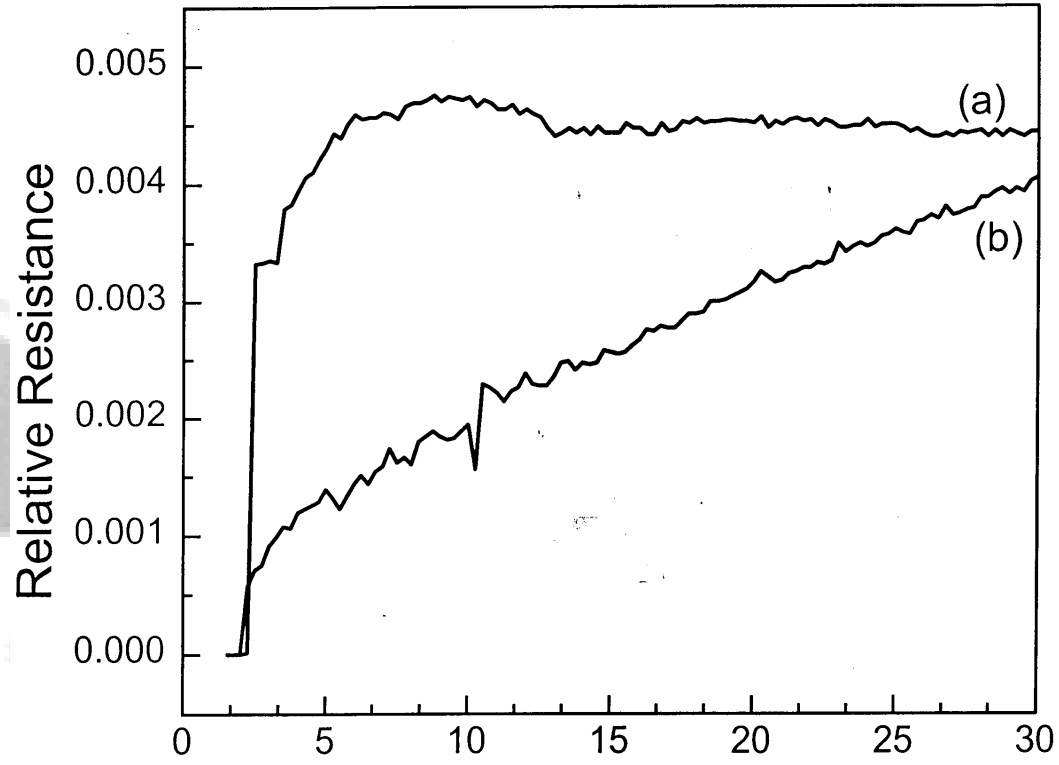
Thermal stability, phase transitions

Substrate resistance

Ion-surface collisions, reaction dynamics at surfaces

Processes on ices

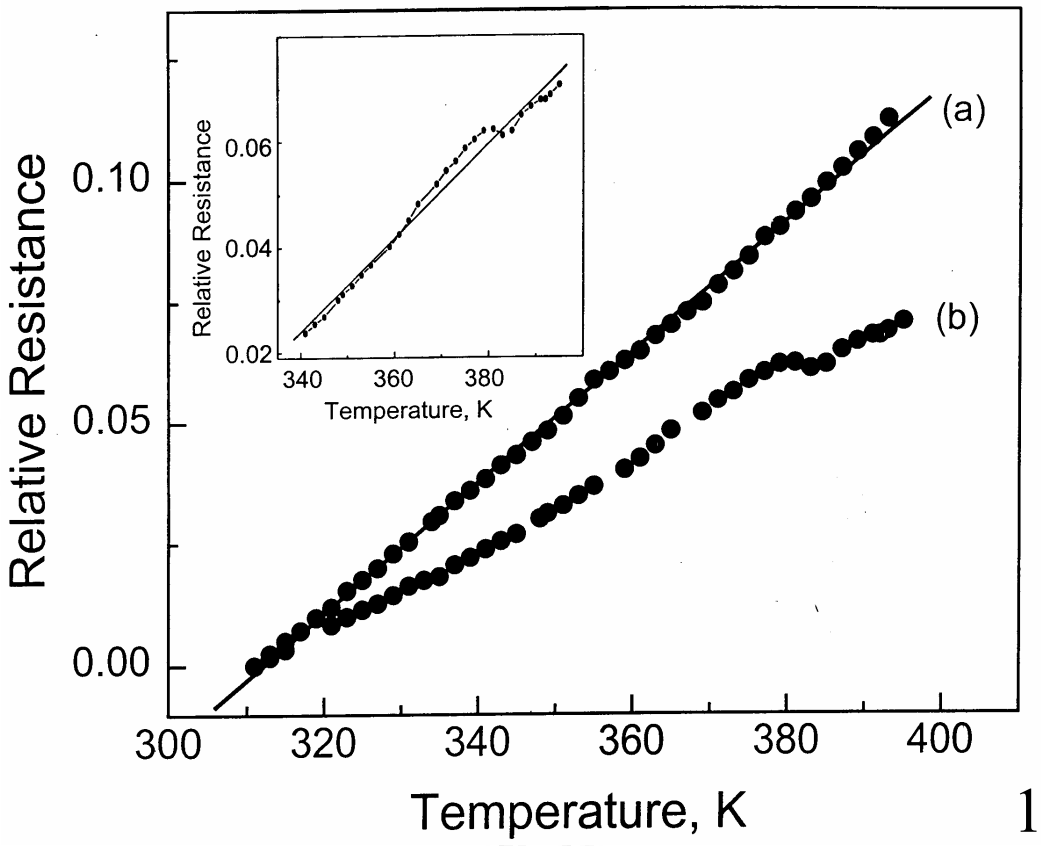
Monolayer formation changes resistance



$$1/\tau=(n^2e^2/M)d\partial\rho/\partial n_a\,|_{na=0}$$

Venkataramanan and Pradeep, Chem. Phys. Lett. 2000

Phase transitions of monolayers with surface resistance



$$1/\tau = (2m\omega_F\Gamma/M)N(E_F)< \sin^2\theta >$$

Venkataramanan and Pradeep, Anal. Chem. 2000

What is new with monolayers?

What happens when thiols adsorb on gold?

$$RS\text{-}H + Au_n^0 \rightarrow RS^- \text{-}Au^+ + \tfrac{1}{2} H_2 + Au_{n-1}^0 \quad (1)$$

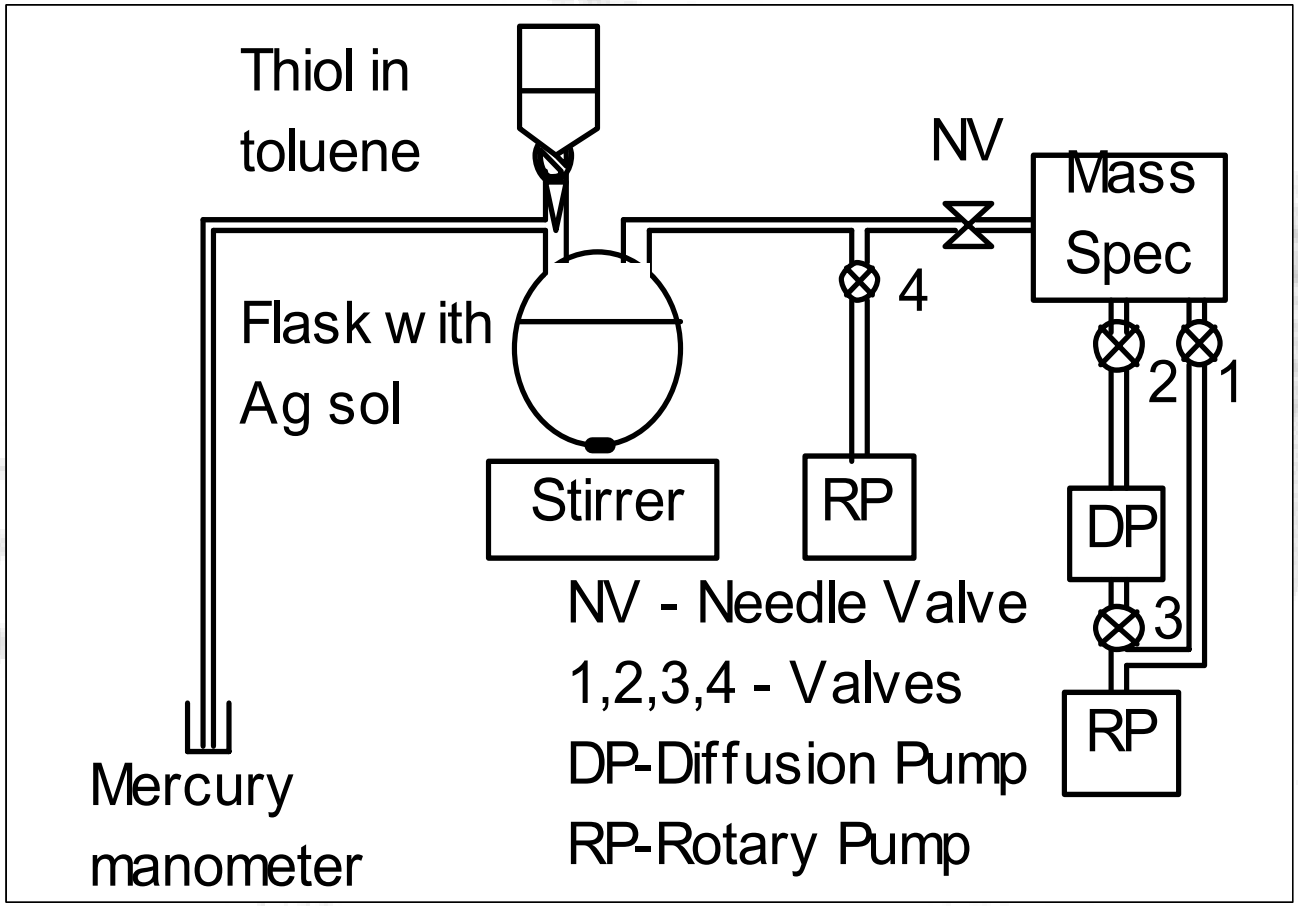
$$RS\text{-}H + Au_n^0 + \text{oxidant} \rightarrow RS^- \text{-}Au^+ + \tfrac{1}{2} H_2O + Au_{n-1}^0 \quad (2)$$

$$RS\text{-}H + Au \rightarrow RS^- \text{–}Au^+ + H^+ + e^- \quad (3)$$

Problem: Number of species and detection

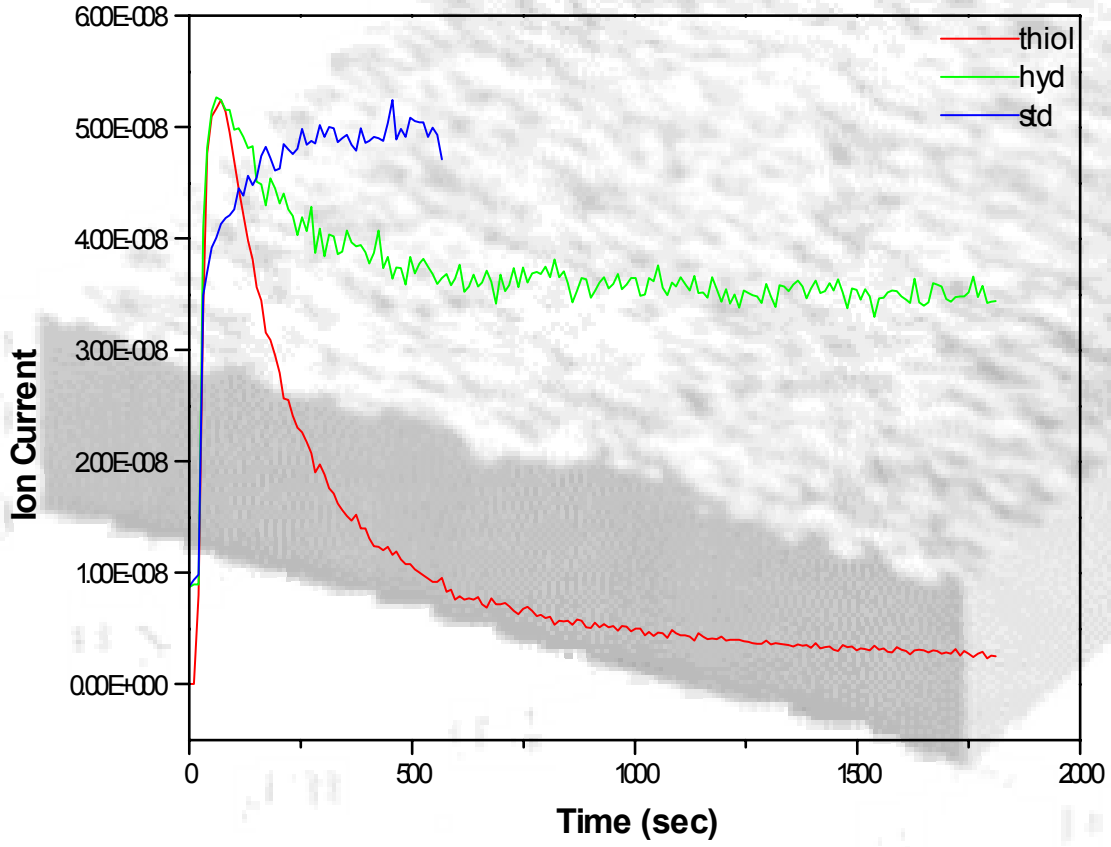
Solution: Increased surface area

Mass spectrometry



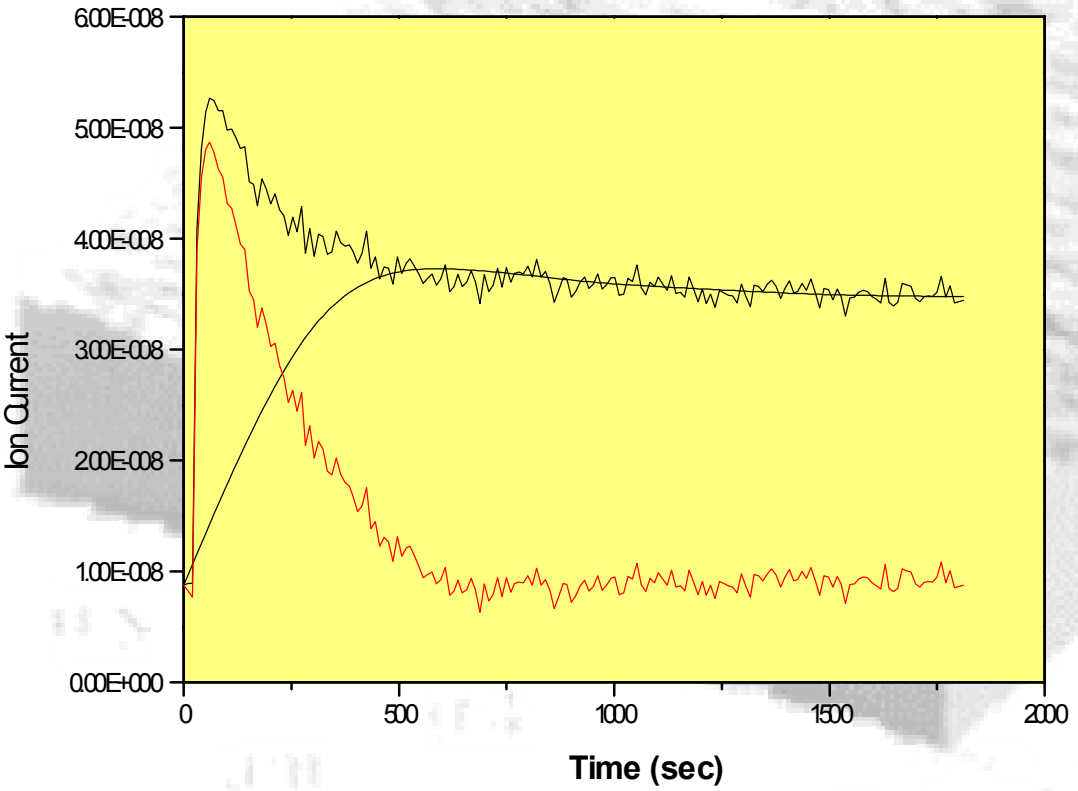
Set-up used to study thiol adsorption

Thiol adsorption on gold films

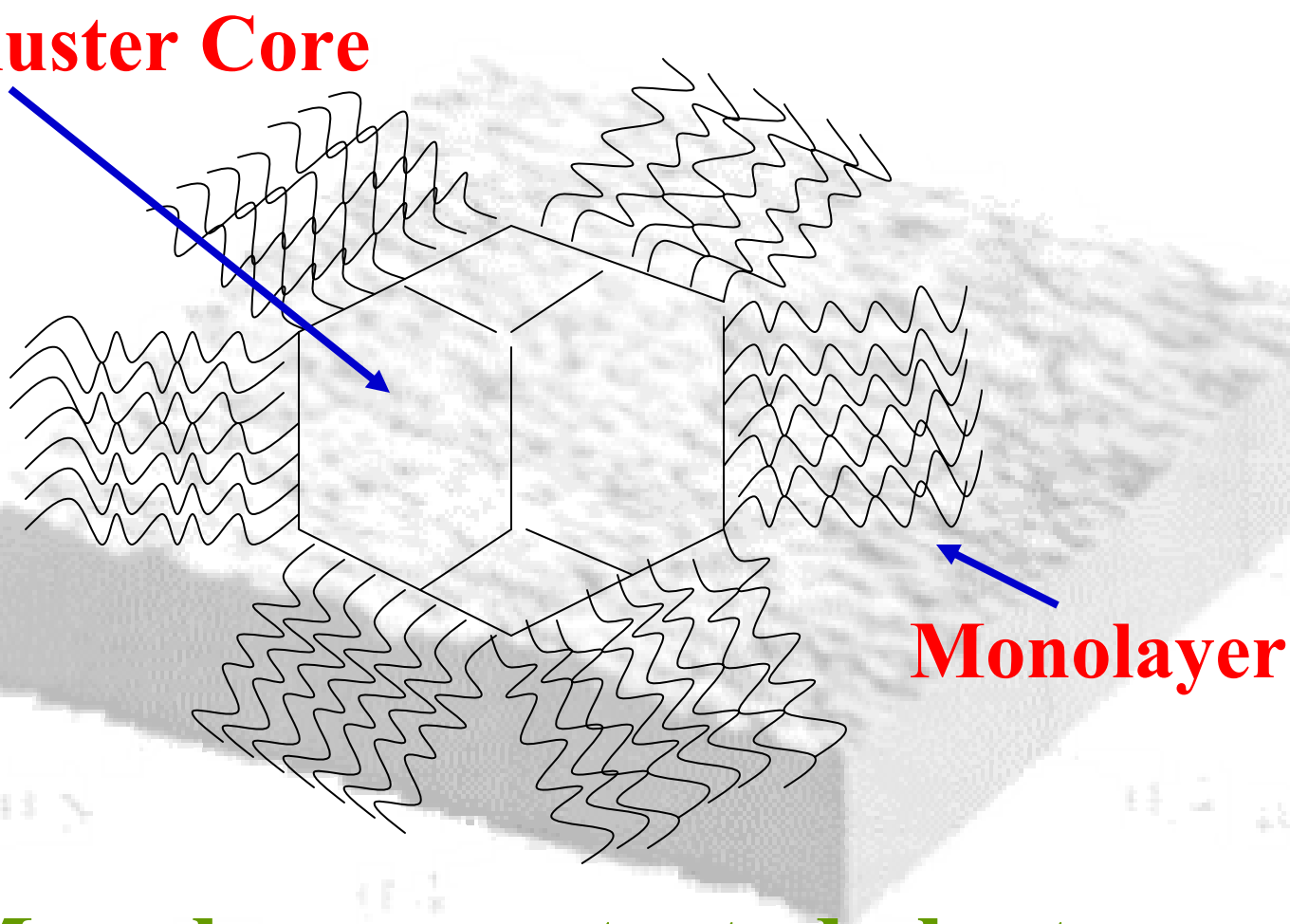


Mass spectral intensities upon thiol adsorption

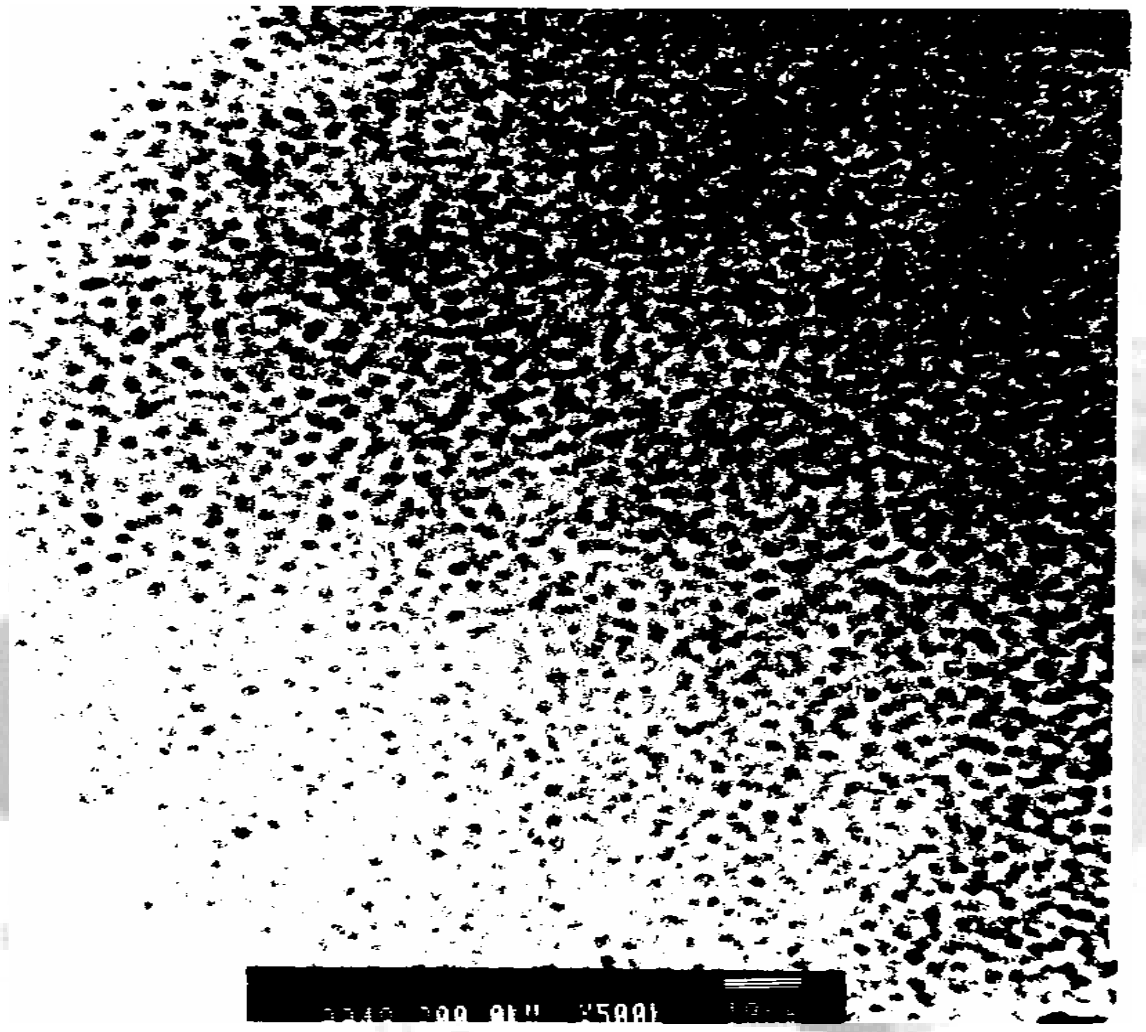
Hydrogen evolution due to adsorption



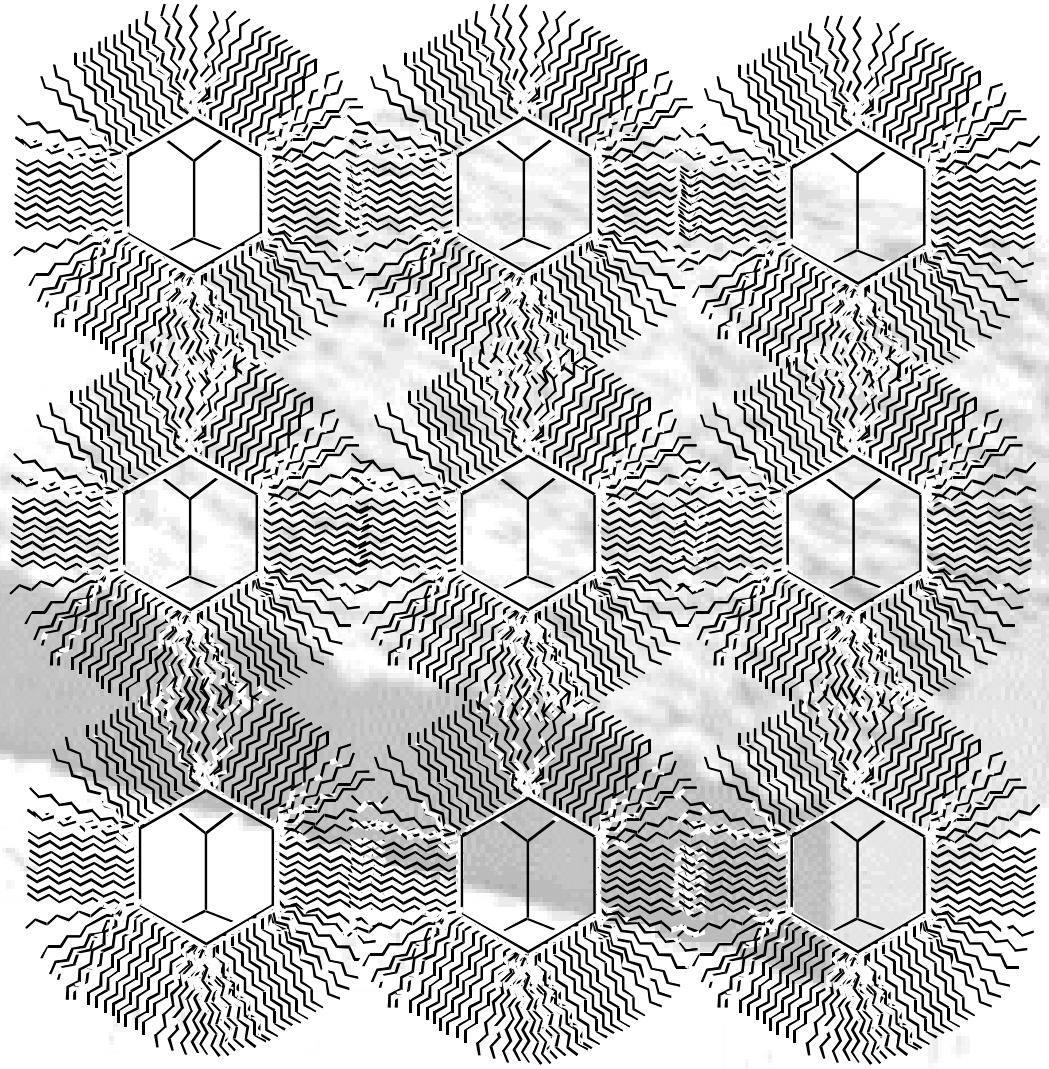
Hydrogen evolution due to adsorption

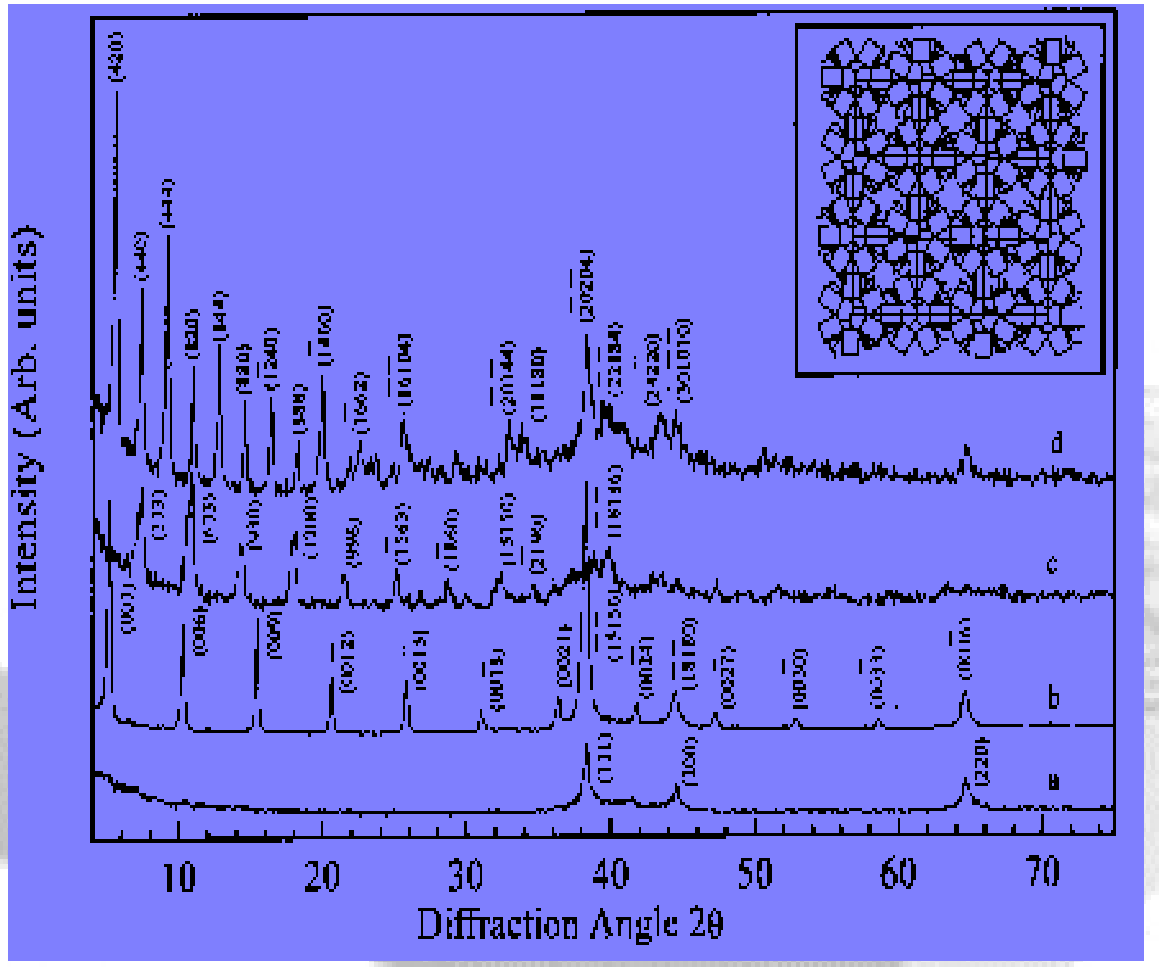


Monolayer protected cluster

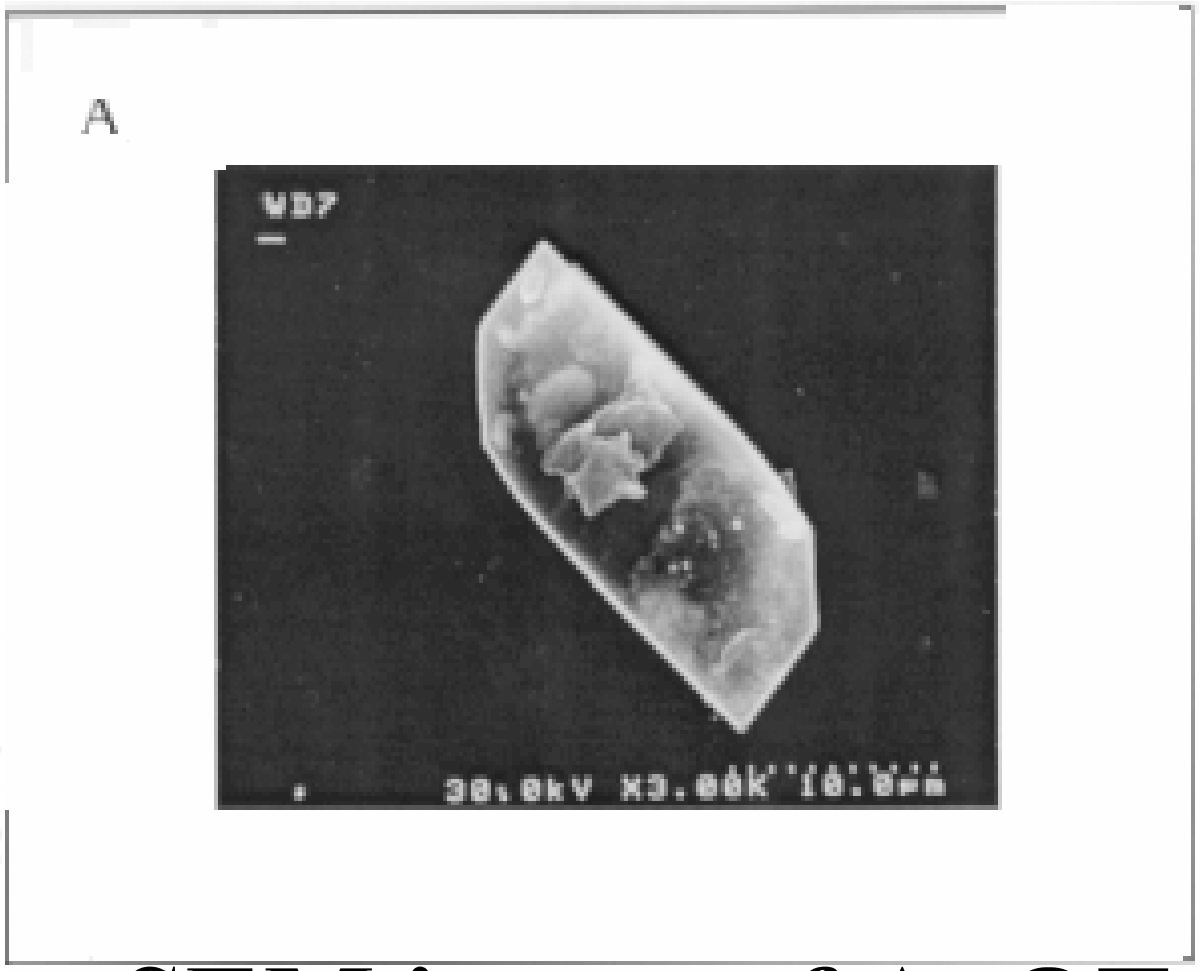


TEM of gold clusters protected with monolayers

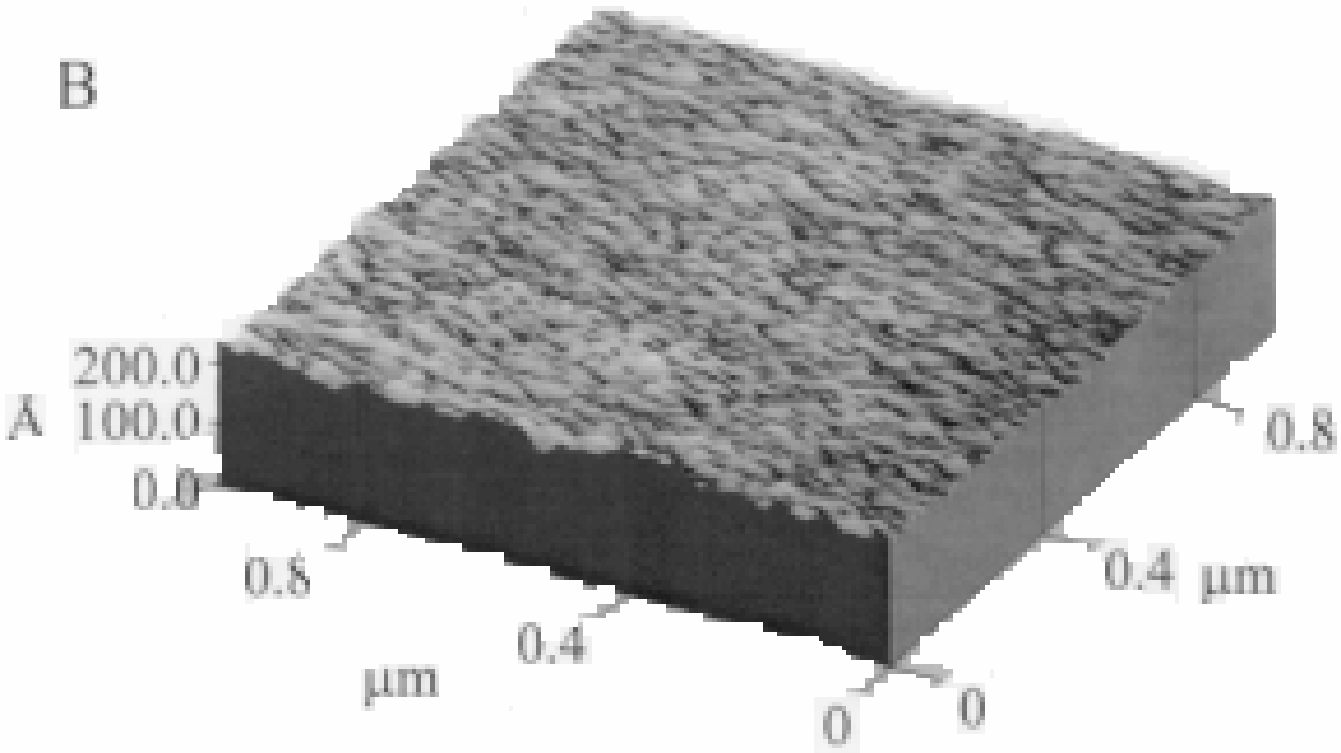




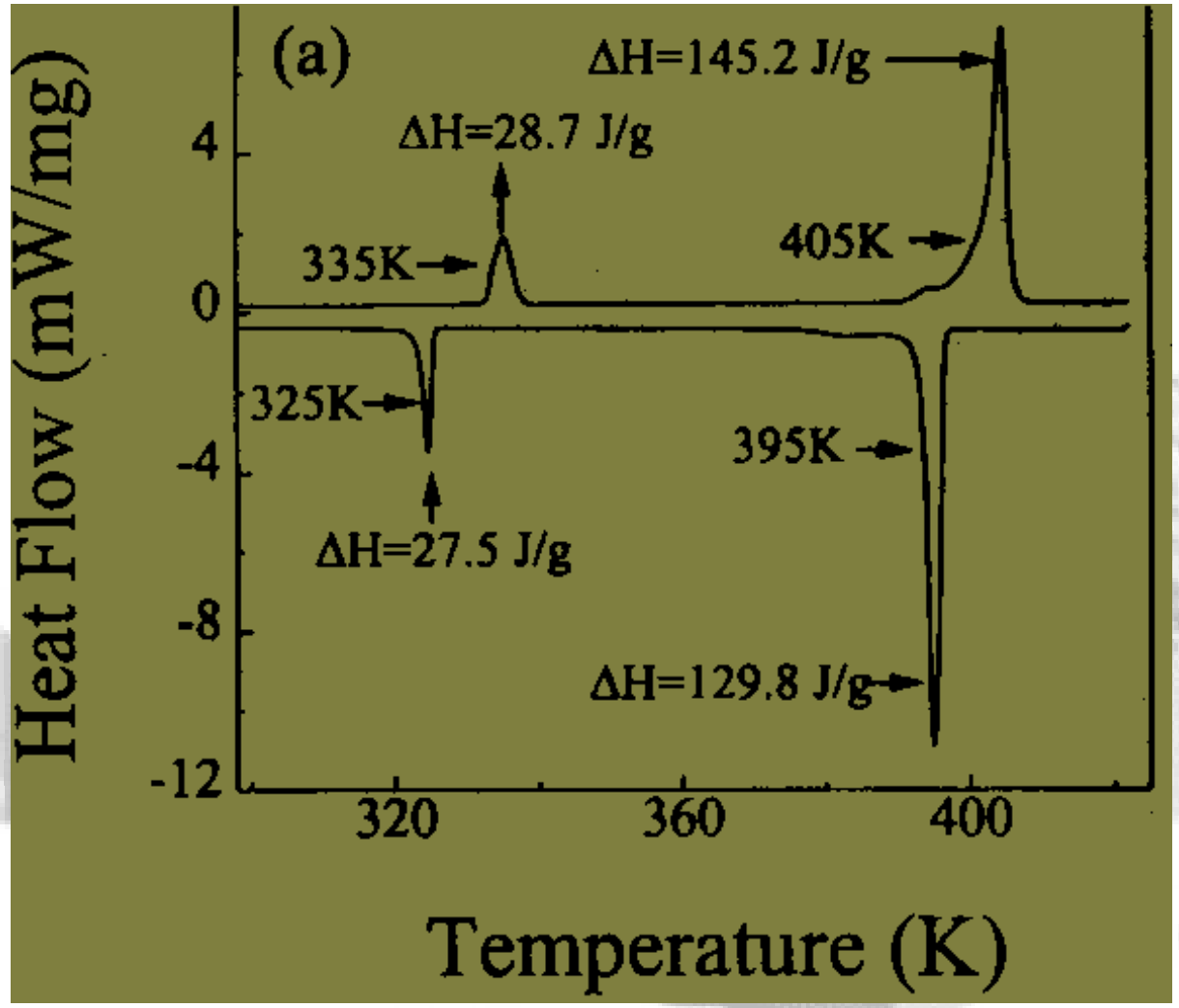
XRD patterns of (a) AgBT, (b) AgPT, (c) AgOT and (d) AgODT



SEM image of AgOT superlattice crystal

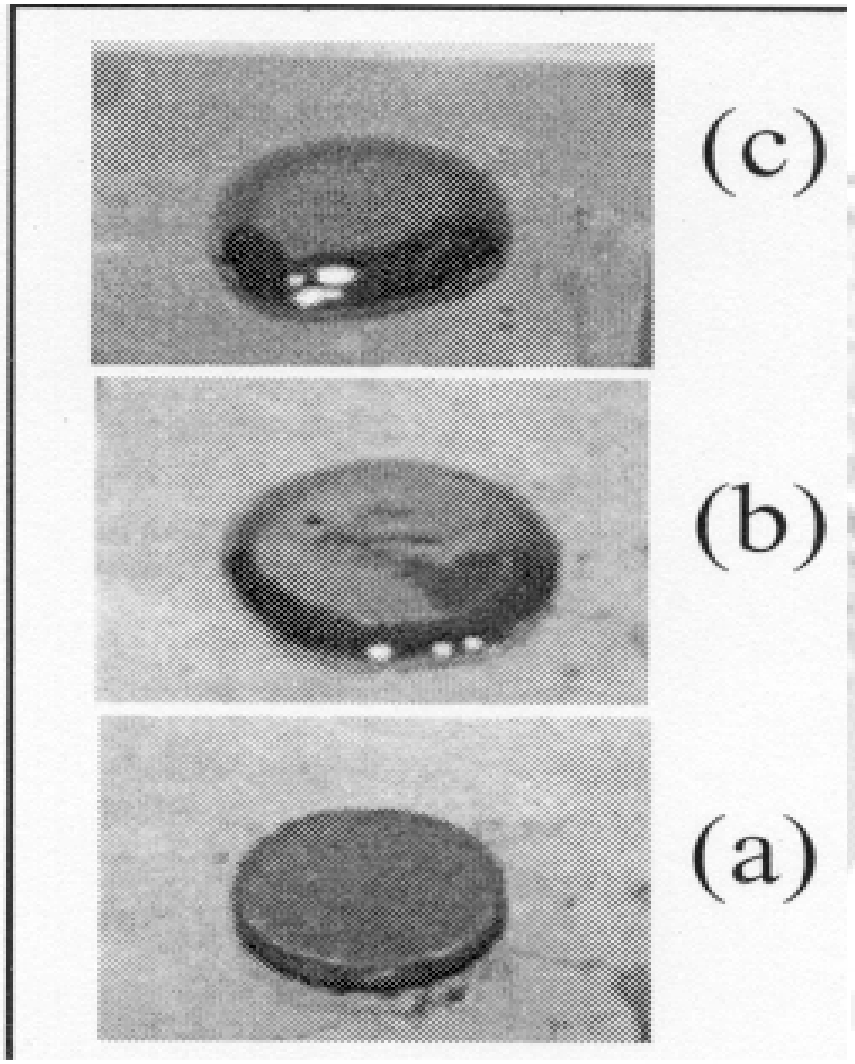


STM morphology of the crystal surface

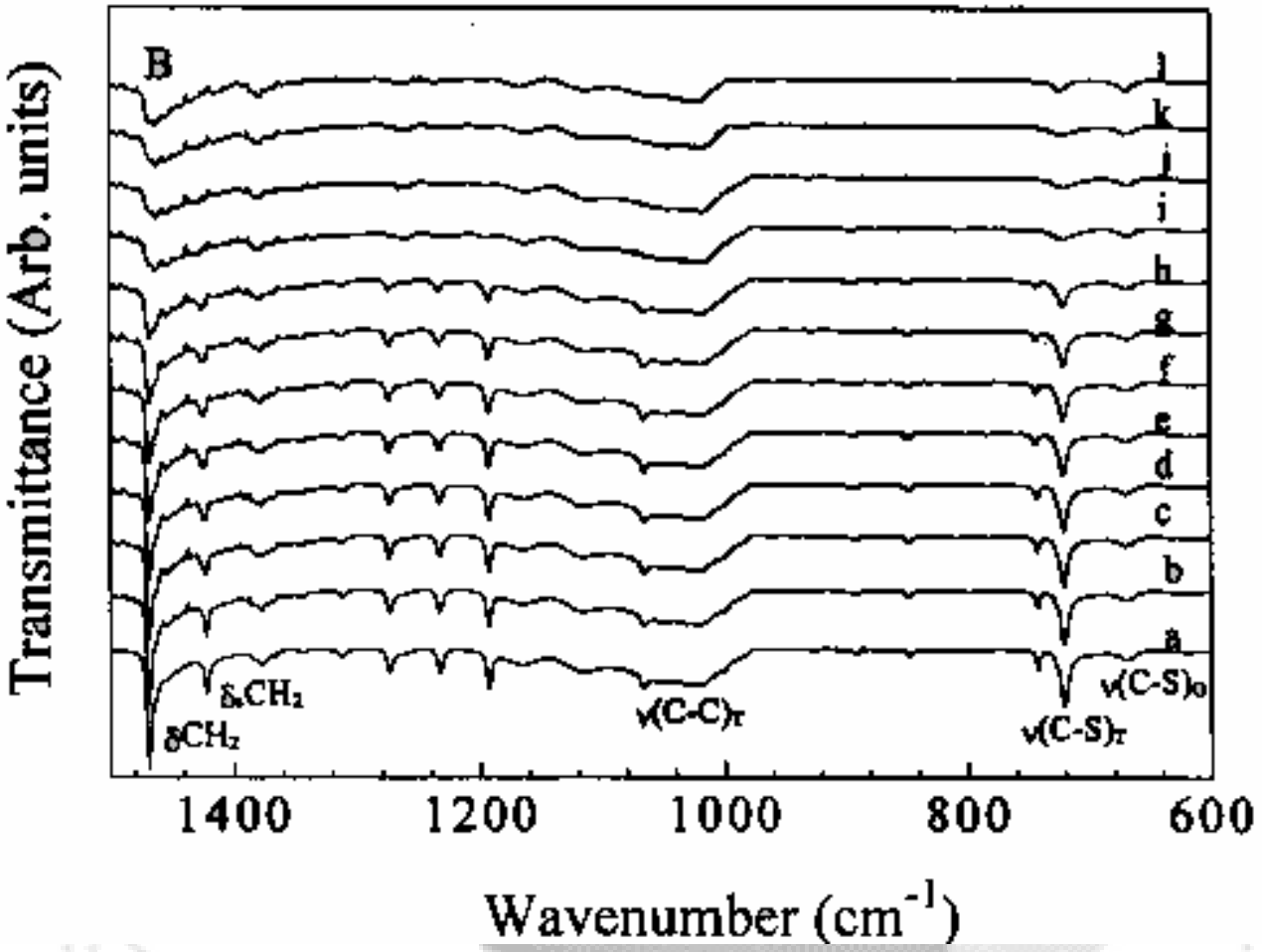


DSC of Au ODT (up to 443 K)

(Sandhyarani et. al. Phys. Rev. B. 2000).



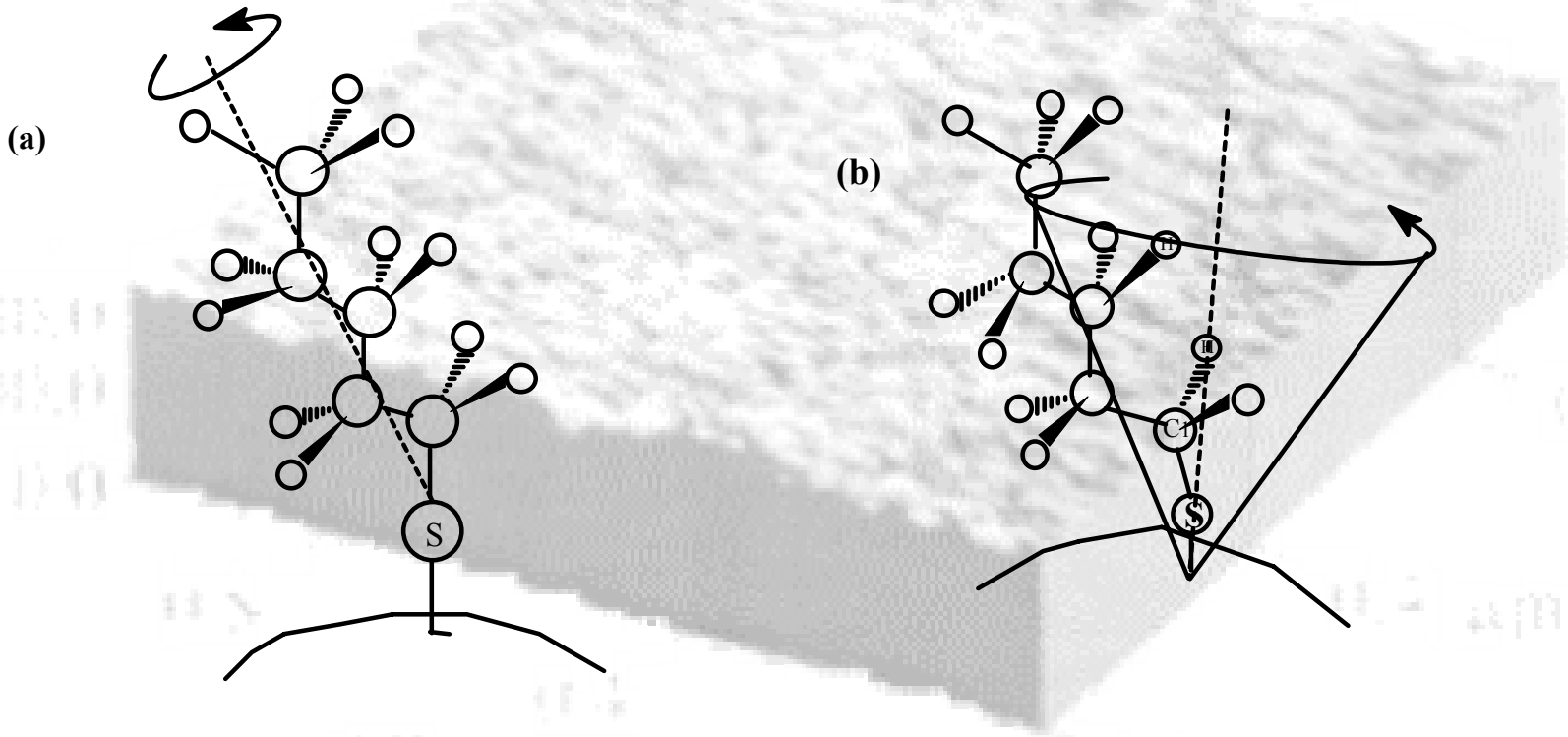
Sandhyarani et. al. Phys. Rev. B. 2000.



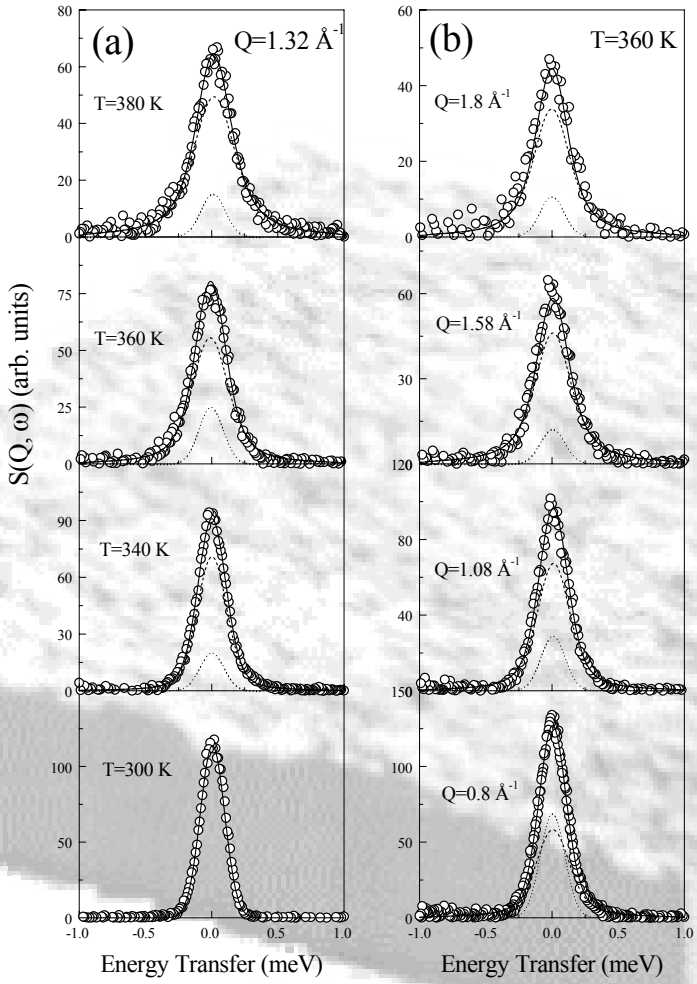
Temperature dependent FTIR of AgOT

(Sandhyarani et. al. J. Chem. Phys. 2000)

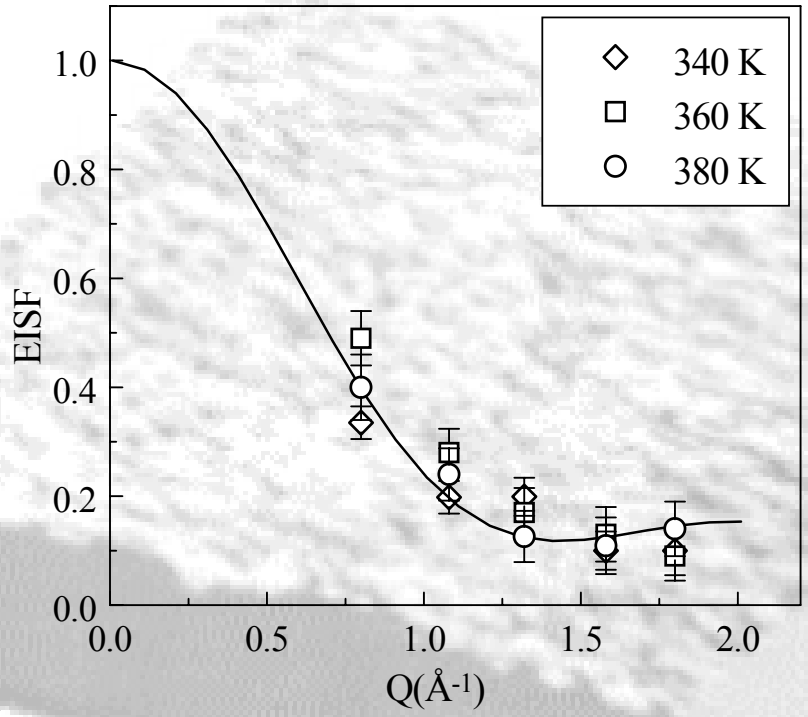
Dynamics of alkyl chains



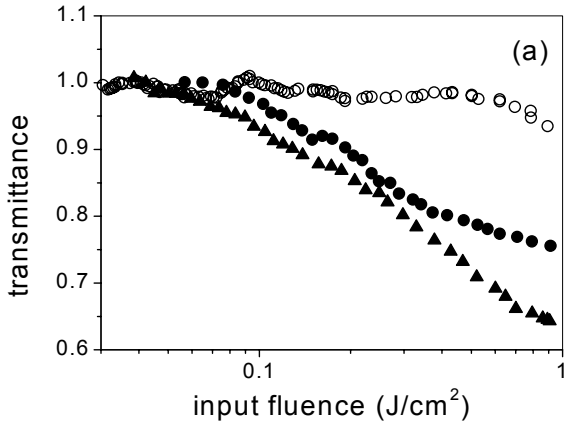
Mukhopadhyay et al. (J. Phys. Chem. B, 2002)



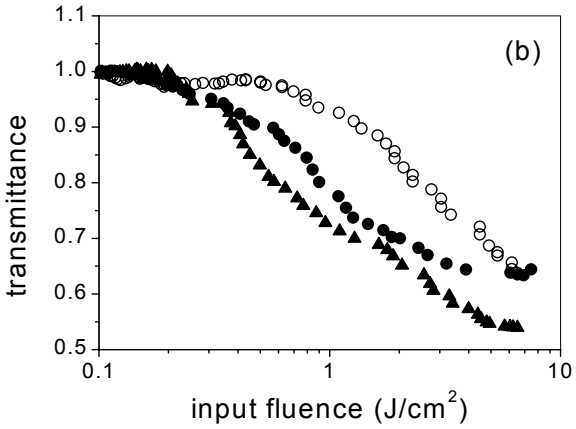
Typical QENS spectra for an isolated nonolayer protected cluster, AuC_{18},
(a) at Q = 1.32 Å^{-1} and at different temperatures (b) at 360 K, but at different
(b) Q values. Dashed and the dotted lines are the quasielastic and elastic
(c) components, respectively.



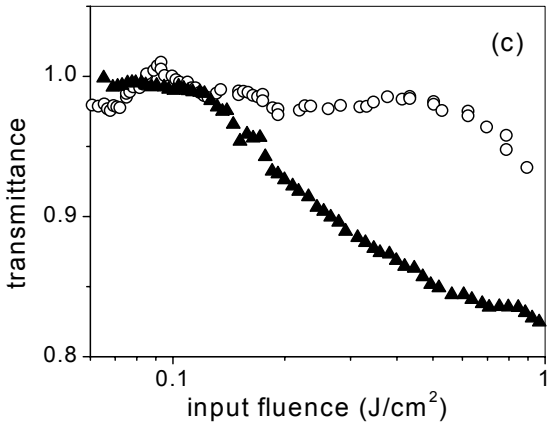
EISF as obtained for AuC_{18} at 340 and 360 K and 380 K. The solid line corresponds to a model in which a particle performs random jumps among N = 6 equivalent sites on a circle with radius, *a* equal to 2.1 Å.



Au Clusters

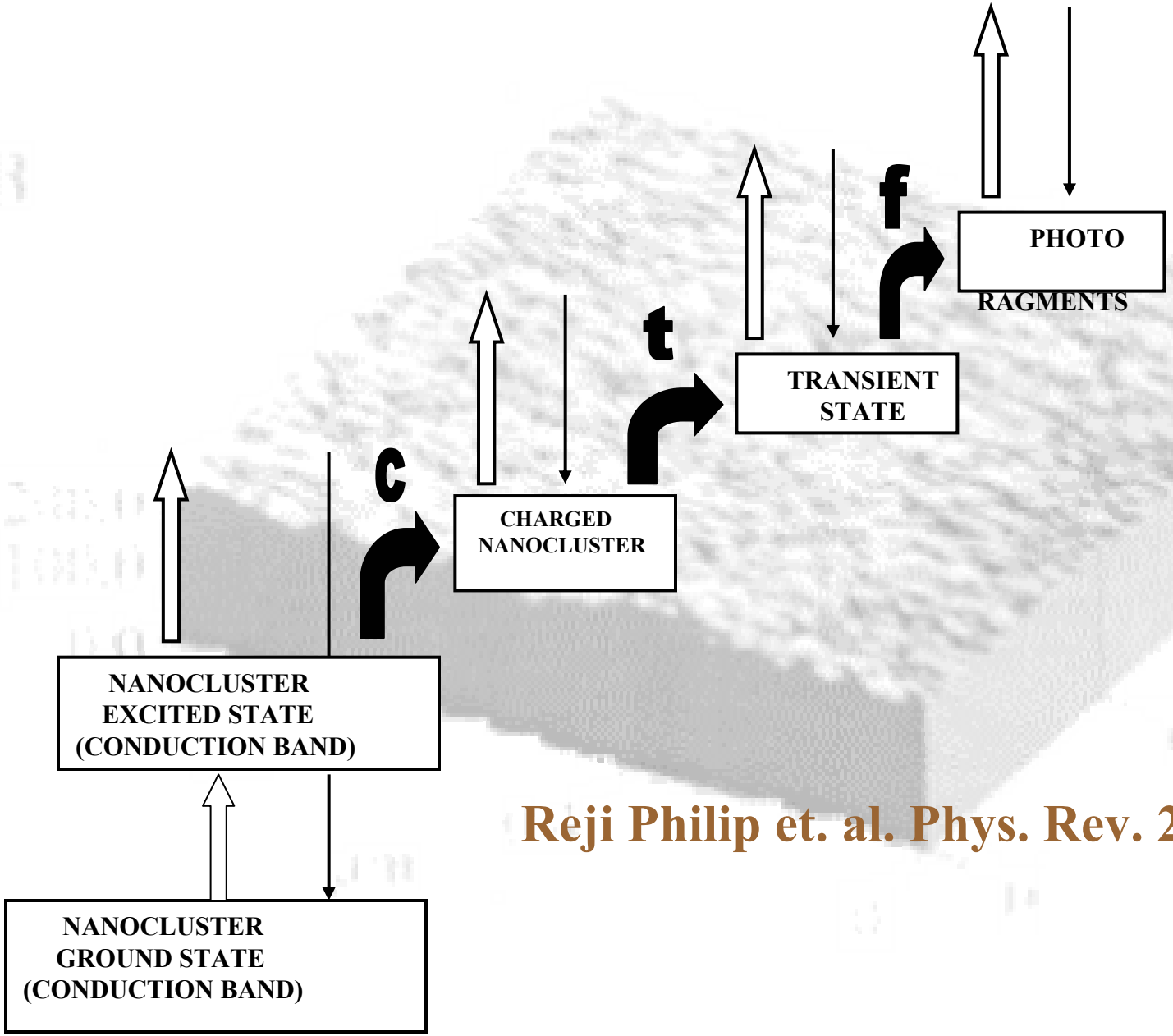


Ag Clusters

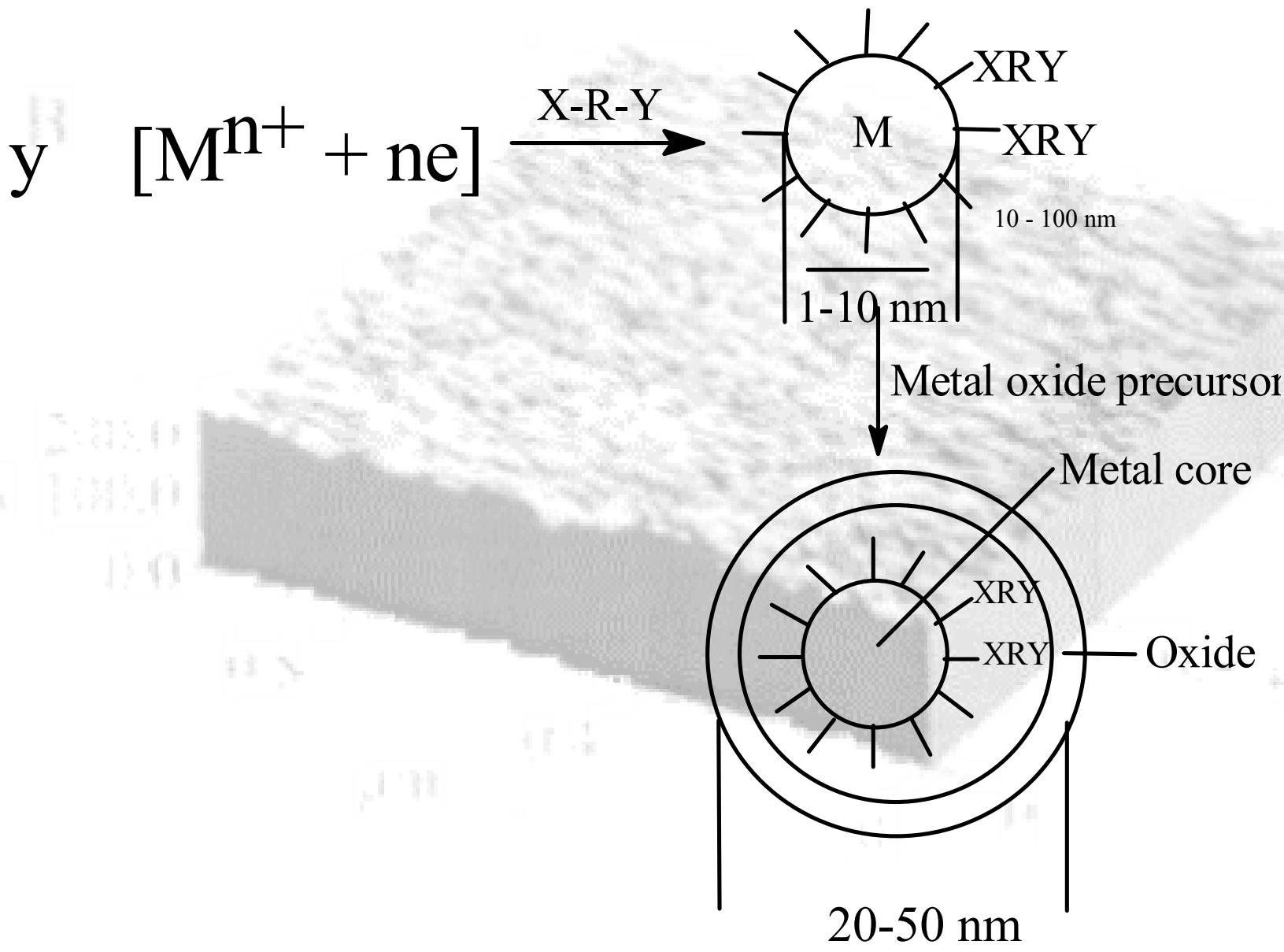


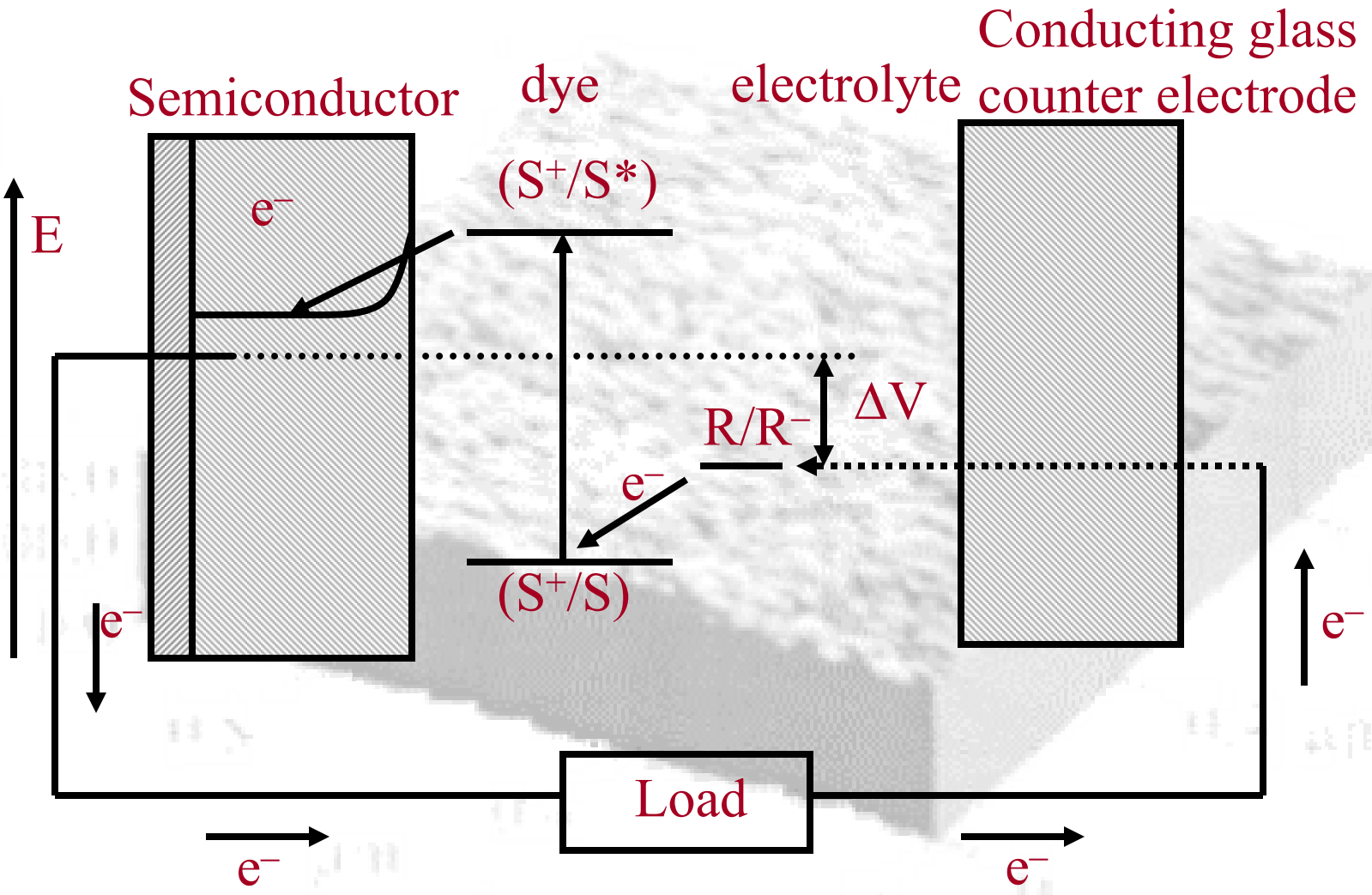
$AuAg_{0.75}$ Clusters

Reji Philip et. al. Phys. Rev. 2000

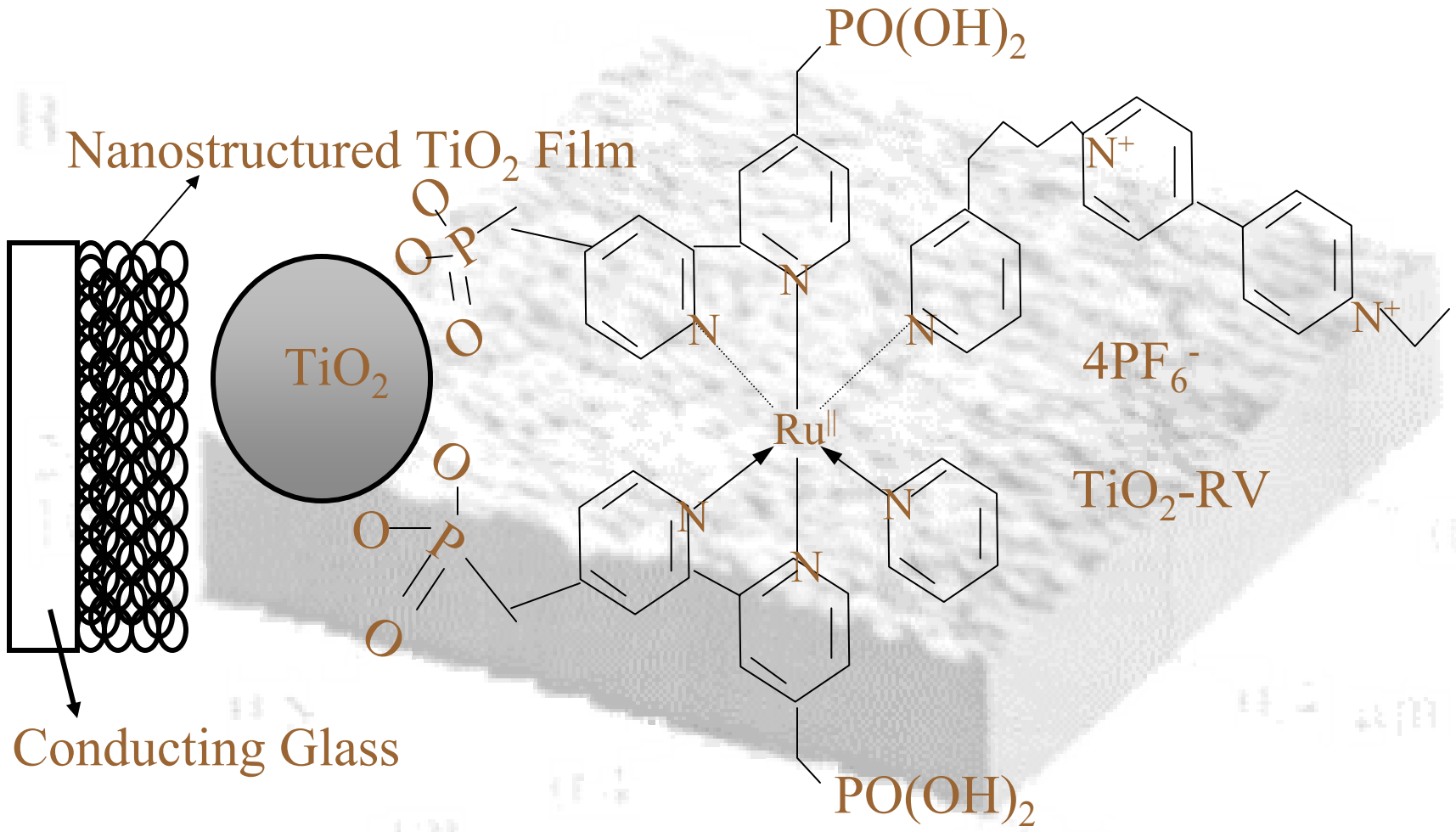


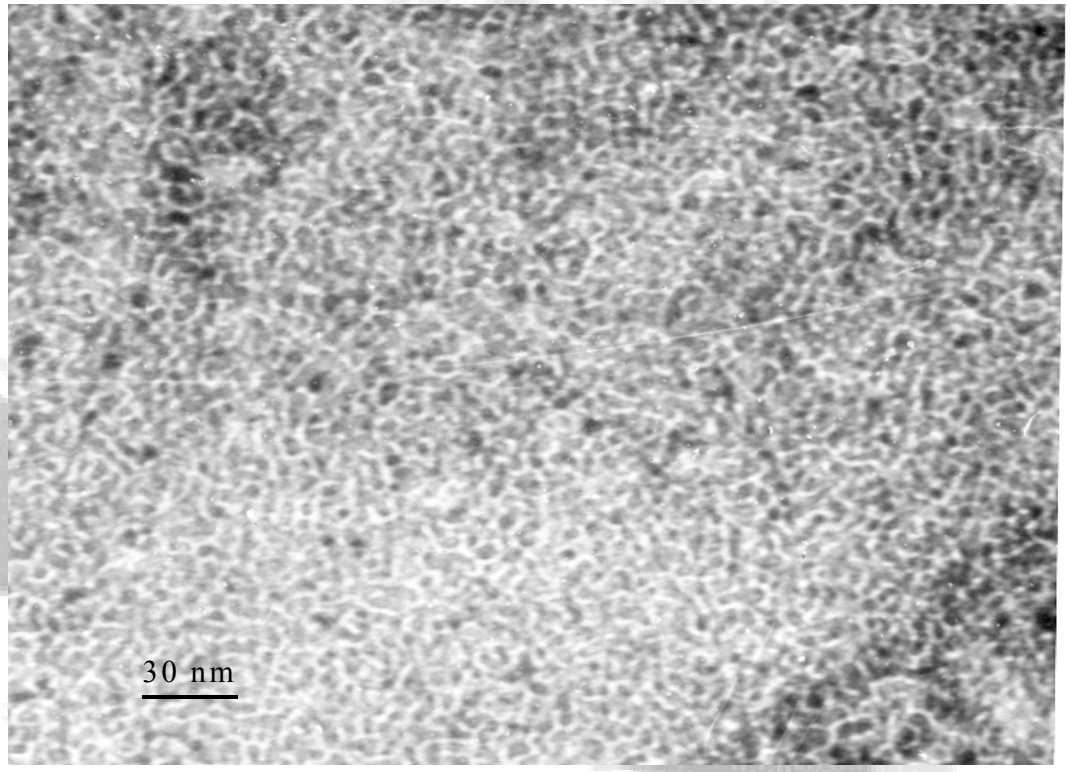
Reji Philip et. al. Phys. Rev. 2000


y [M^n+ + ne]
X-R-Y
M
XRY
XRY
10 - 100 nm
1-10 nm
Metal oxide precursor
Metal core
XRY
XRY
Oxide
20-50 nm

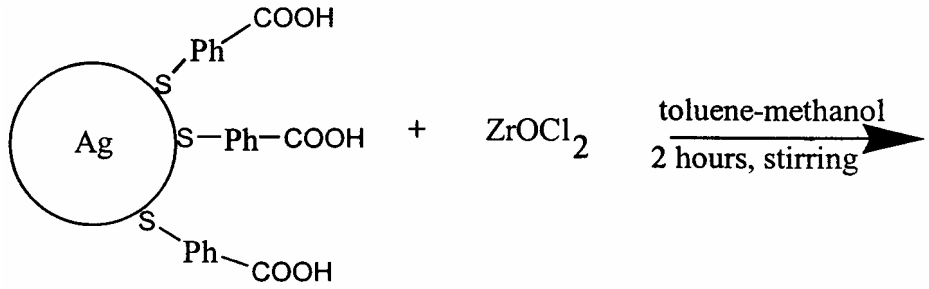


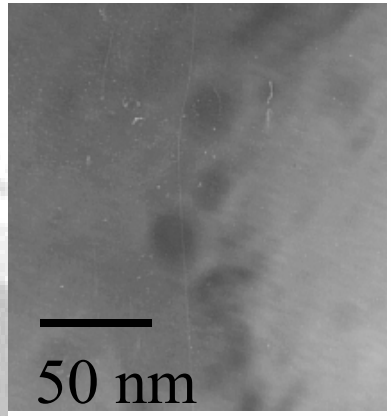
B. O'Regan and M. Gratzel, Nature 353 (1993) 737.

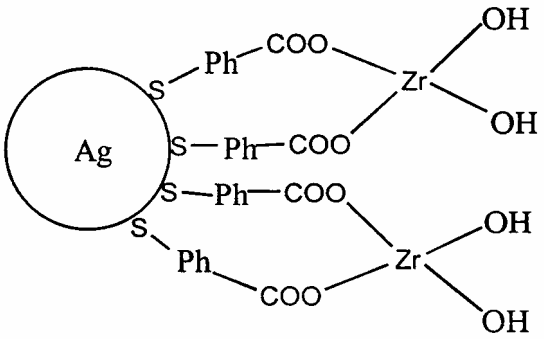

Nanostructured TiO_2 Film
TiO_2
Conducting Glass
$PO(OH)_2$
$PO(OH)_2$
Ru^{II}
$4PF_6^-$
TiO_2-RV

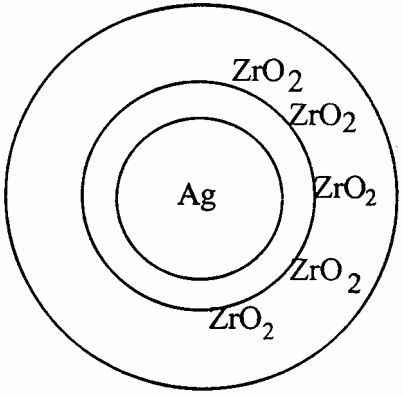


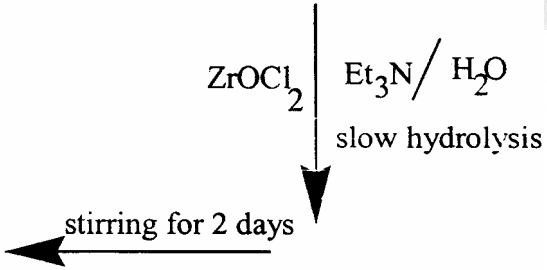
Mercaptopropionic acid protected Au cluster

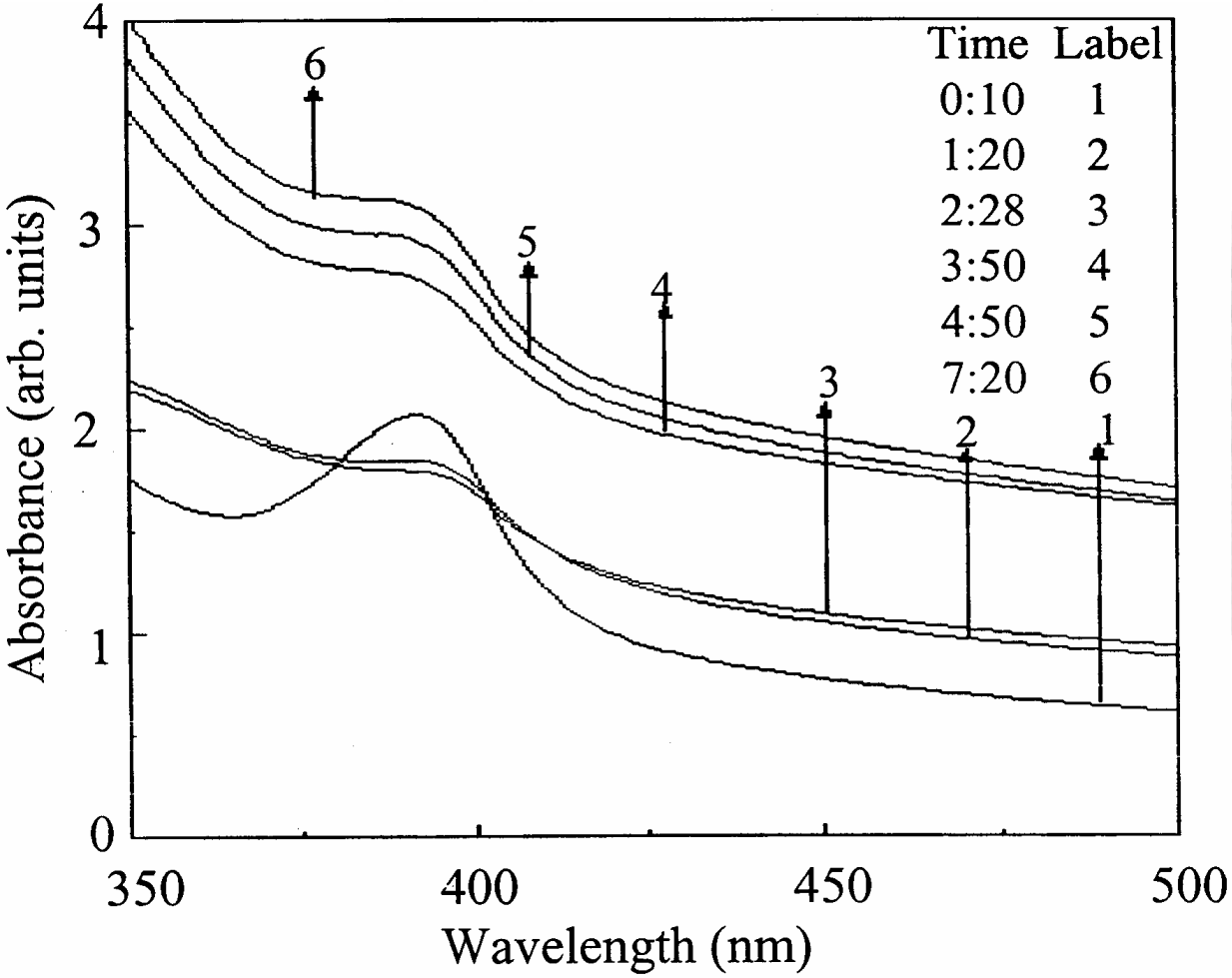

COOH
Ph
S
Ag
S—Ph—COOH
S
Ph
COOH
+
ZrOCl2
toluene-methanol
2 hours, stirring

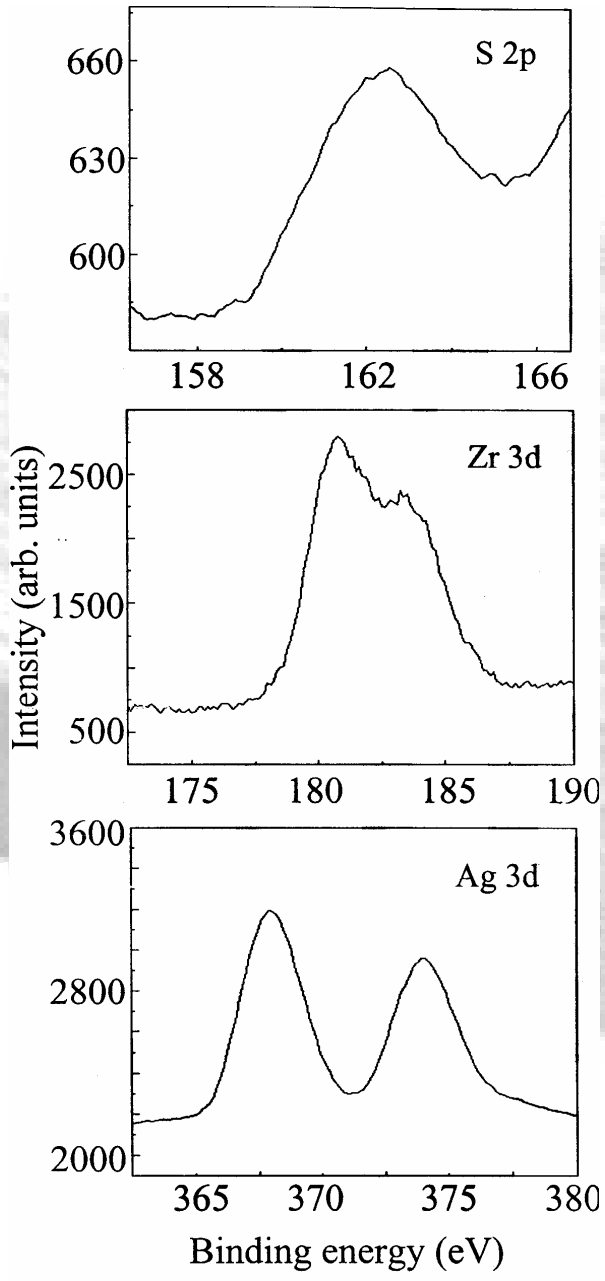

50 nm

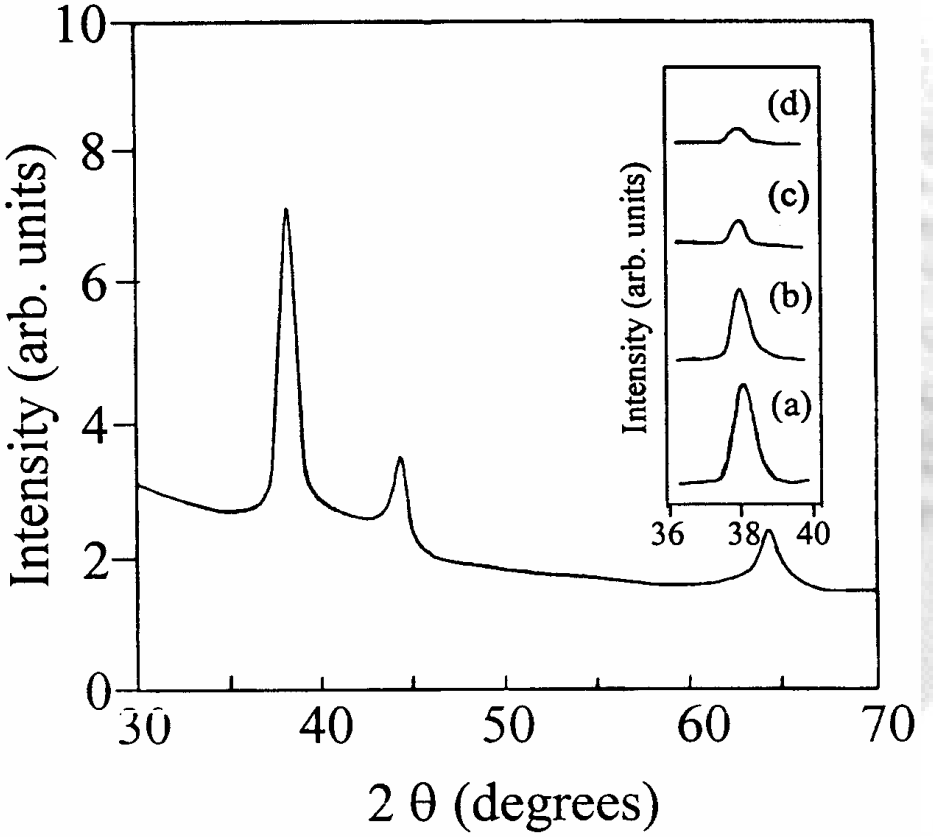

OH
Ph
COO
Zr
S
OH
Ag
S—Ph—COO
S—Ph—COO
S
OH
Ph
Zr
COO
OH


ZrO2
ZrO2
Ag
ZrO2
ZrO2
ZrO2

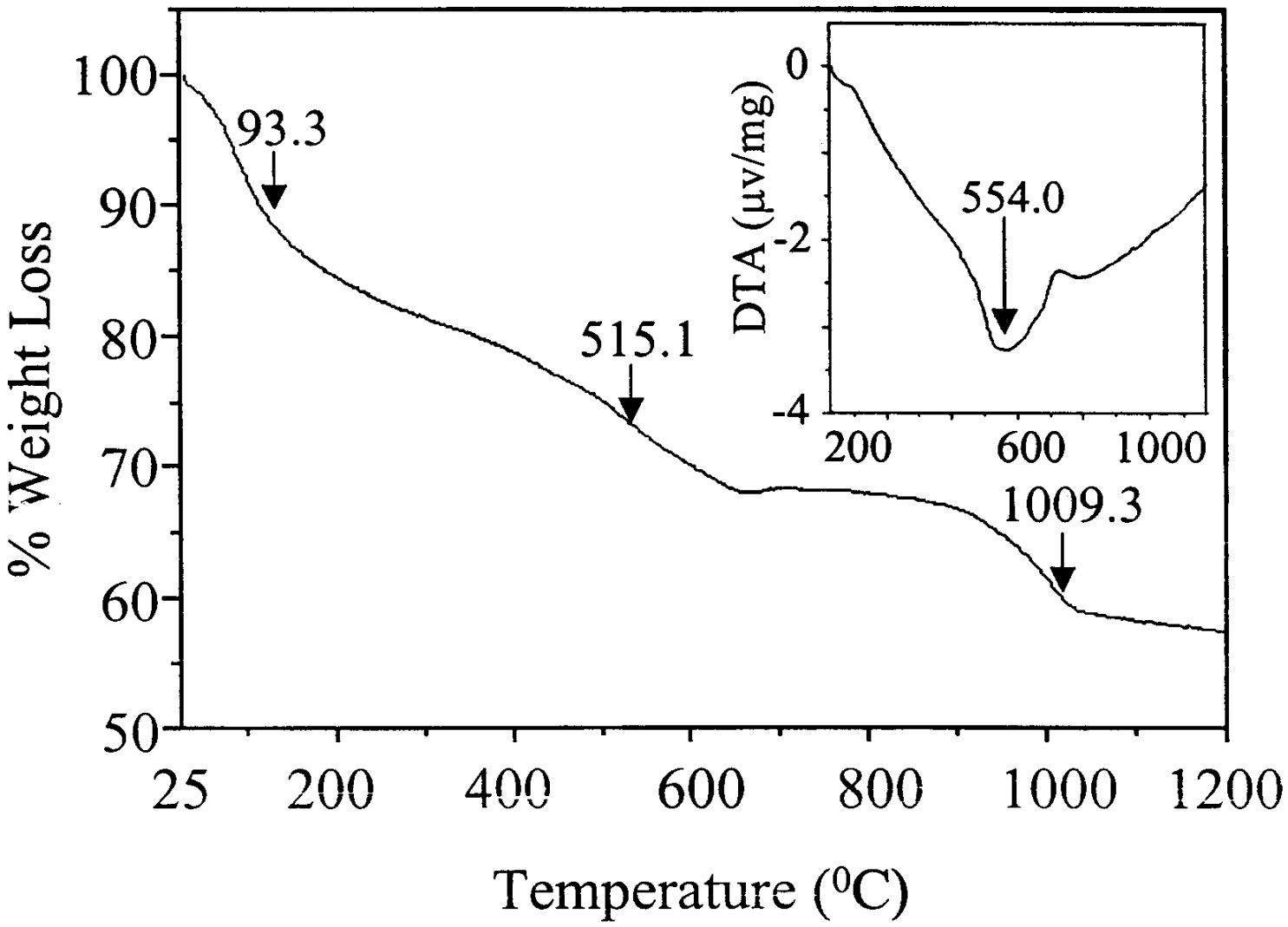

ZrOCl2
Et3N / H2O
slow hydrolysis
stirring for 2 days


Time Label
0:10 1
1:20 2
2:28 3
3:50 4
4:50 5
7:20 6
6
5
4
3
2
1
Absorbance (arb. units)
0
1
2
3
4
350
400
450
500
Wavelength (nm)

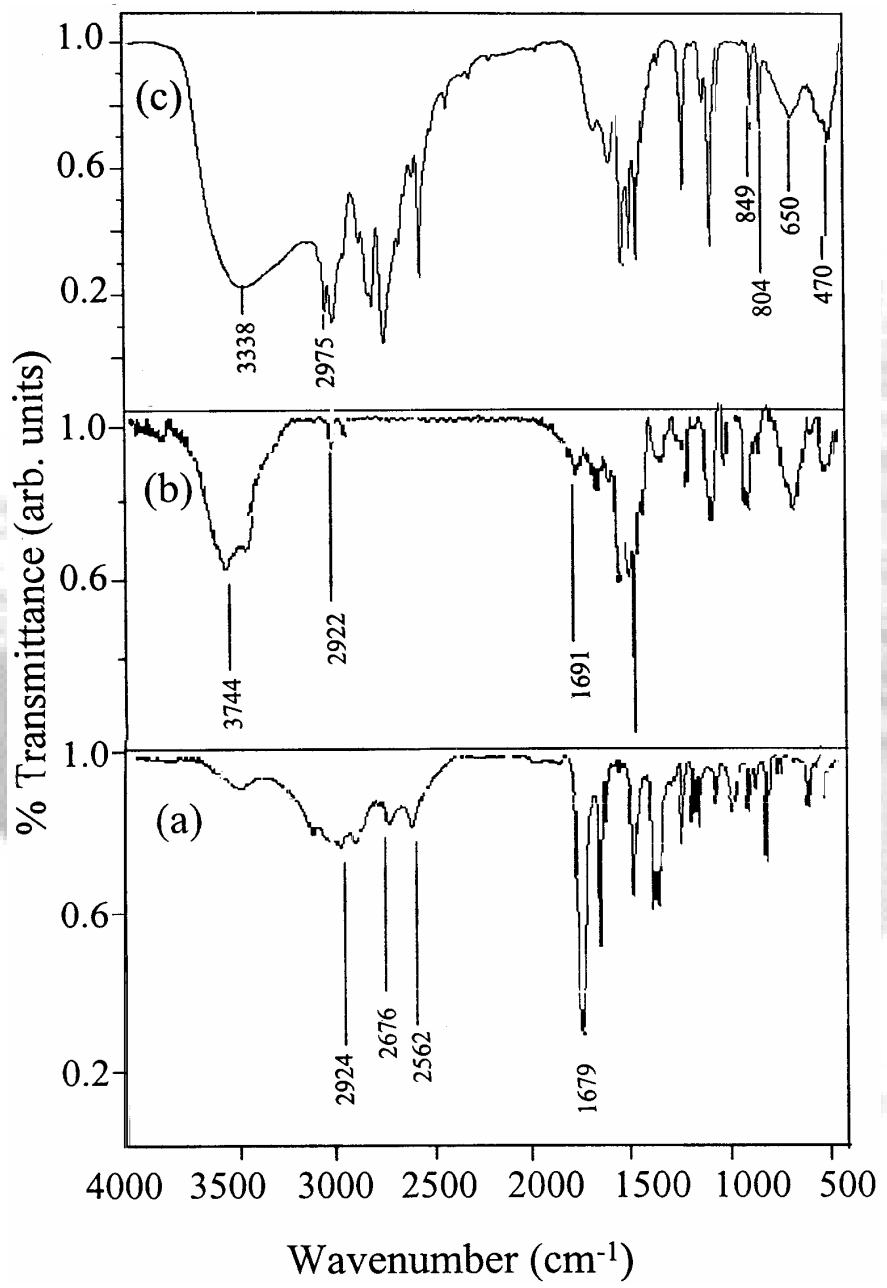

S 2p
660
630
600
158
162
166
Zr 3d
2500
1500
500
175
180
185
190
Ag 3d
3600
2800
2000
365
370
375
380
Intensity (arb. units)
Binding energy (eV)



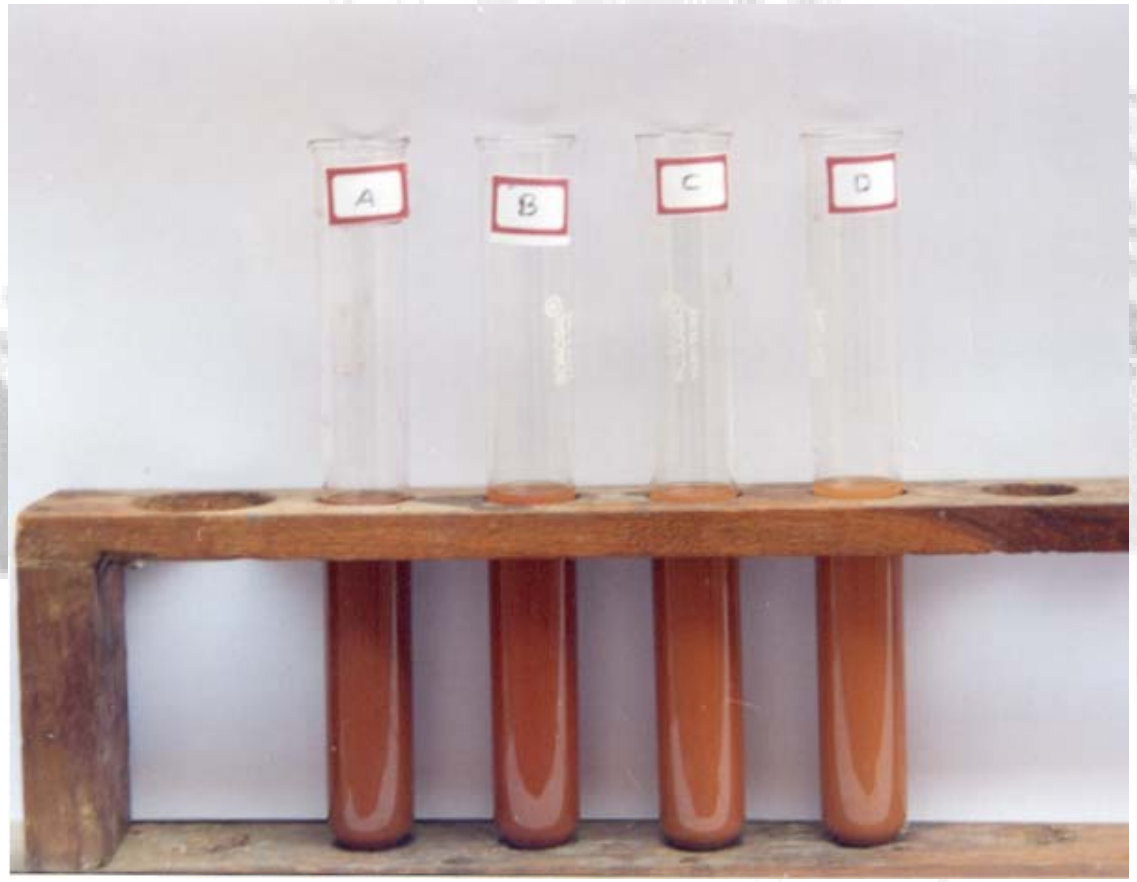
XRD upon increase in shell thickness

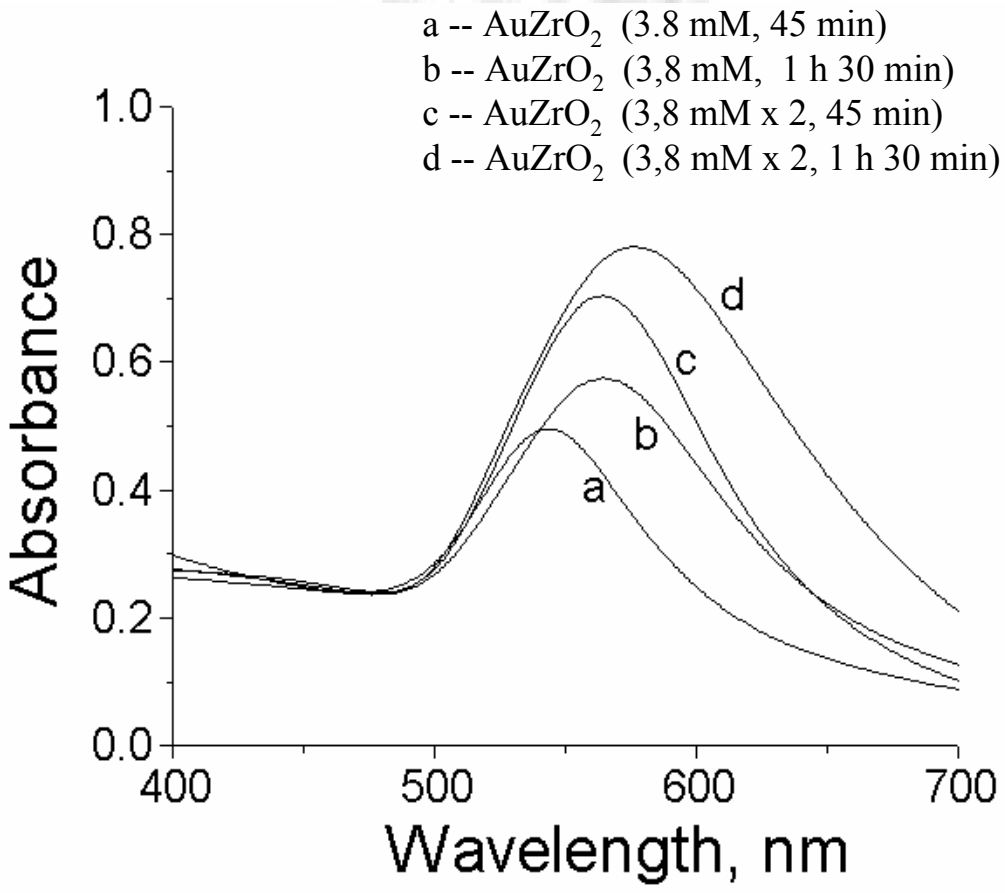


TG of Ag-MBA-ZrO_2

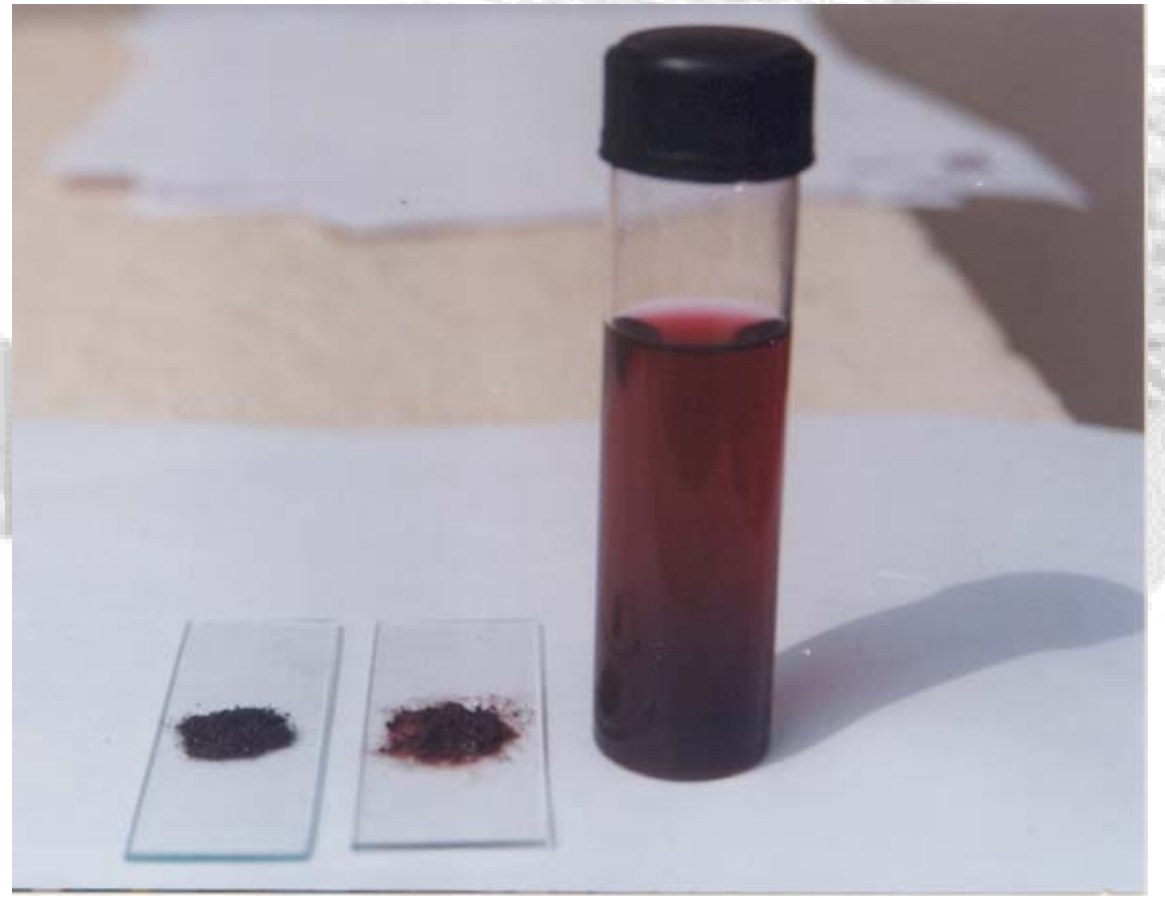

(c)
(b)
(a)
1.0
0.6
0.2
3338
2975
849
804
650
470
3744
2922
1691
2924
2676
2562
1679
% Transmittance (arb. units)
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)

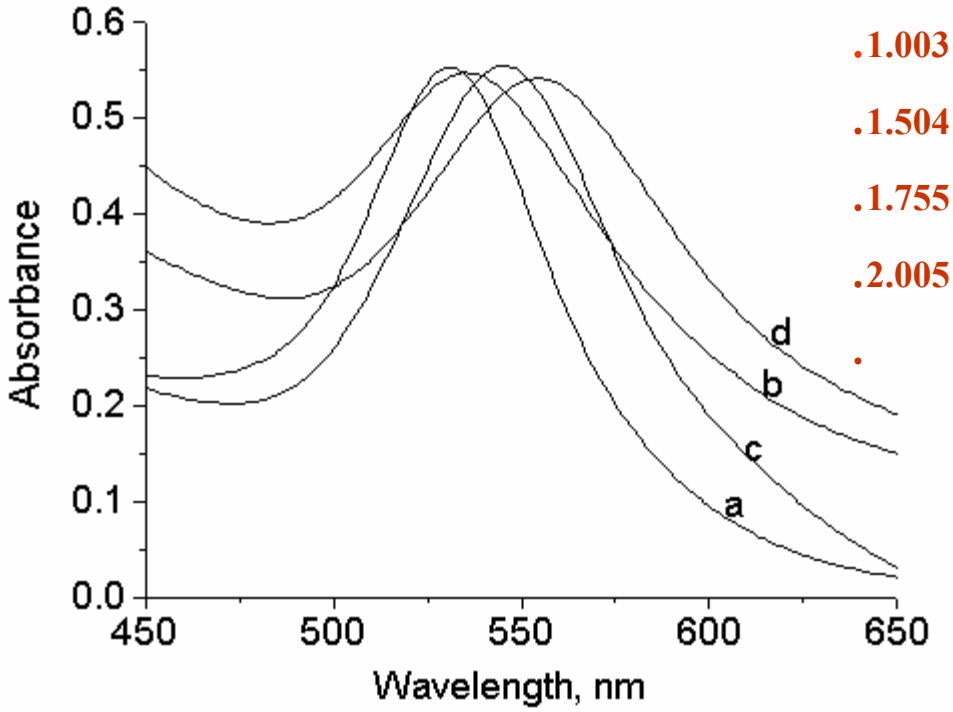
ZrO_2 covered Au cluster solutions




a -- AuZrO2 (3.8 mM, 45 min)
b -- AuZrO2 (3,8 mM, 1 h 30 min)
c -- AuZrO2 (3,8 mM x 2, 45 min)
d -- AuZrO2 (3,8 mM x 2, 1 h 30 min)
Absorbance
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
Wavelength, nm
a
b
c
d

TiO_2 covered Au in various forms





.1.003 mM (λ max = 531nm)

.1.504 mM (537 nm)

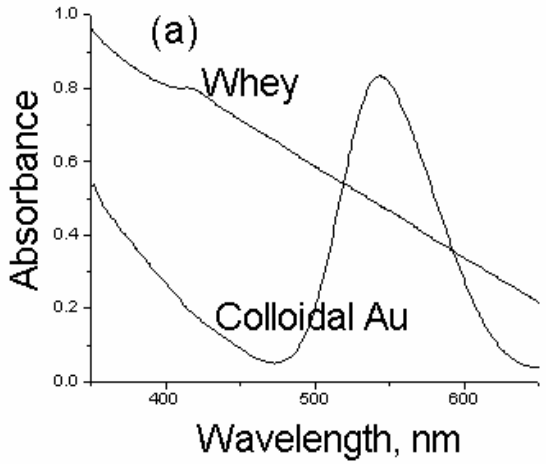
.1.755 mM (547 nm)

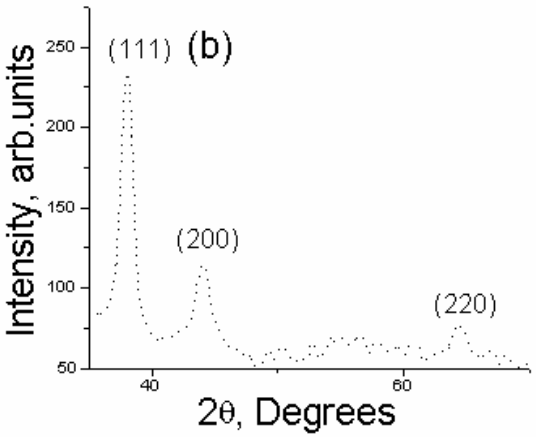
.2.005 mM (554 nm)

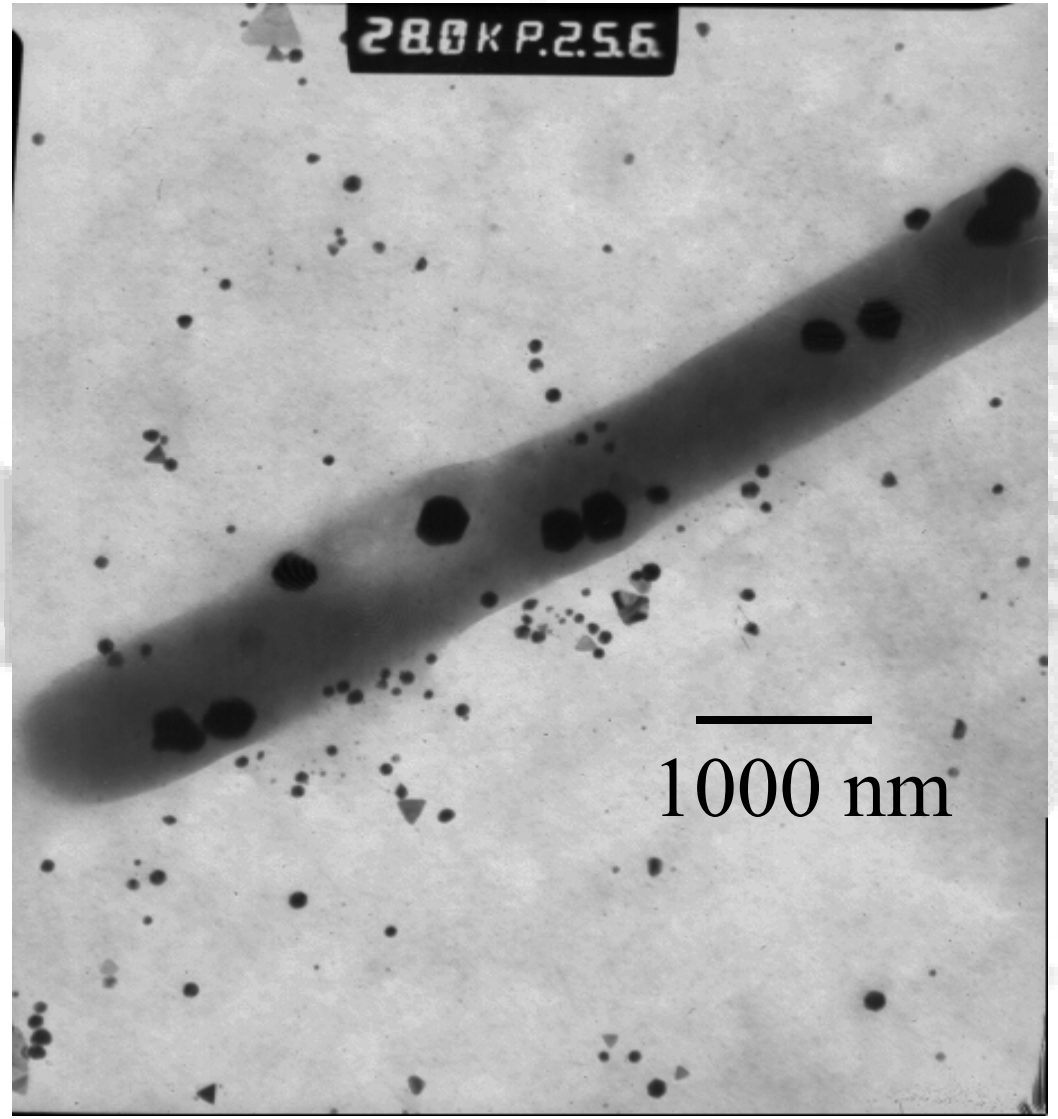
.

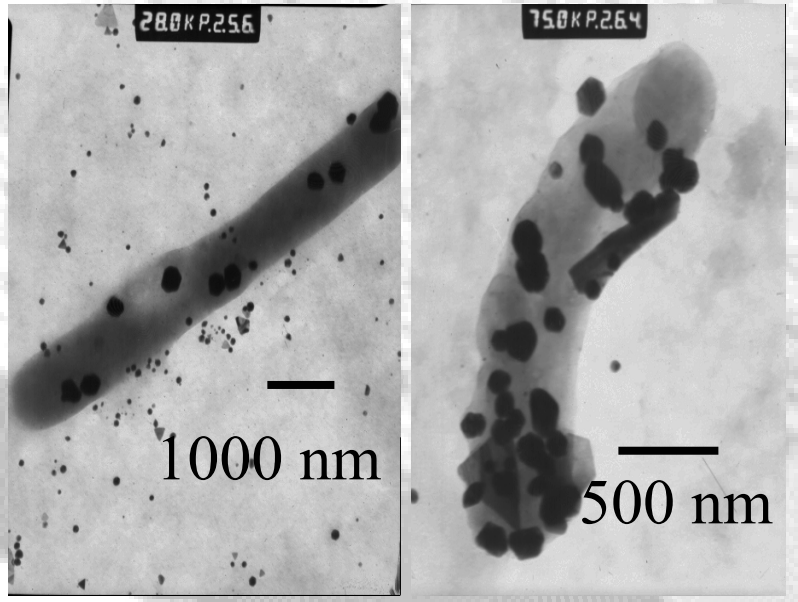
UV-VIS of titania covered gold nanoparticles

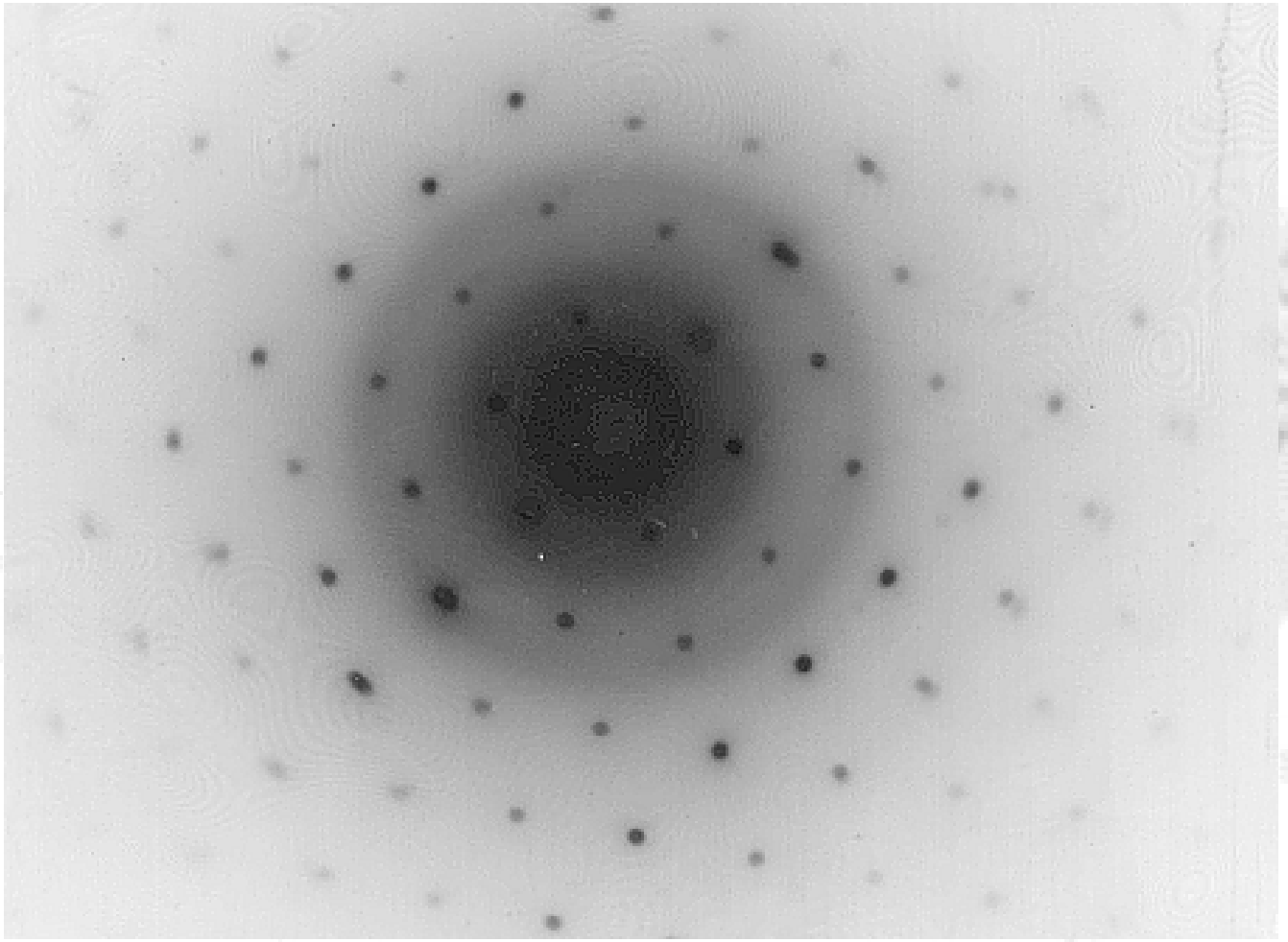
Bio-clusters!



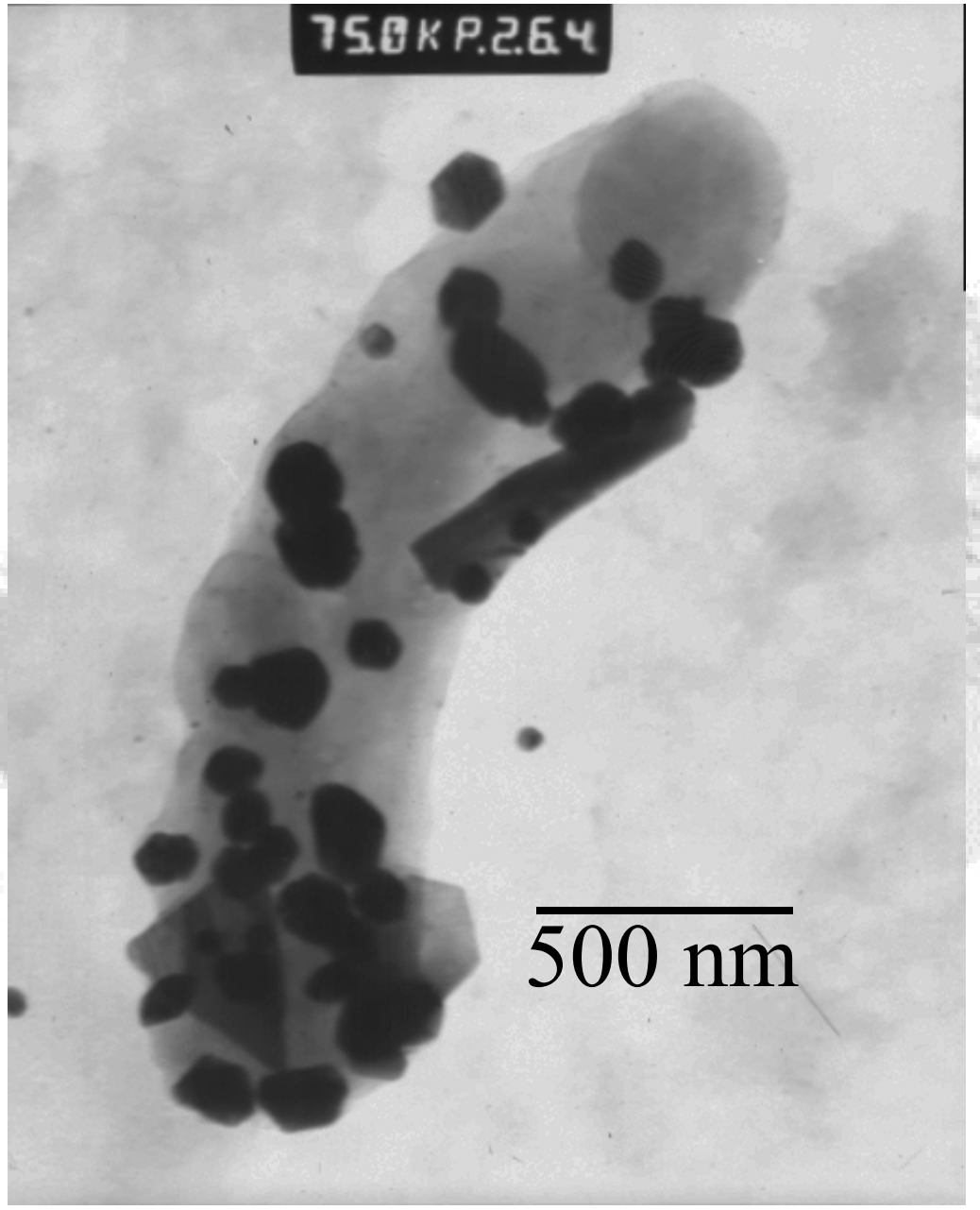


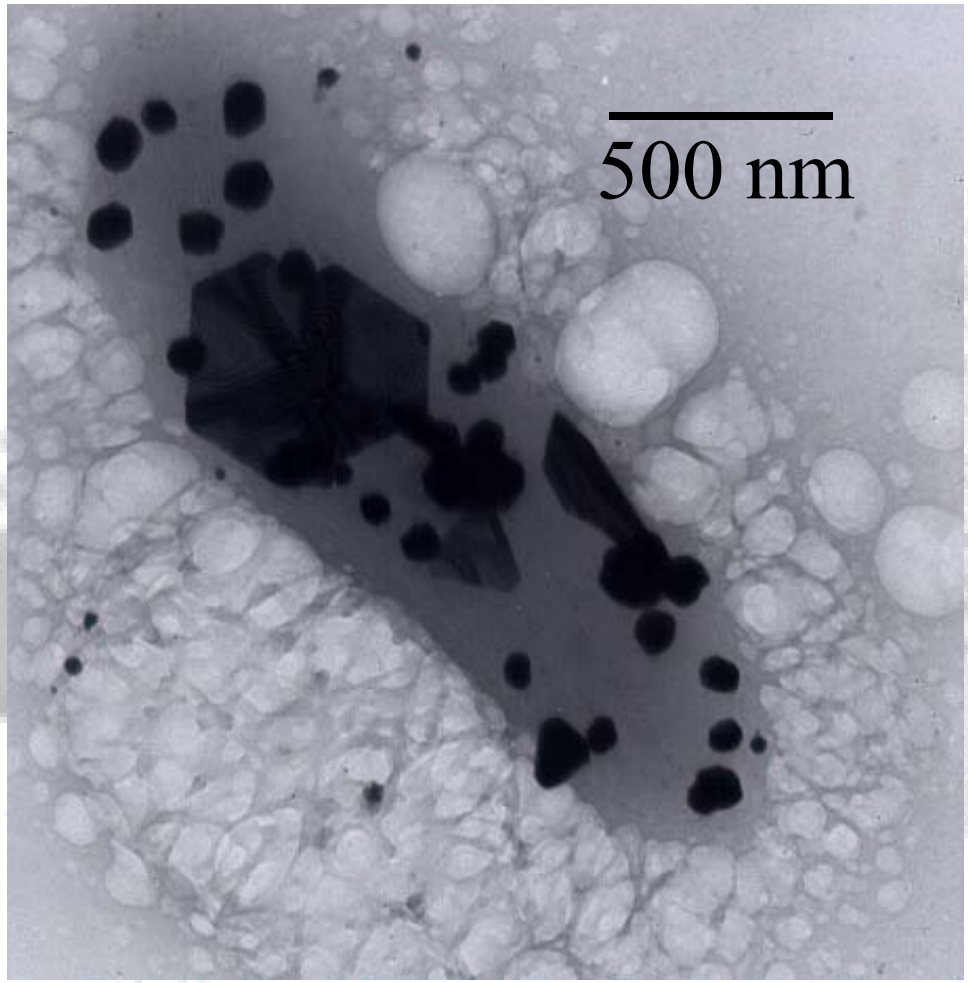

28.0K P.2.56
1000 nm

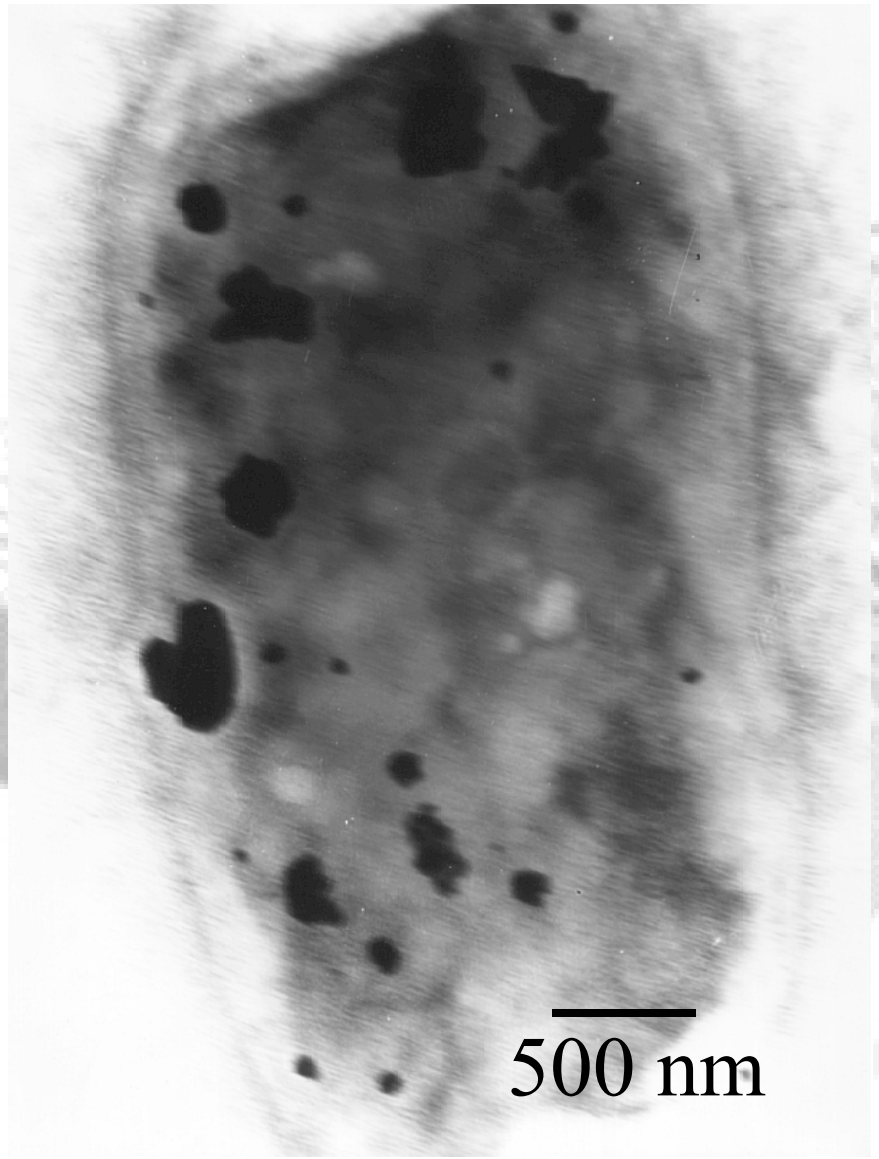

28.0KP.2.56
1000 nm
75.0KP.2.64
500 nm

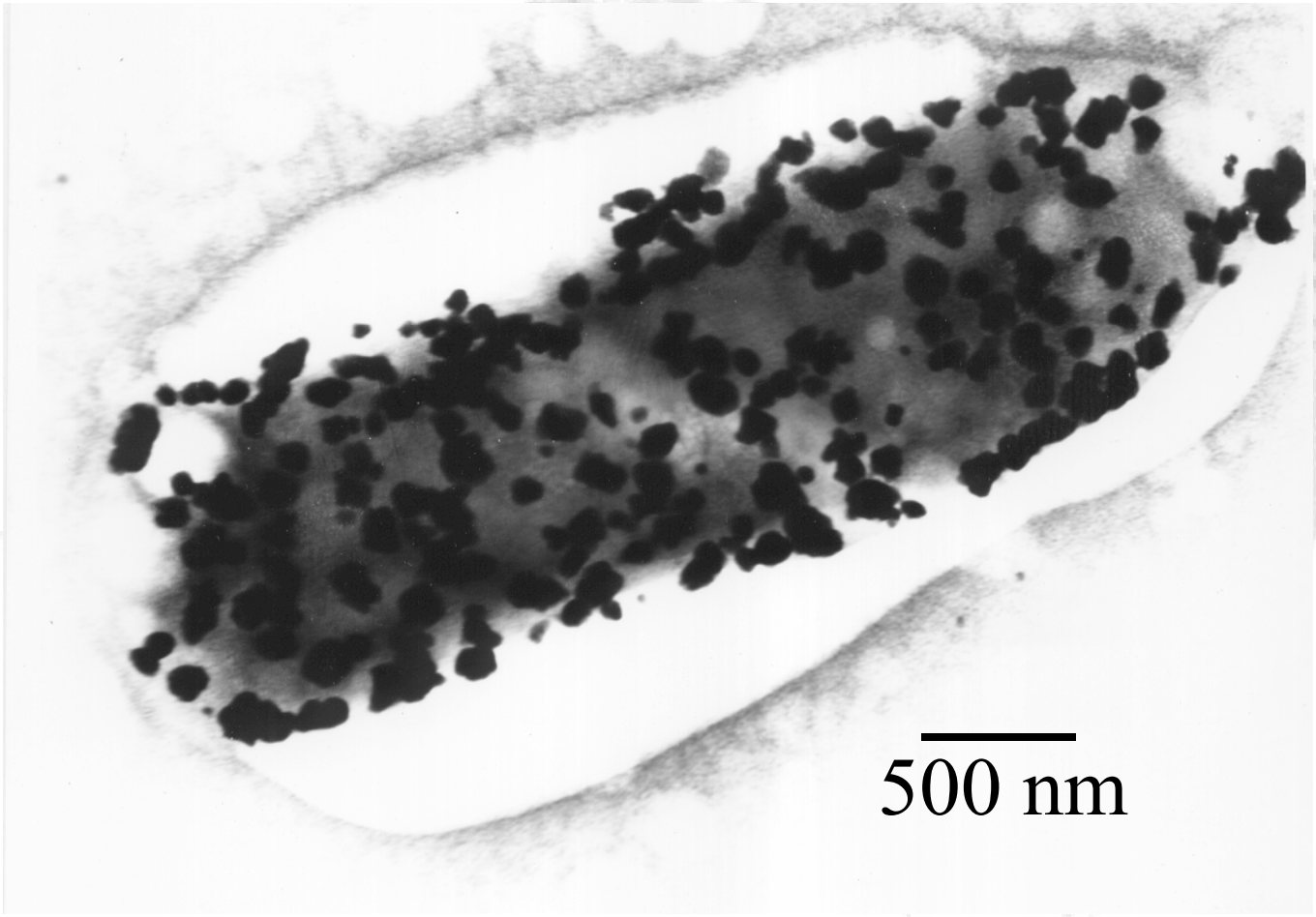


Along [111] zone axis


75.0K P.2.64
500 nm


500 nm


500 nm


500 nm

Bacterial gold film (111) orientation

Summary

Materials through monolayers: a viable approach

Thiol adsorb on gold with hydrogen evolution

Oxide protected metal clusters can be synthesised in bulk

Properties can be tuned depending on the dimensions of both oxide and metal

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