

A photograph of a sunflower field at sunset. The sky is a gradient from blue to orange and yellow. A small crescent moon is visible in the upper left corner. In the foreground, several sunflowers are silhouetted against the setting sun, their heads turned towards the right. A paved path or road curves through the field on the left side.

# Nanoscience A New World Coming

Chris Sorensen

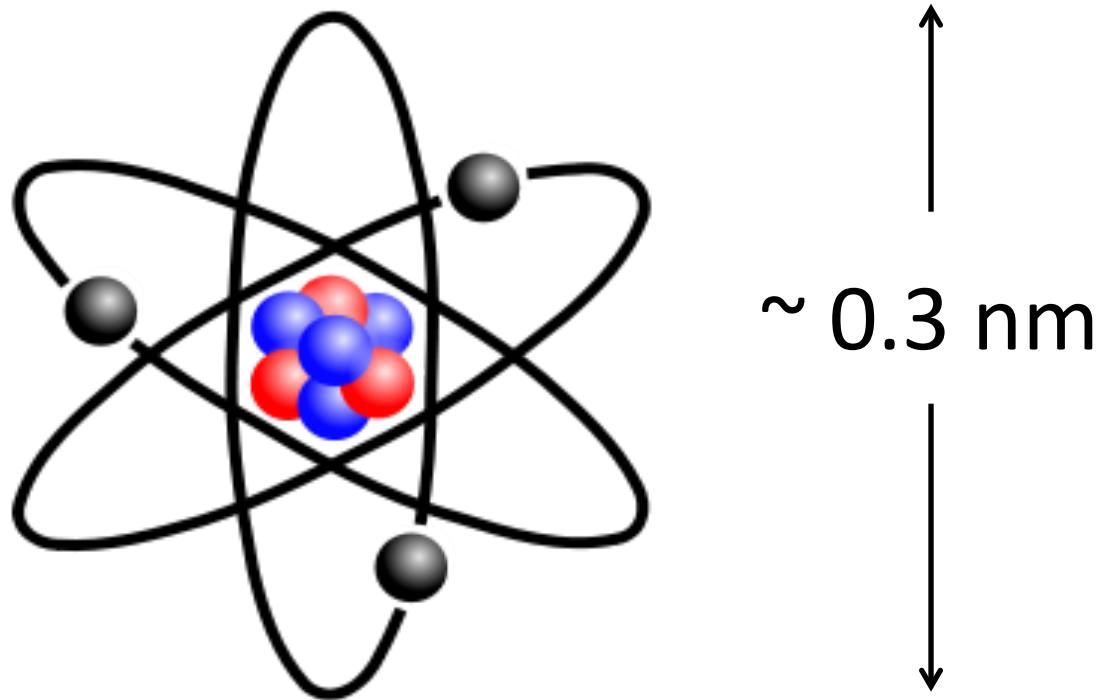
Physics

Kansas State University

# What if...

you cut a piece of iron in half,  
what would you get?

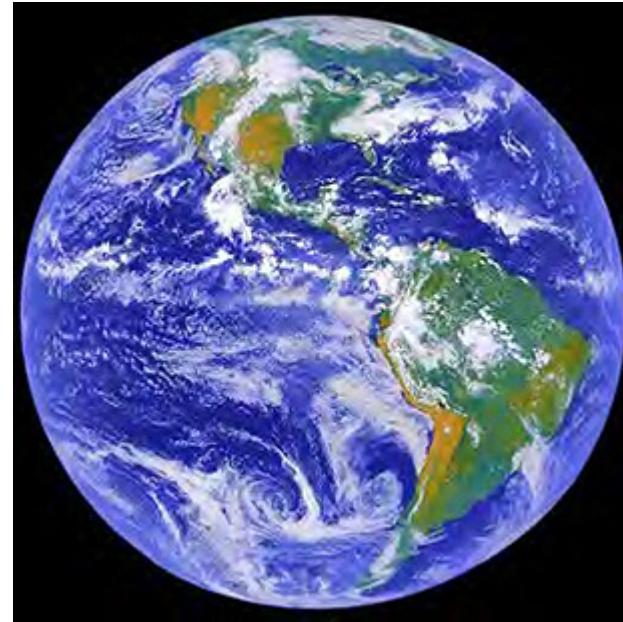
An atom...



is a few tenths of a nanometer  
in size.

Nano = one billionth =  $10^{-9}$

One nano-Earth



Is a marble!



Nanomaterials have size dependent chemical  
and physical properties!

Nano is different than bulk

Nano is different than atomic

Nano is something in between

Why?

Bulk effects

Surface effects

# Quantum mechanics 951

Schrodinger equation

$$[\frac{-\hbar^2}{2m} \nabla^2 + V] \Psi = i\hbar \frac{\partial}{\partial t} \Psi$$

# Energy is quantized.

For an oscillator or a photon it comes in pieces (quanta) with size

$$E = hv$$

v is the frequency

h is Planck's constant

=  $6.6 \times 10^{-34}$  Joule.sec.

But why is energy quantized?

Because:

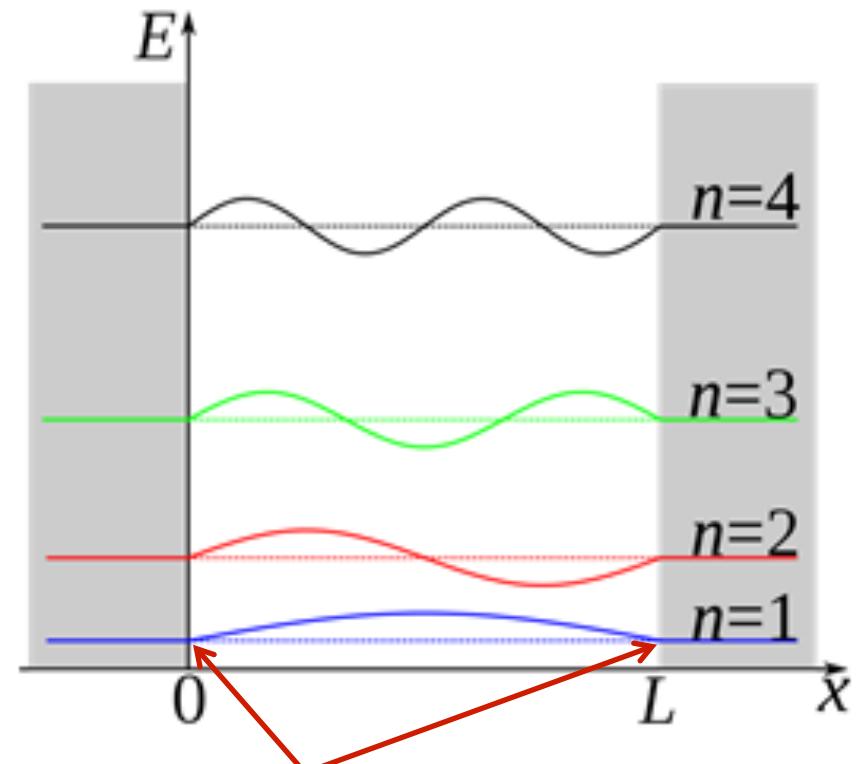
1. everything has a wave nature; de Broglie  $\lambda = h/p$
2. confined wave resonate at only specific frequencies

# The Particle in a Box

Quantum mechanics tells us that all particles are waves too (including you!).

The wave/particle duality of Nature

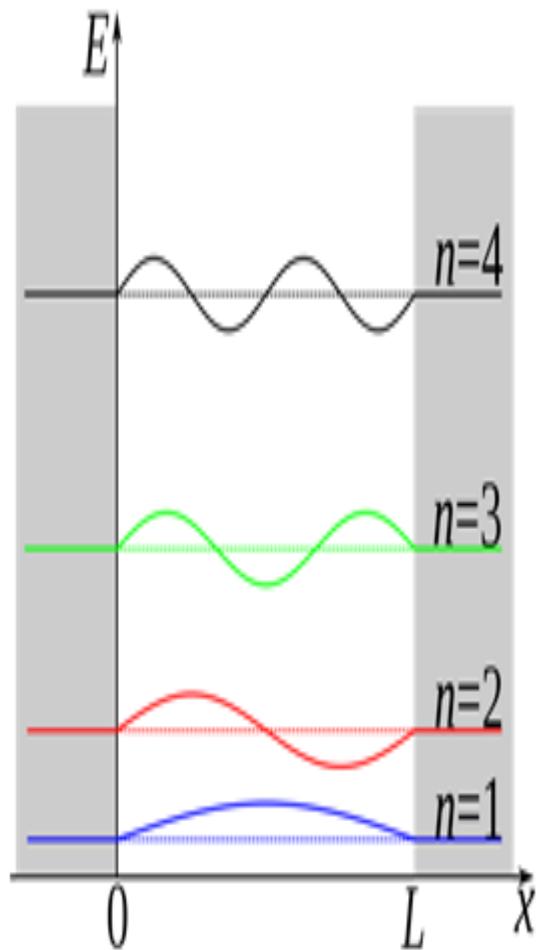
When a particle like an electron is confined to a “box”, e.g. an atom or a nanoparticle, its waves exist in only certain resonances called “eigenstates”, as drawn to the right.



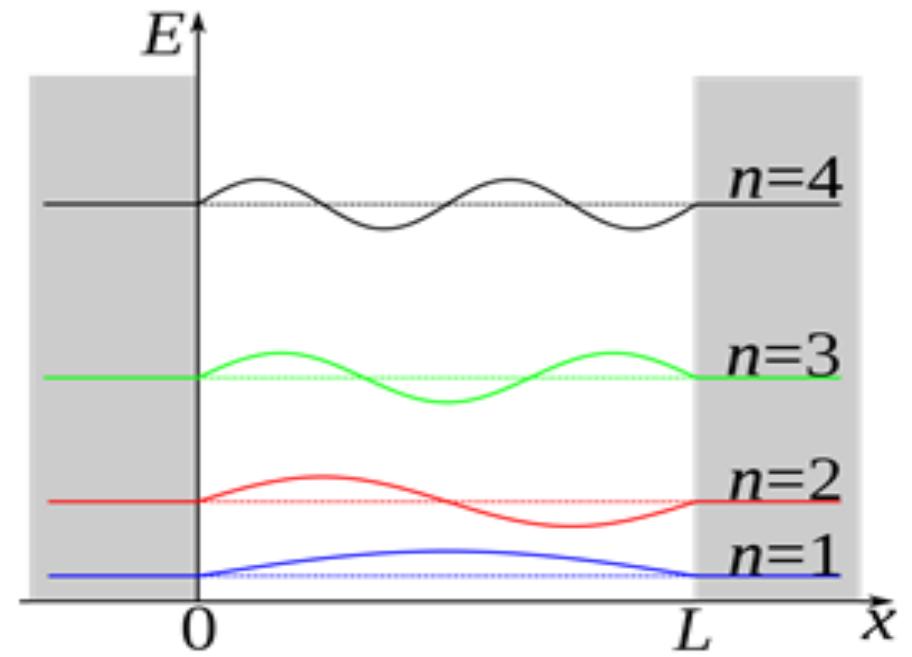
Boundary conditions, wave  $\psi = 0$  at boundaries.

# Particles in Different Boxes

Small boxes,  
higher frequencies,  
bigger energies

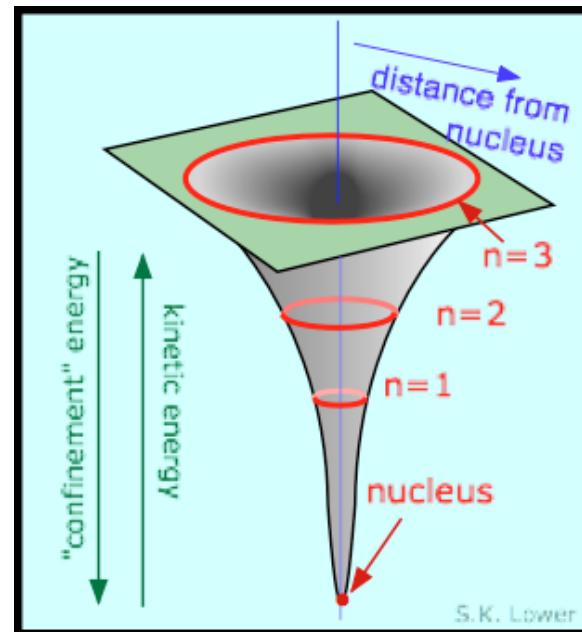


Big boxes,  
lower frequencies,  
smaller energies



The atomic “box”. Size  $\sim 0.3$  nm.

Confinement of the electron  
by the attraction of the nucleus



Energy level spacings of 1 to 10 eV.

Quantum mechanics rules!

Note: green light photon carries 2.5 eV

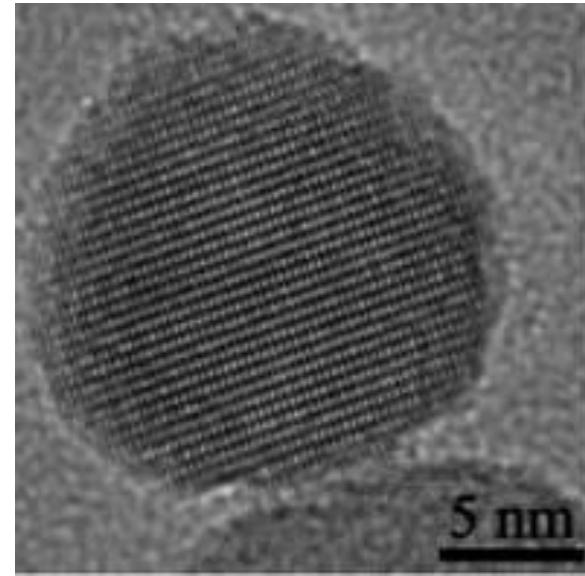
A penny, size  $\sim 1$  cm ( $10,000,000$  nm)

Confinement of the electrons  
by the limits of the penny.



Energy level spacings  $10^{-14}$  to  $10^{-12}$  eV.  
essentially a continuum of energy...  
no quantum effects.  
A “sea” of electrons!

A nanoparticle box,  $\sim 10$  nm  
Confinement of the electrons  
by the walls of the particle.

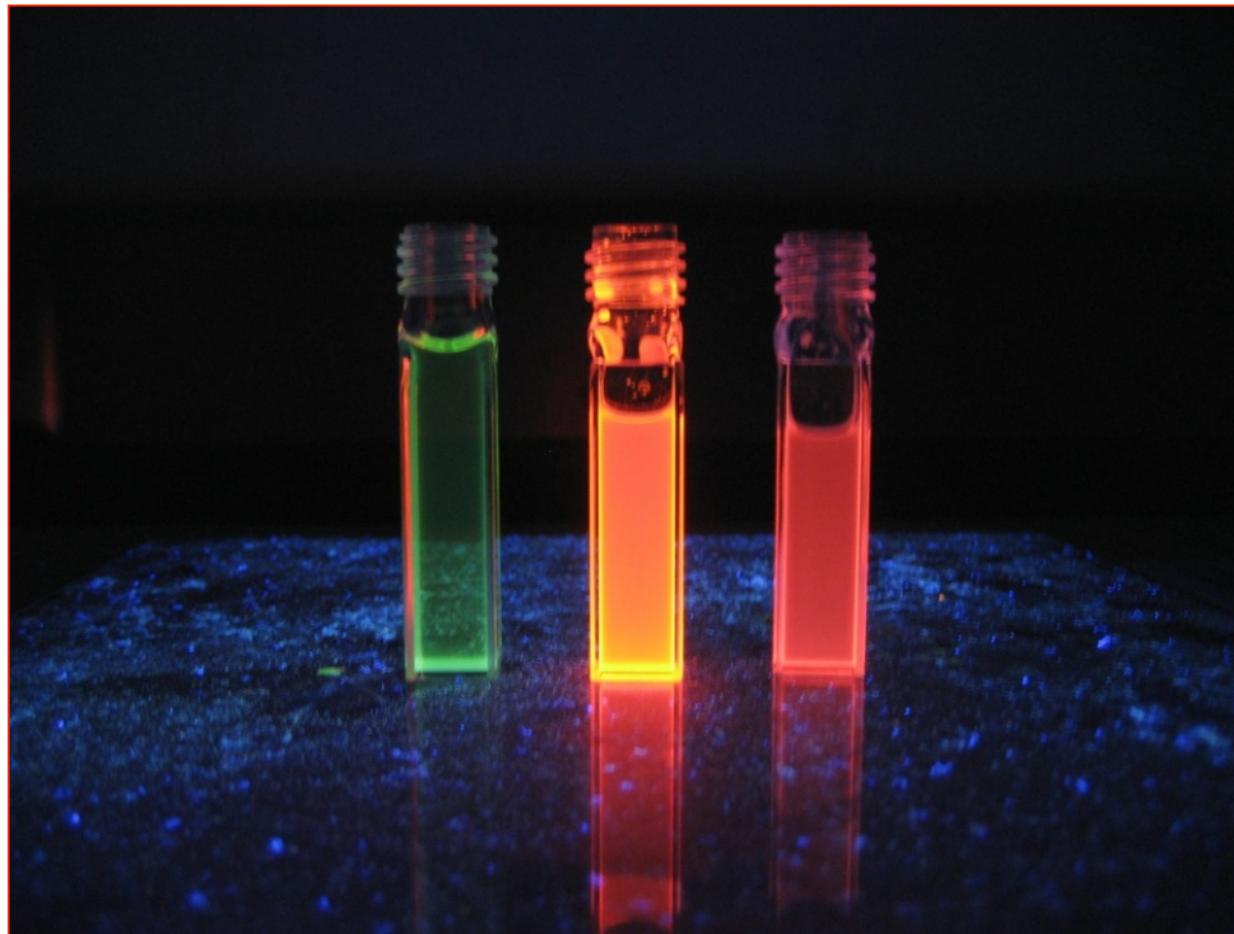


Energy level spacings 0.1 to 1 eV.  
Quantum mechanics still important.

# CdTe nanoparticles

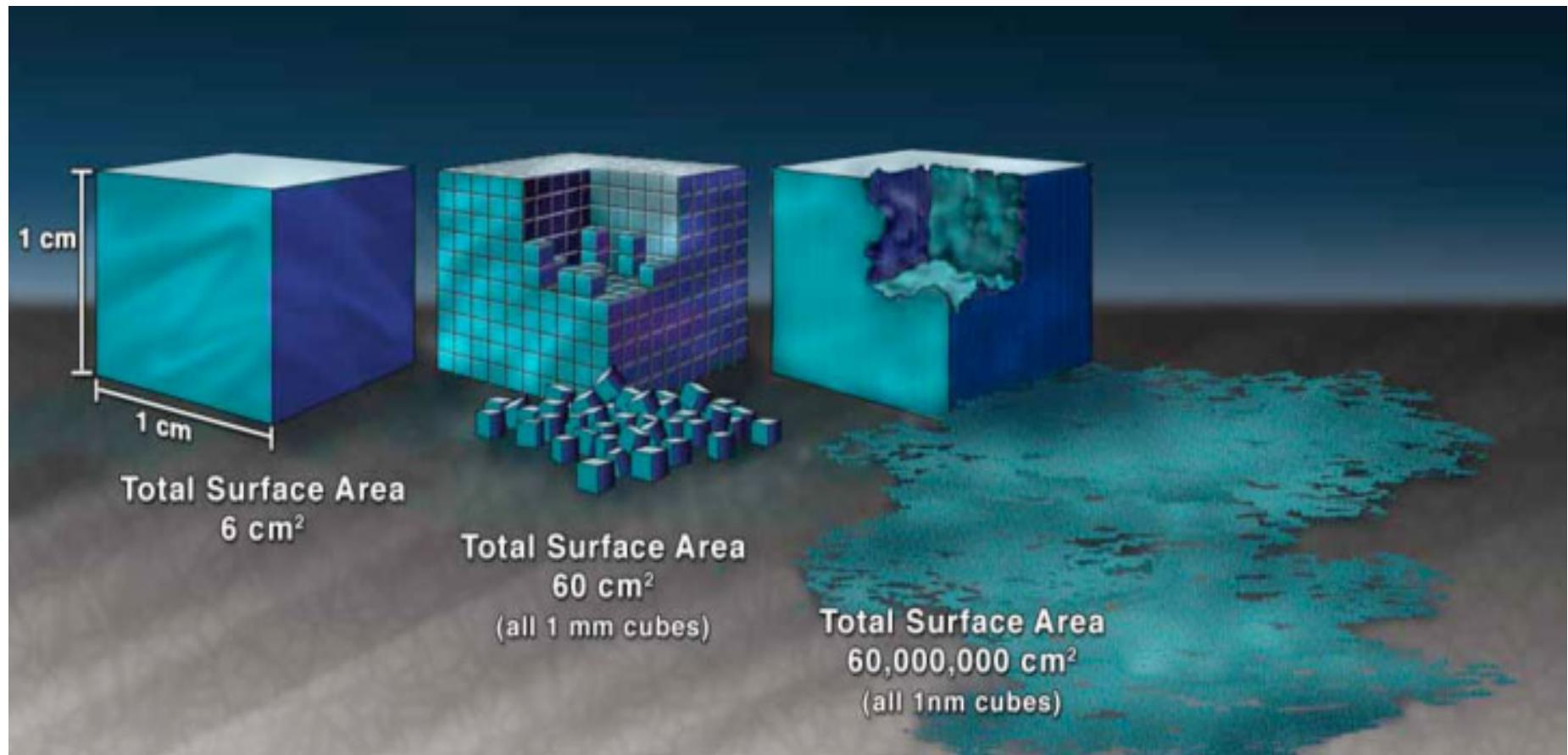
## Different sizes

### UV light(fluorescence)



Small medium large

# Nanostuff is surface stuff





# Surface Fraction

You:  $4 \times 10^{-7}$  % (4 parts in a billion) of all your atoms are on your surface.

Everyday things are bulk stuff.

Most of the atoms are hidden beneath the surface.

A 5 nm nanoparticle: 36% of all the atoms are on the surface.

A nanoparticle is surface stuff!

Many of the atoms are exposed!

# Galileo's notebook

Ali 7. di Giugno 1610 Giove si vedeva con l'occhio ai  
3. stelle appaesi <sup>et non</sup> delle quali solo il minore  
minore si vedeva <sup>con</sup> à di 3. apparire così <sup>et</sup> era dunque  
piuttosto retrogrado come s'pone i calulatori.  
Ali 9. fu regolato à l'uso di Galileo così <sup>et</sup> vi è di  
quale si la più occidentale si stella multo appena si può credere.

Ali 11. ora in questa posizione <sup>con</sup> era la stella più vicina  
à Giove era latitudine minore dell'altra, et vicinissima all'alba  
dove che le altre sare erano le dette stelle apparse tutte tre  
di qual grandezza et tra di loro qualche contorno; dal che  
appare intorno à Giove esser 3. altre stelle erranti invisibili ad  
ogniuno sino à questo tempo.

Ali 14. si vedde in tale costituzione <sup>con</sup> era la stella  
occidentale poco minor delle orientali, et giaceva in mezzo intorno  
la luna et dall'altra parte il suo diametro è circa: et forte era  
una terza piccola et vicinissima à l'uscente oriente; e se pur si era  
veramente la più diligente osservata, se n'ebbe più intrinseca  
notte.

Ali 13. havendo tenuto fermato lo strumento si veddono vicinissimi à Giove  
4. stelle in questa costituzione <sup>et</sup> è meglio così <sup>con</sup>  
e tutte apparsiono della med. grandezza, lo splazio delle 2. occidentali  
ad est maggiore del diametro di 3. et erano fra di loro notabilmente  
più vicine che le altre sere; ne erano in linea retta appuntite come  
di aquila in media distanza videlicet ora appena elevata, i vero la  
più occidentale alquanto depresso; sono queste stelle tutte molto lucide certe  
lucidissime et altre fine l'apparizione della med. grande sta in sere  
con splendore.

Ali 14. fu regolato. Ali 15. ora così <sup>con</sup> è presso à  
3. era la minore et le altre 2. meno è meno maggiore: gli interstizi  
tra 2. et la 3. regolarmente erano quasi il diametro di 3. ma la 4. era di  
mezza della 3. et il doppio circa: ed faceva  
lung. 71.38 lat. <sup>Merid.</sup> 1.13° <sup>con</sup> erano veramente lucide retta, ma non molto  
<sup>et</sup> per esempio, erano al solle lucidissime se ben pungere  
le estreme scintillavano come un'elliptica

# You gotta have the right equipment

## BEETLE BAILEY

By Mort Walker



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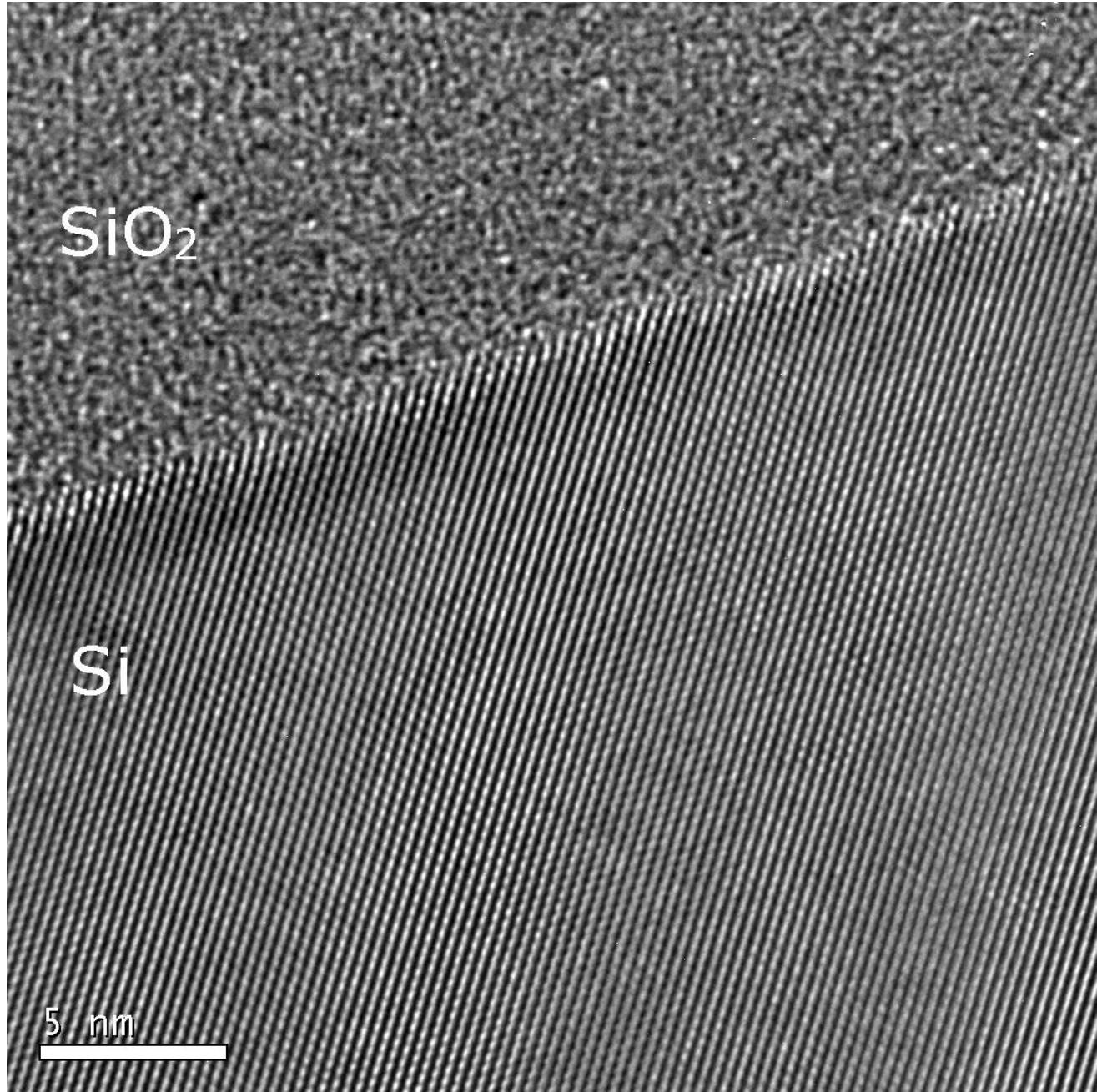


# Microscopy

# The electron microscope

Ernst Ruska





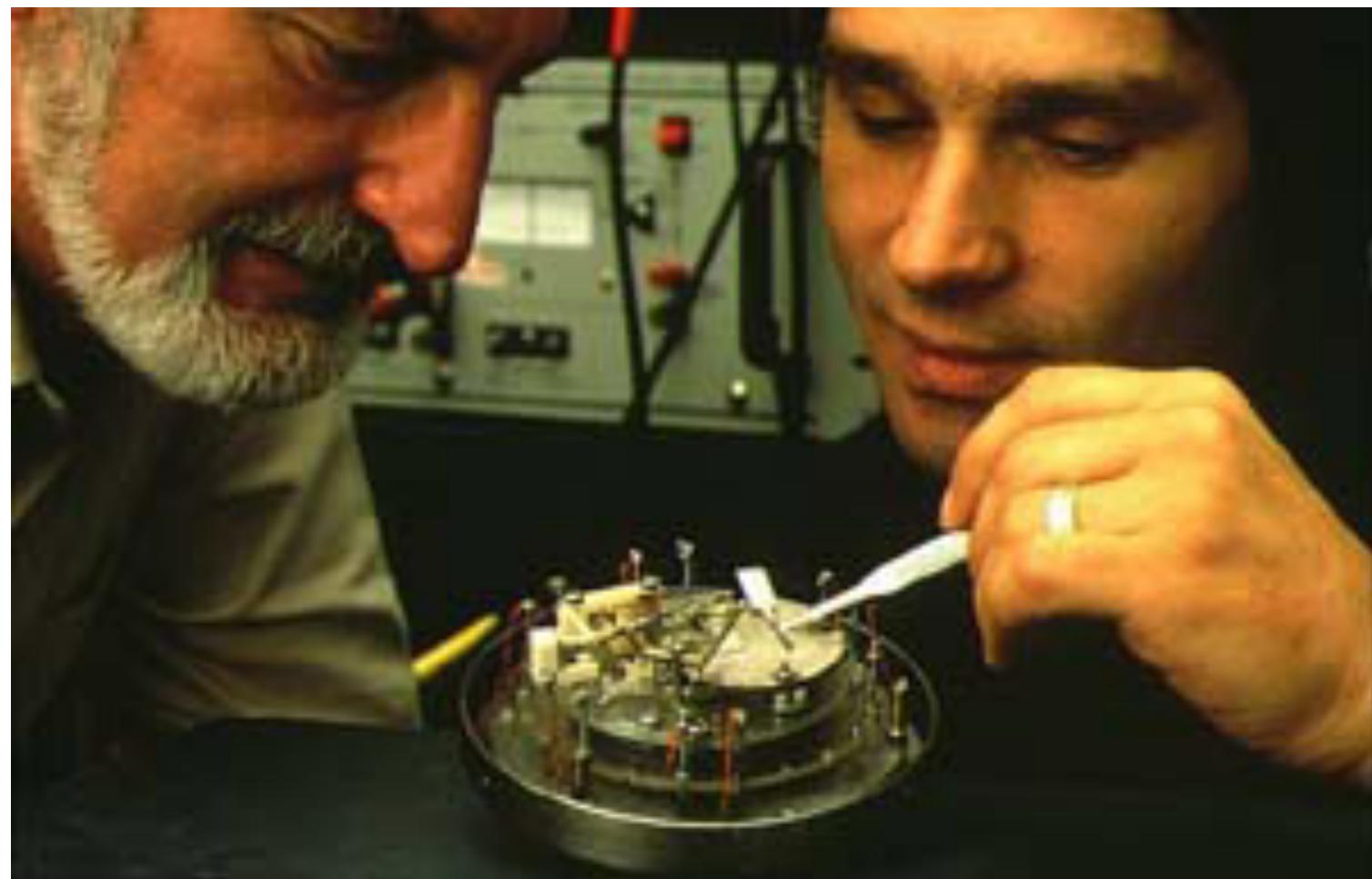
Duc The home page

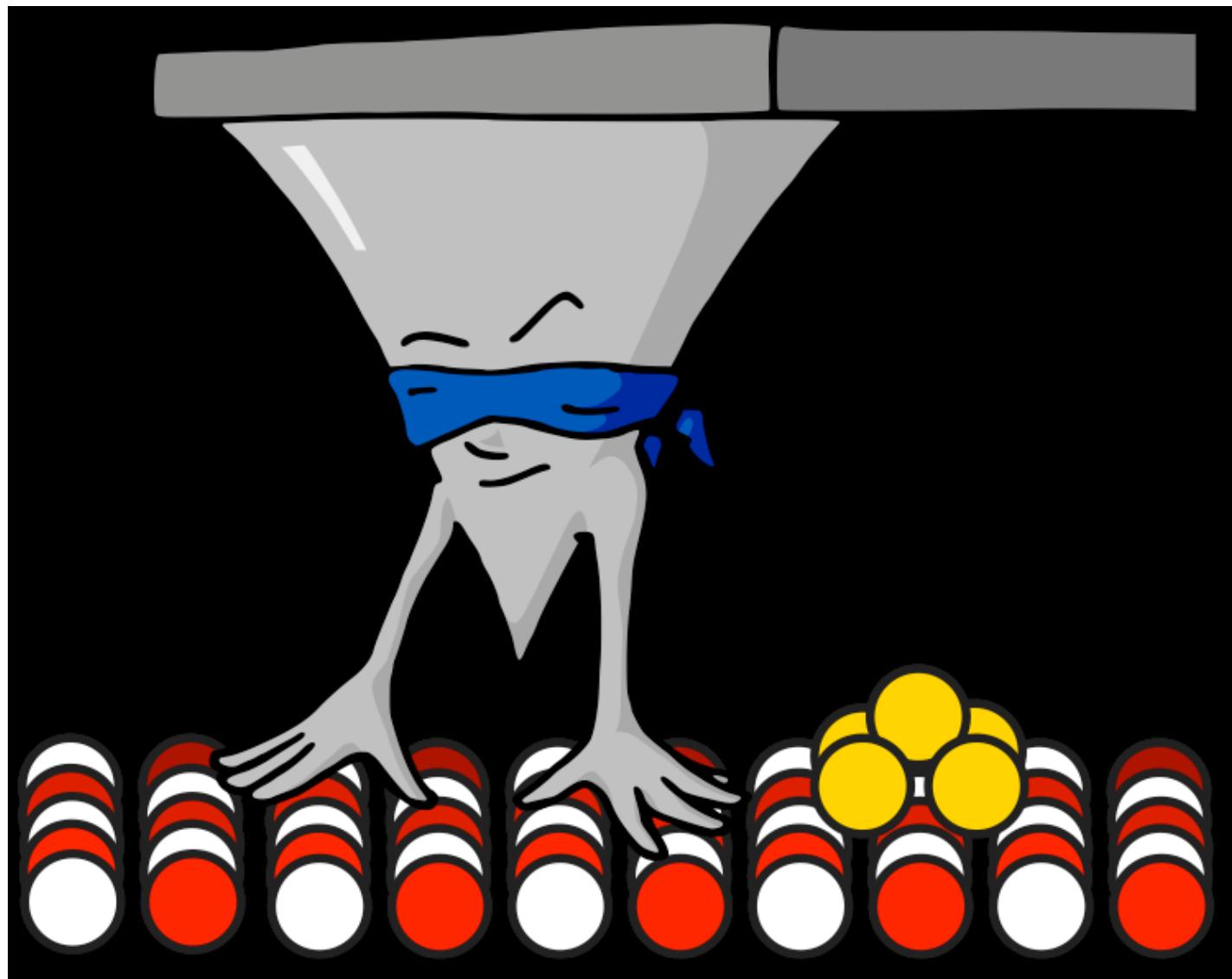
# Feeling is Seeing

Binnig and Rohrer and their scanning tunneling microscope  
Nobel prize 1986



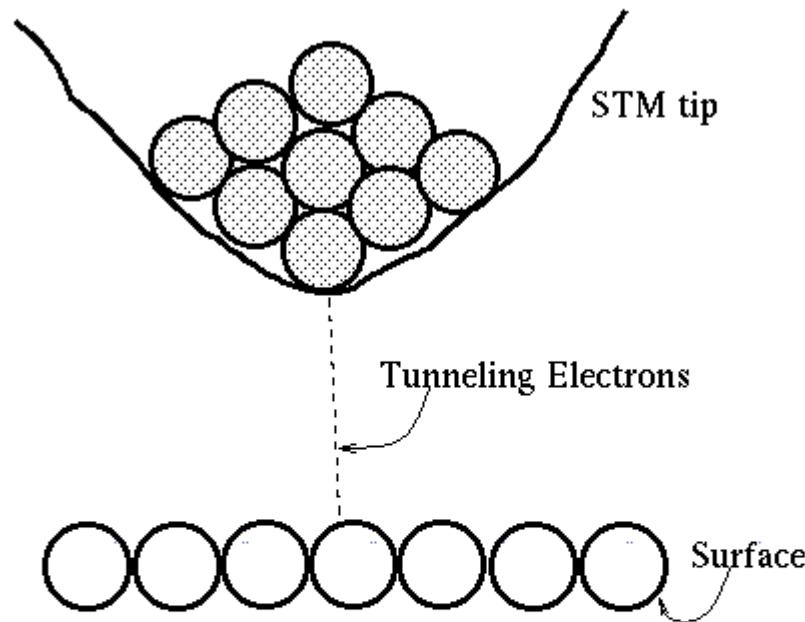
Scanned at the American  
Institute of Physics





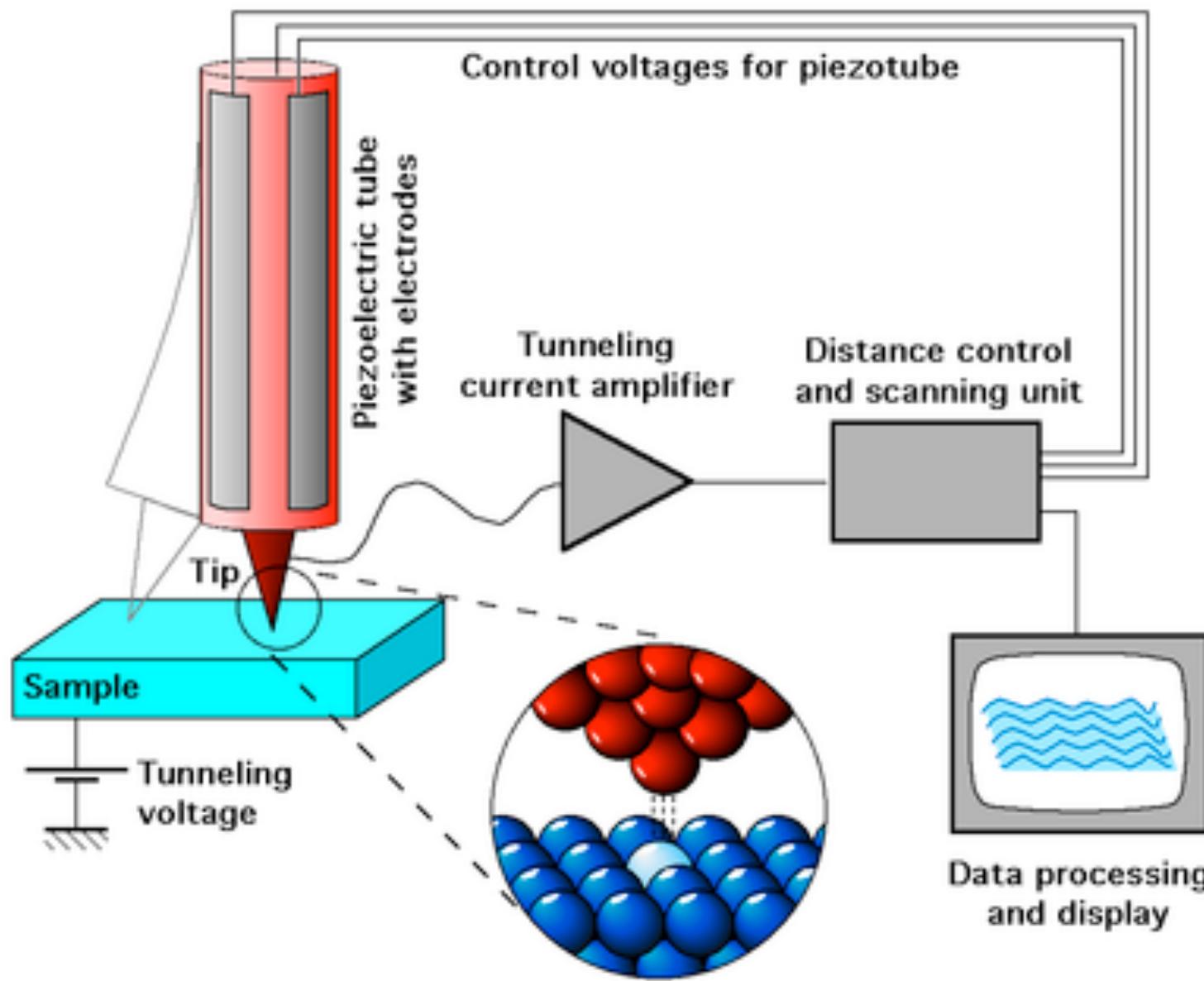
Tampere University of Technology, Physics

# The Scanning Tunneling Microscope



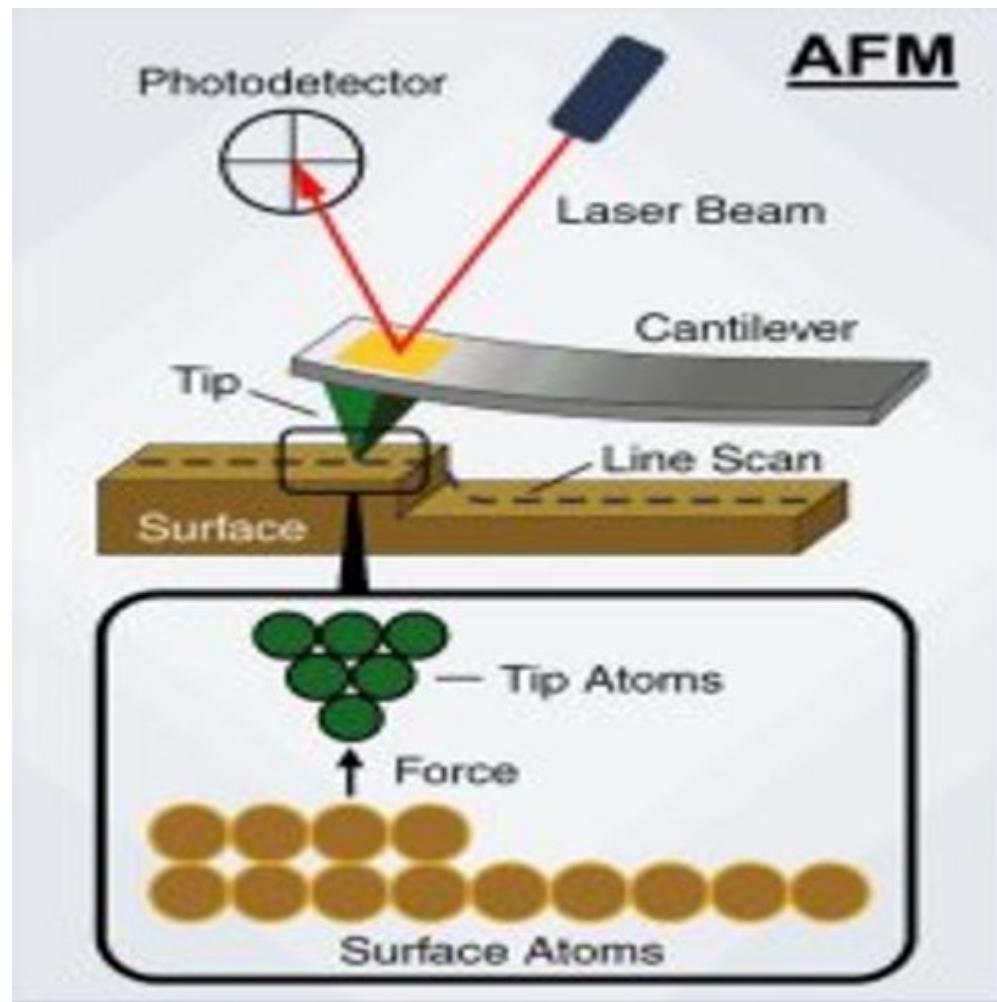
The Scanning Tunneling Microscope (STM) was developed by Gerd Binnig and Heinrich Rohrer at IBM. When a metal tip is brought near a conducting surface, electrons can tunnel from the tip to the surface or vice-versa. Because the tunneling probability is exponentially dependent on the distance the contours of the surface can be mapped out by keeping the current constant and measuring the height of the tip. In this way, atomic resolution can be obtained. For their work, Binnig and Rohrer shared the 1986 Nobel Prize.

# STM layout

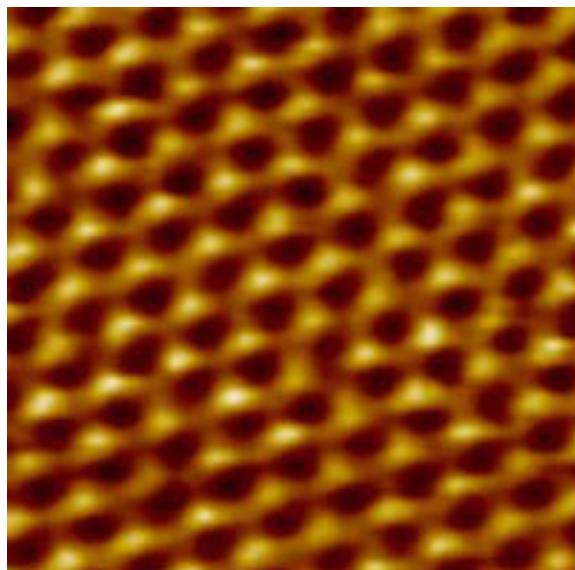


wikipedia

# Atomic Force Microscope



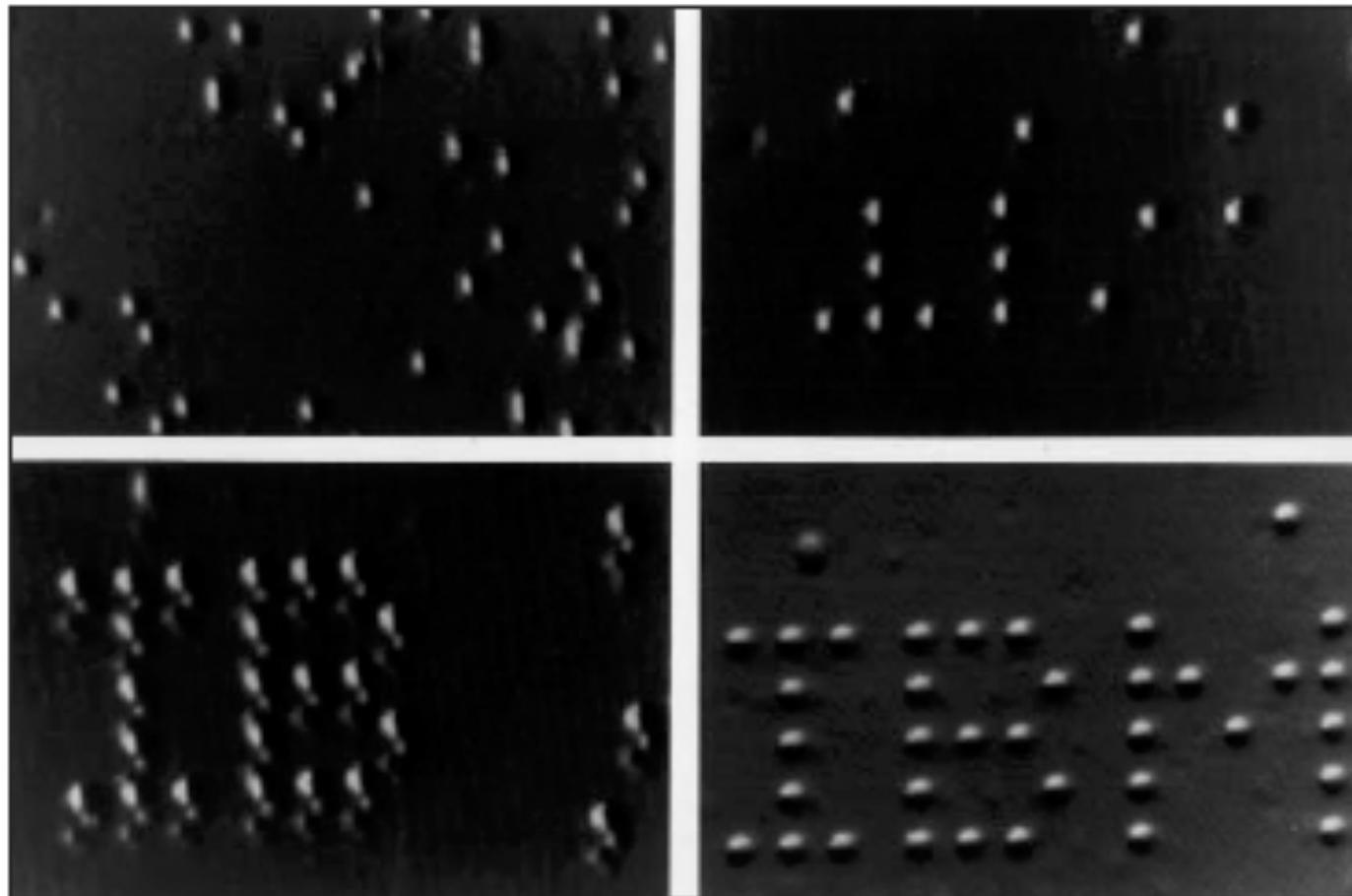
Graphite individual bumps are C atoms.  
Overall size is 2 nm by 2 nm.



← 2 nm →

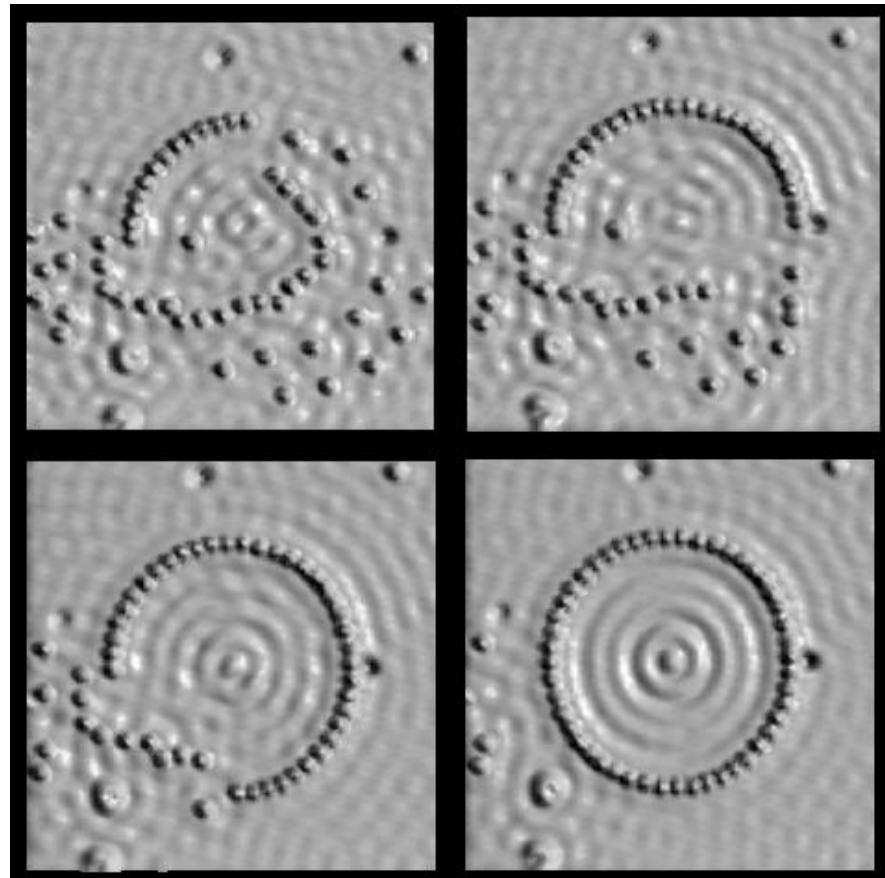
Image is courtesy of Nanosurf AG

# STM manipulation of argon atoms



# Construction of a quantum corral

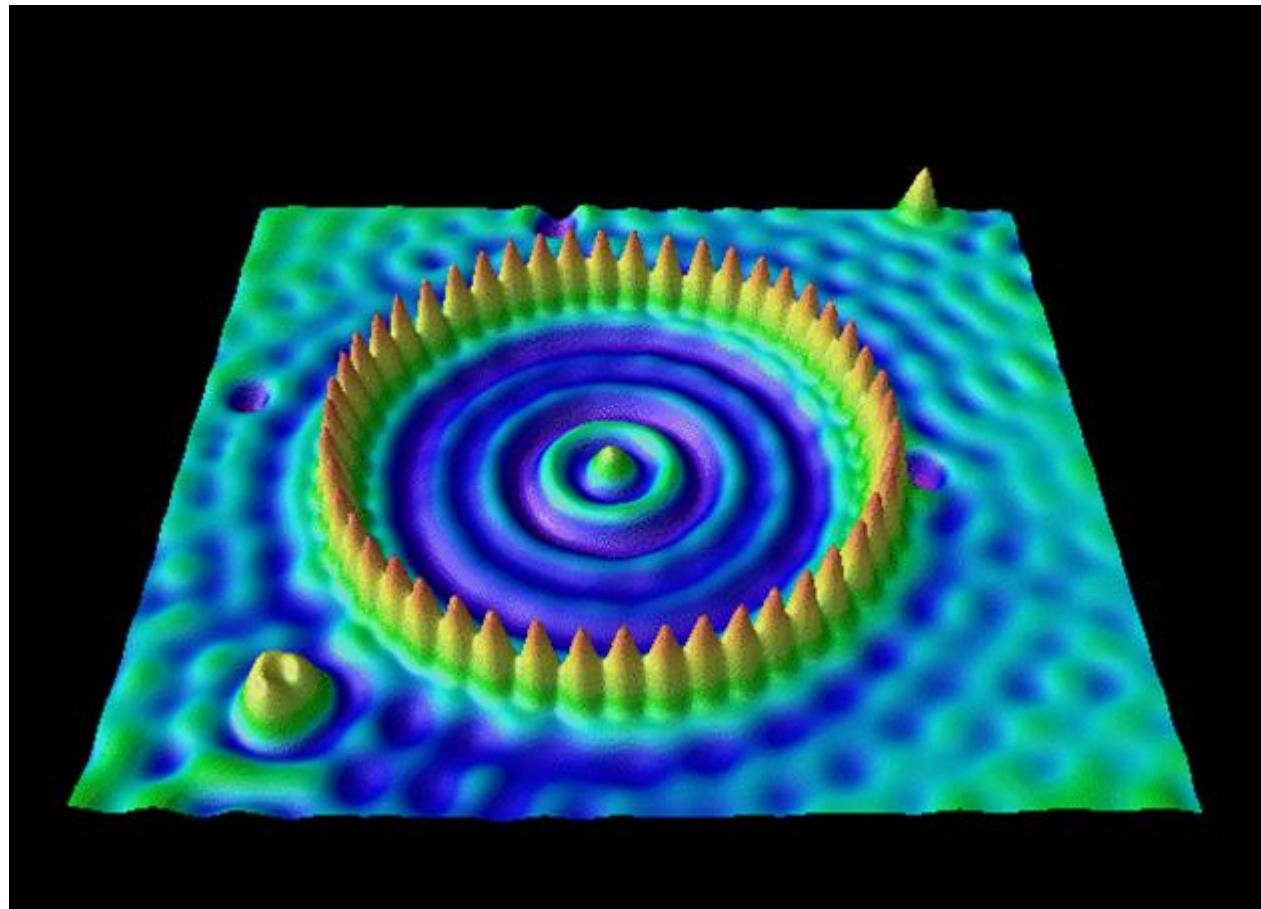
48 iron atoms on a copper surface being pushed around with an STM tip. The diameter of the corral is 7.13 nm



Note how once the corral is complete (lower right), nice rings form inside the corral. These are the standing electron waves, Quantum states expected via the particle in the box.

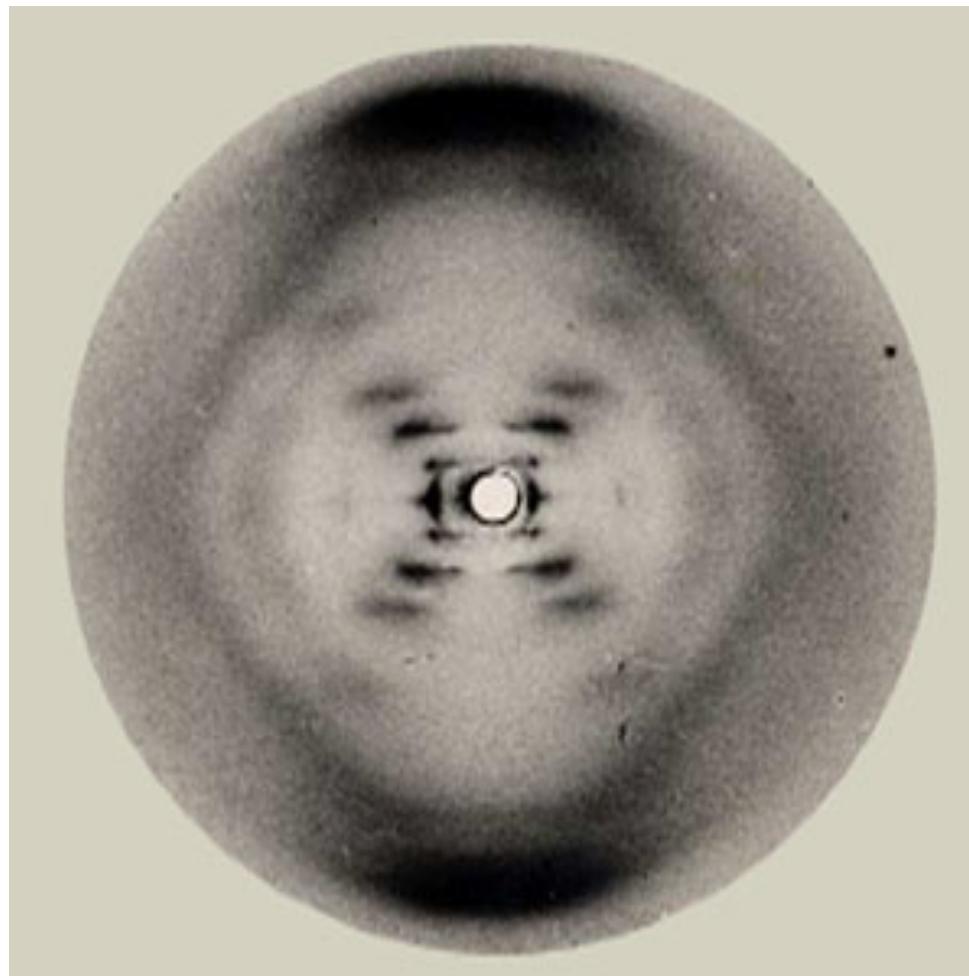
Crommie et al. Science 262, 218 (1993)

# The Quantum Corral



# Diffraction

Example: Rosalind Franklin's DNA work



# Advanced Photon Source (APS)

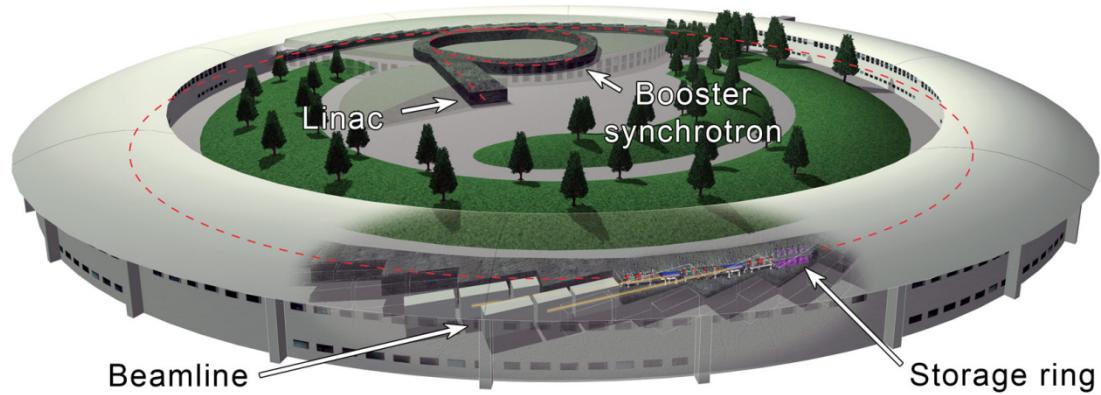
## Argonne National Laboratory

### Argonne, IL



# Synchrotron Radiation

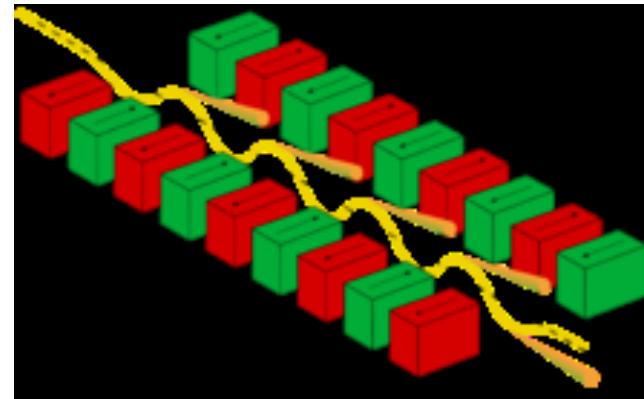
Accelerating charges radiate “light”.



Acceleration around  
A curve.

ESRF

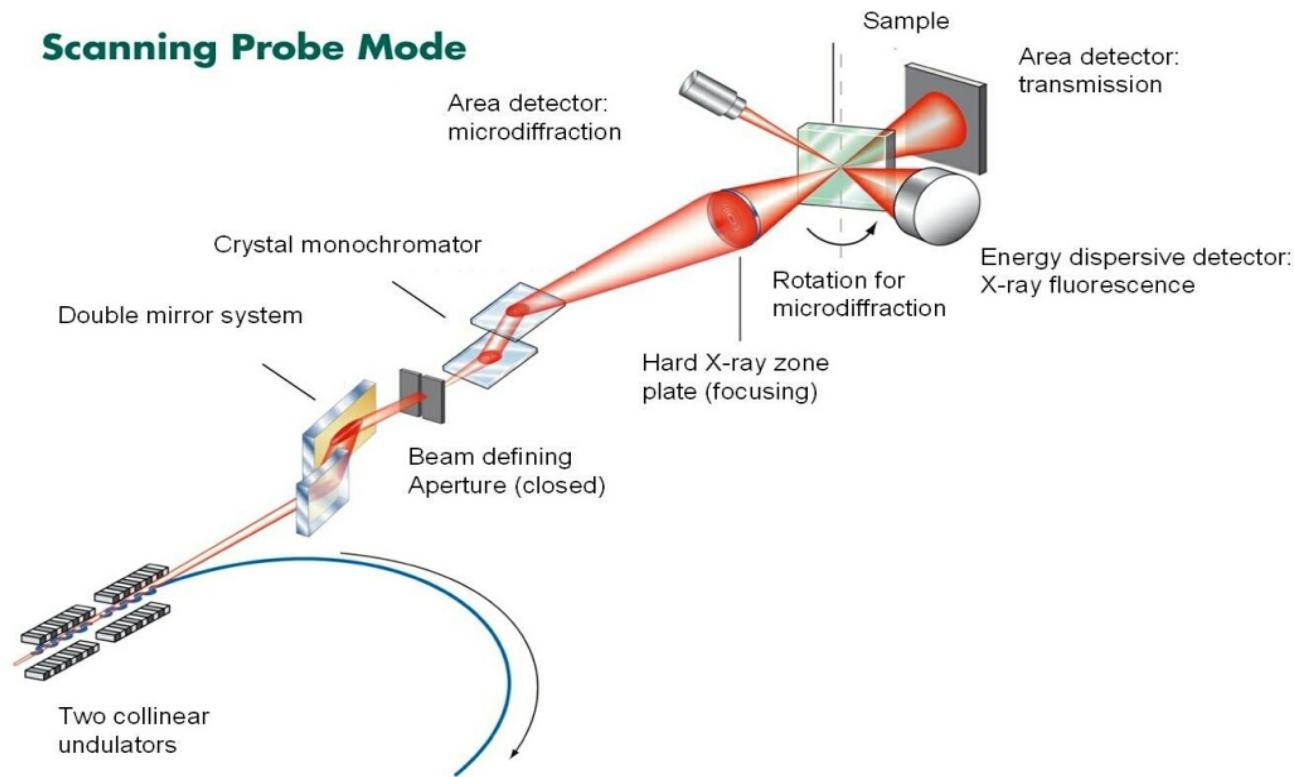
Acceleration in  
an undulator



Wikipedia

# CNM Nanoprobe at the Advanced Photon Source

## Scanning Probe Mode



# Nanoparticle Synthesis

# The Chemistry

Some examples:

Borohydride reduction



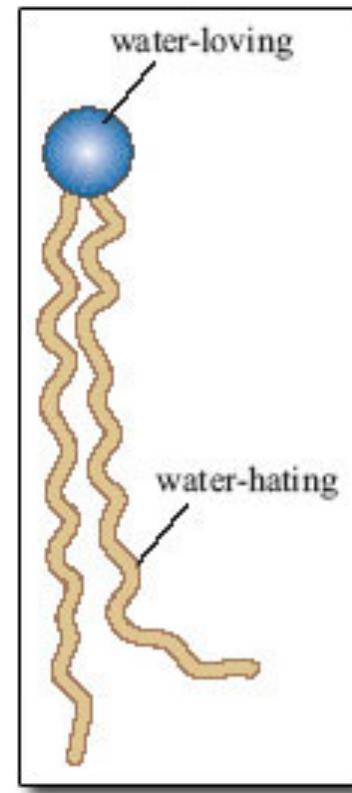
Organic chemistry



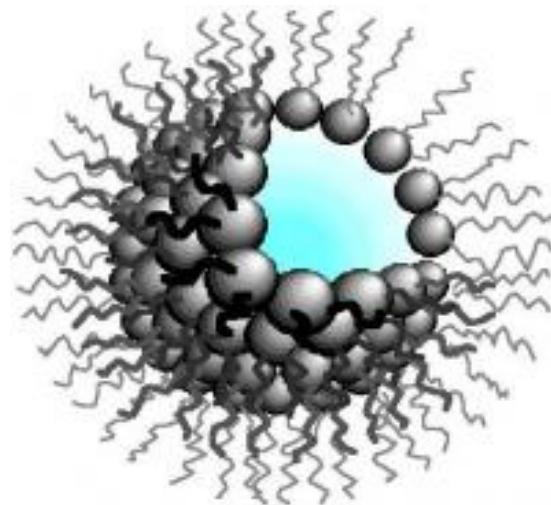
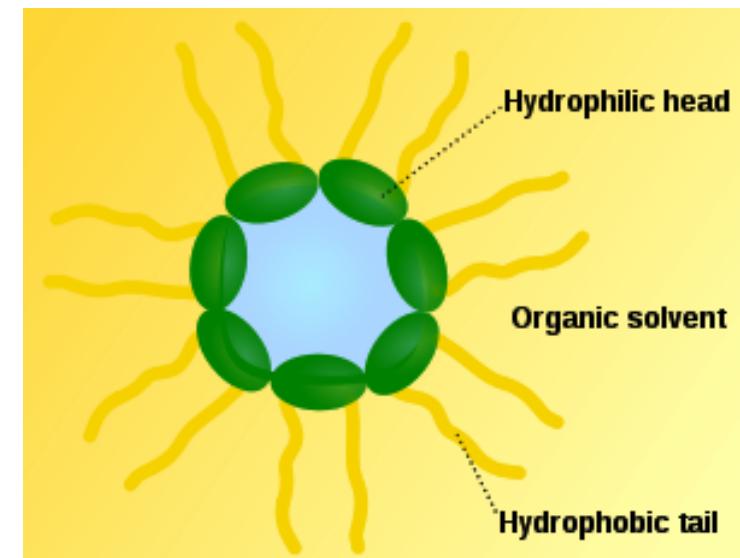
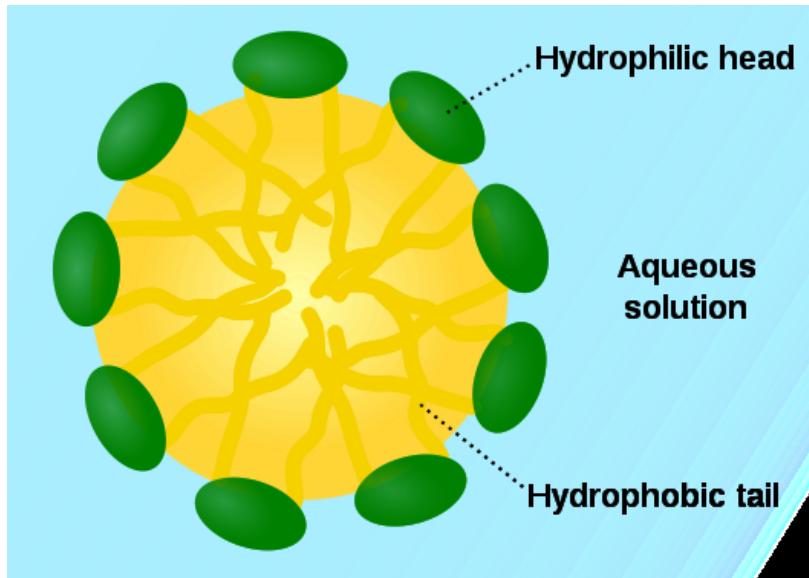
# Surface active molecules

## Surfactants

Soaps with hydrophilic (water loving)  
e.g.  $\text{RCOOH}$ ,  $\text{NR}_4$   
and hydrophobic (water hating,  
but oil loving) parts, e.g. R = alkanes.



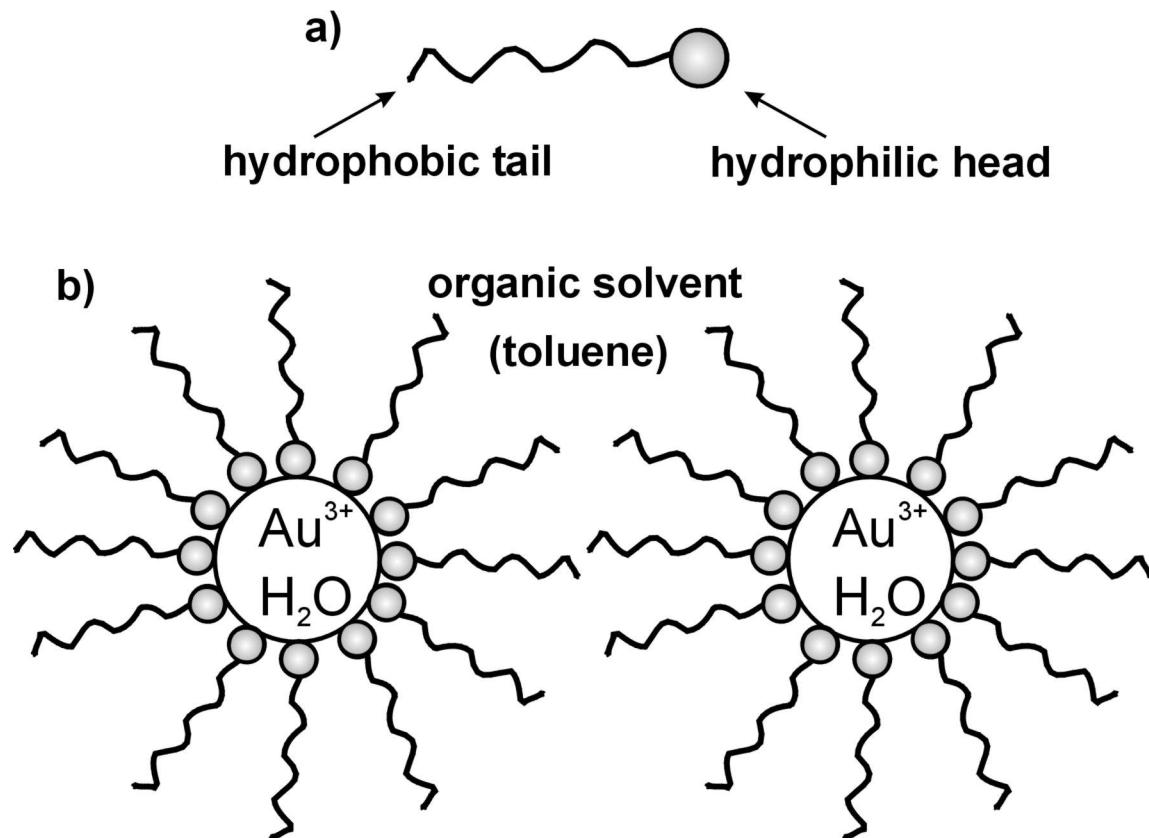
# Micelles and Inverse Micelles



# Inverse Micelles

as

## Nanoscale reactors



Ultra-Fast Synthesis

&

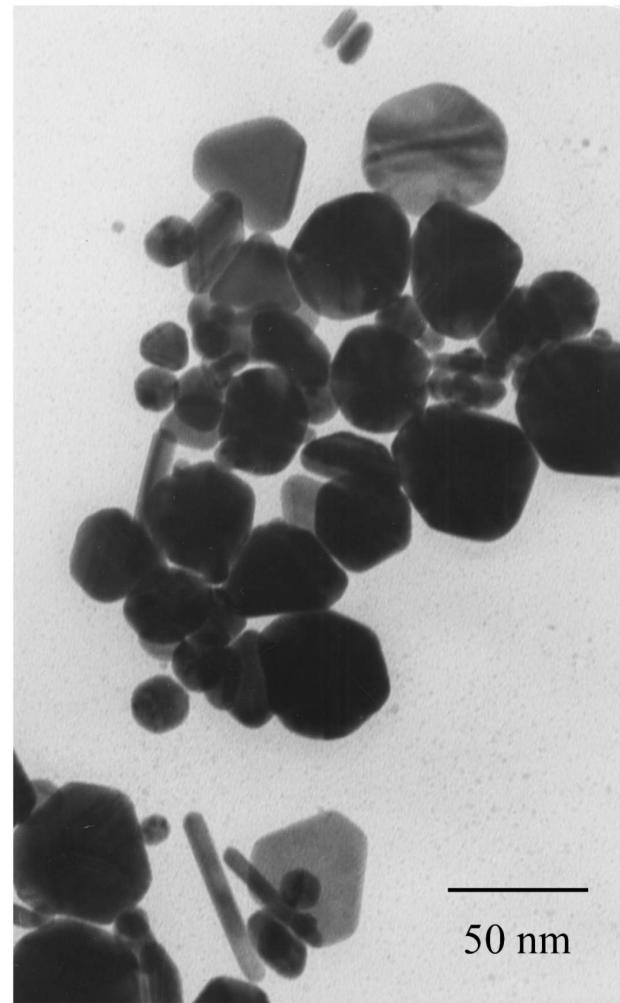
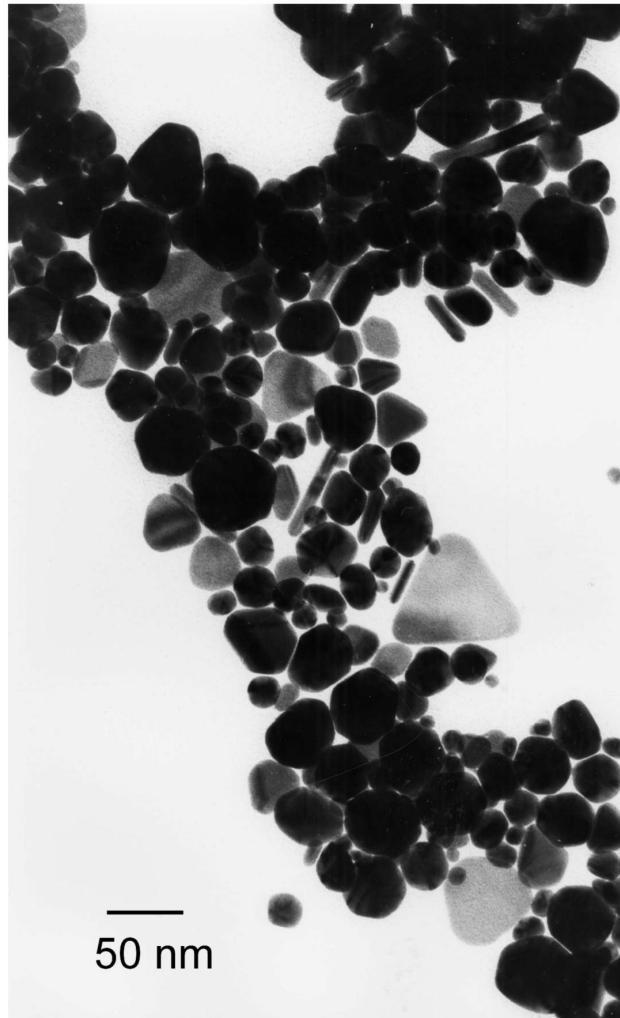
Ultra-Simple 2D Self-Assembly

of

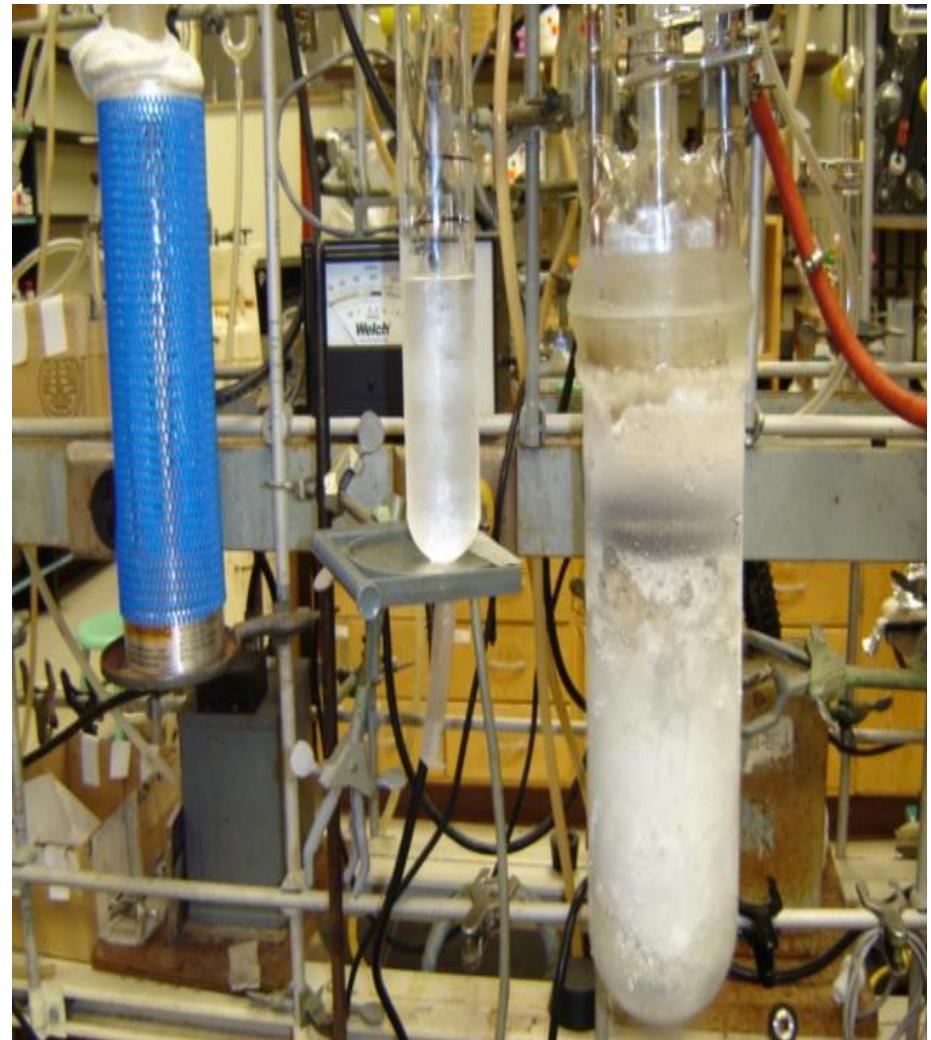
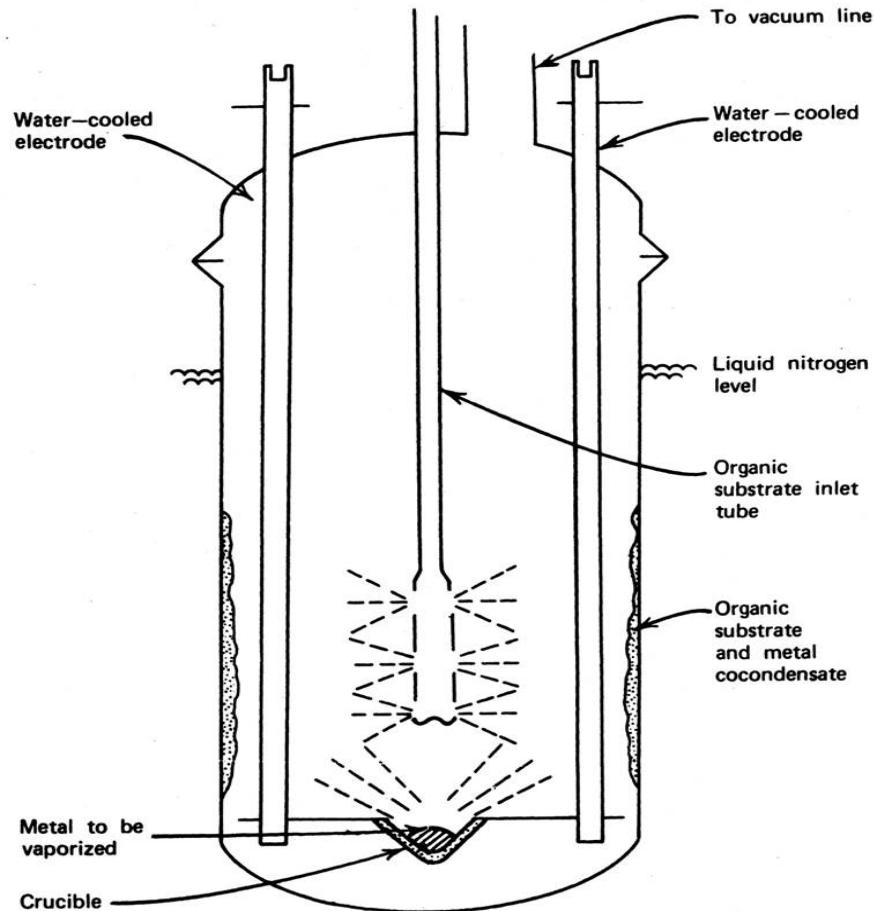
Monolayer-Protected  
Gold Nanoparticles

# TEM OF AS-PREPARED GOLD COLLOIDS BY THE INVERSE MICELLE METHOD

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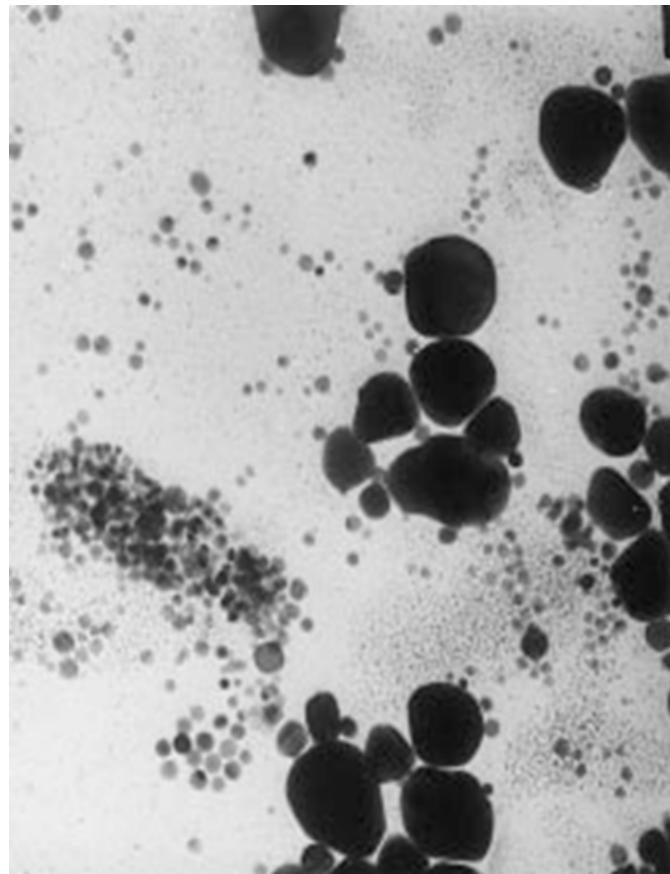
# Solvated Metal Atom Dispersion Reactor



*Synthetic Method Developed by Dr. Kenneth J. Klabunde, Kansas State University .*



# Gold particles made via the SMAD process



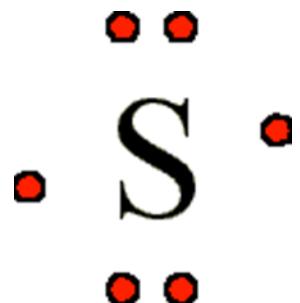
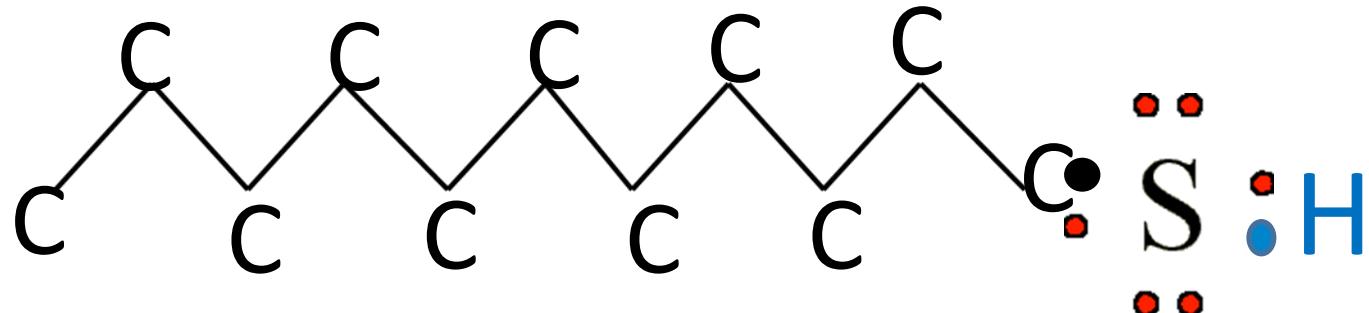
50 nm

# Some chemistry ... Thiols

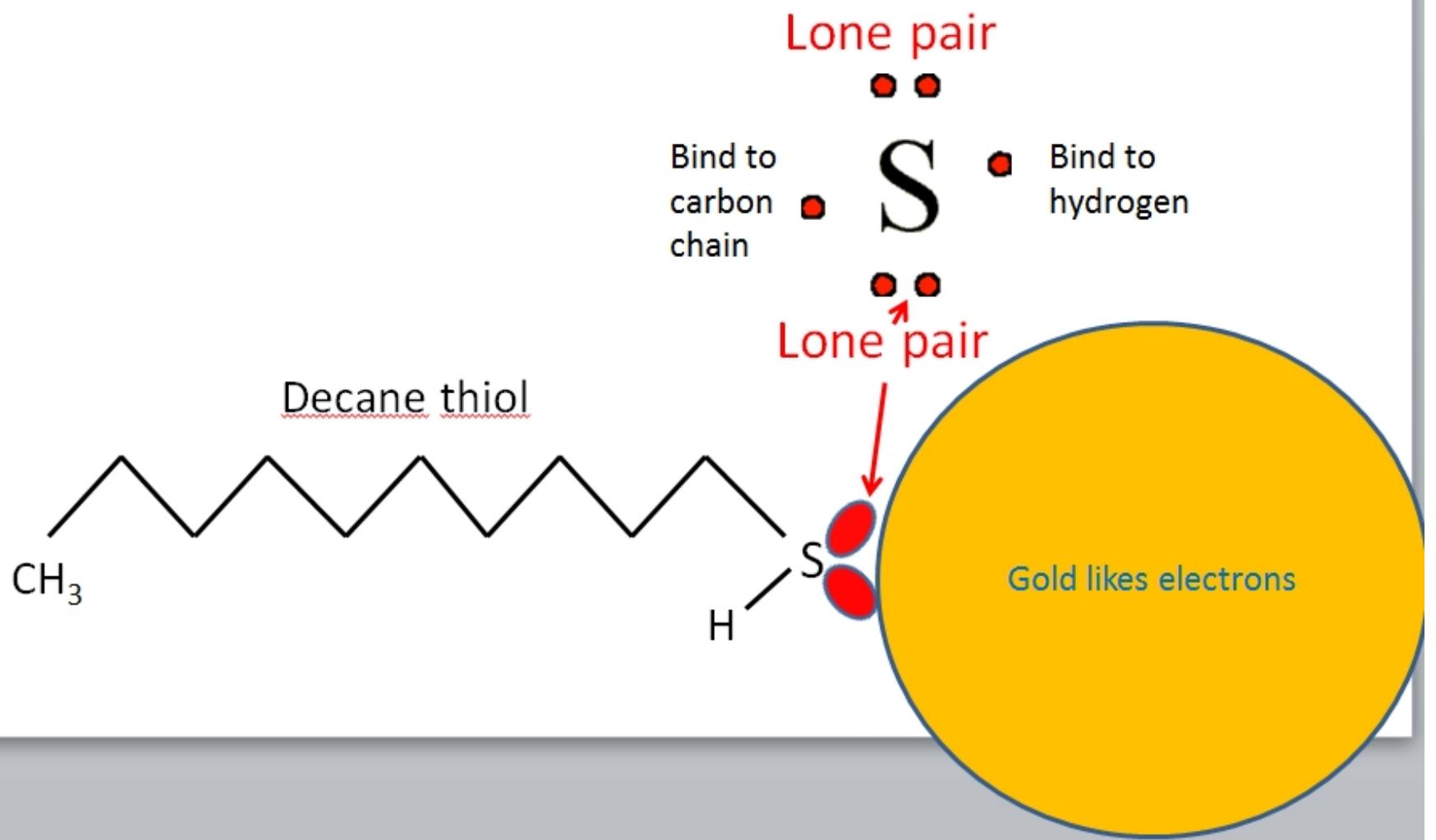


1 H															2 He		
3 Li	4 Be																
11 Na	12 Mg																
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

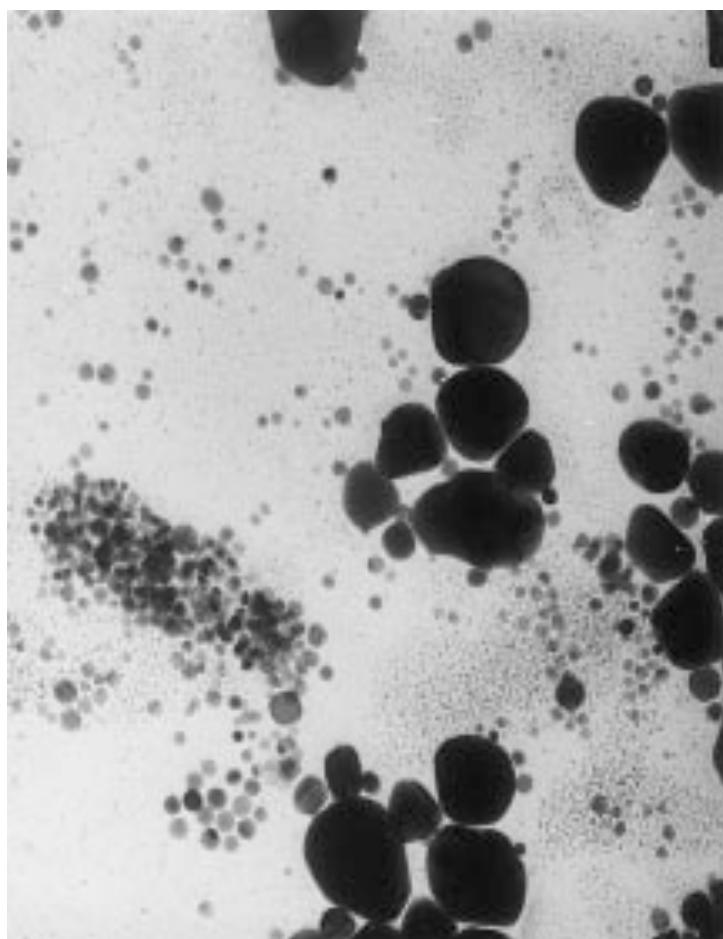


# Ligation

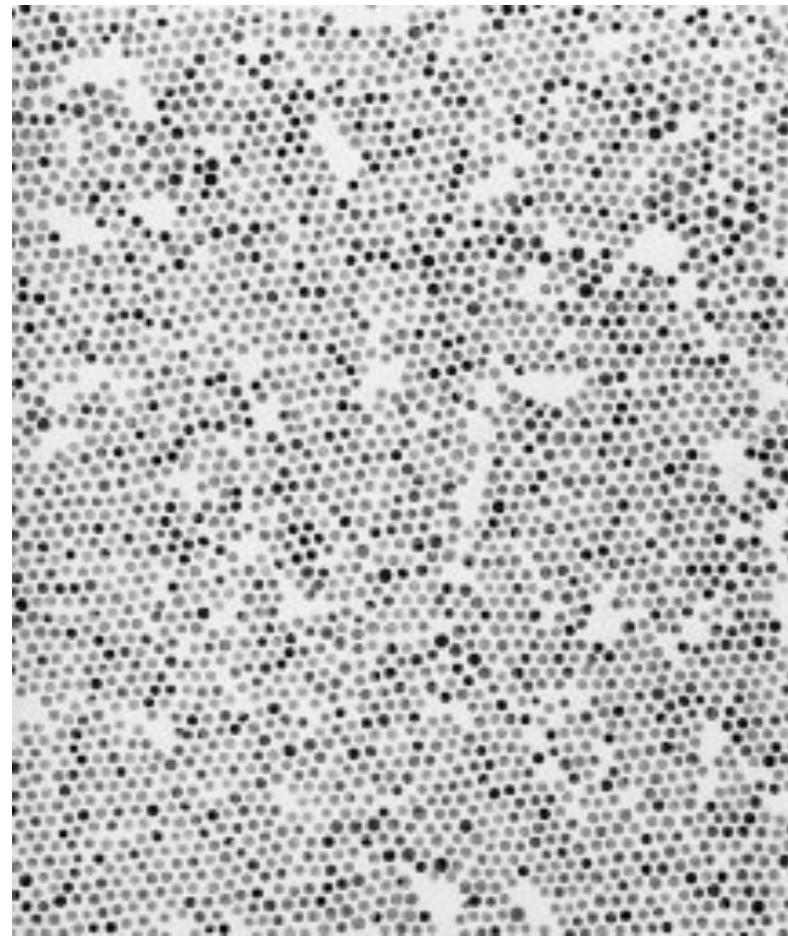


# Digestive Ripening:

Transformation of a polydisperse colloid into a nearly monodisperse colloid by cooking under reflux with excess ligand.

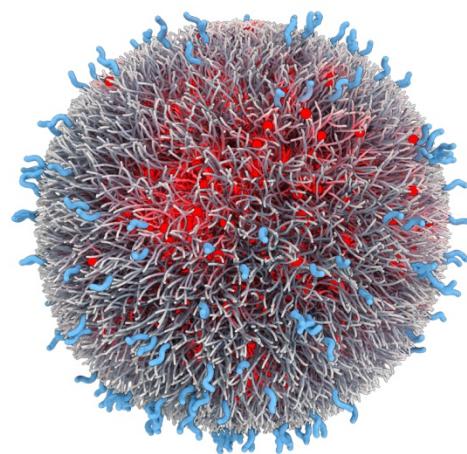
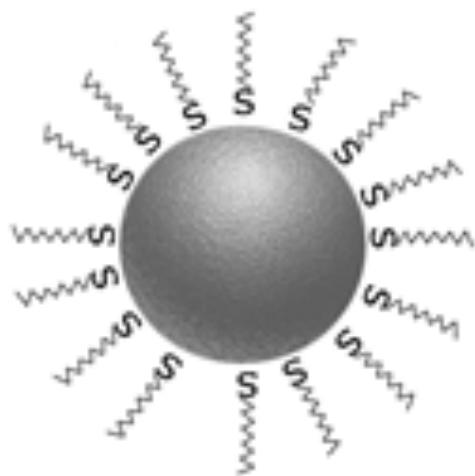


Before



After

# Ligated nanoparticle



# Ligands for Digestive Ripening

Alkane thiols      e.g.  $(C_{12}H_{25})SH$  or  $C_8$  through  $C_{16}$

amines       $RNH_2$

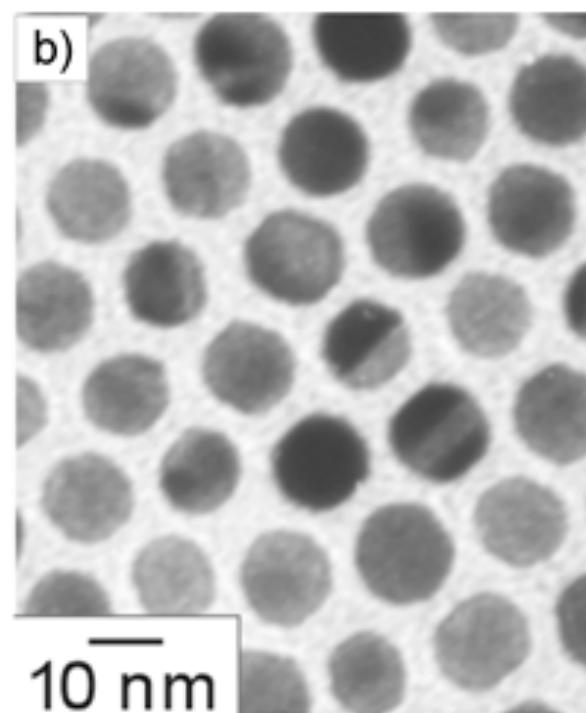
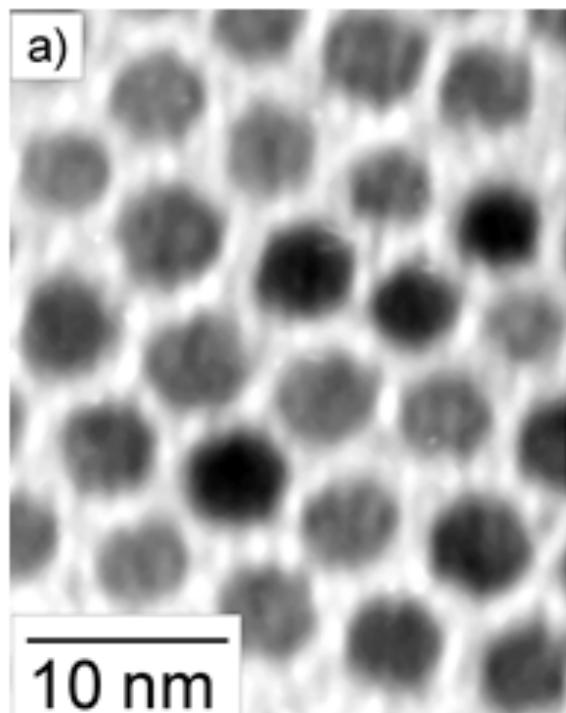
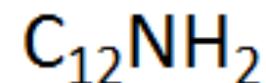
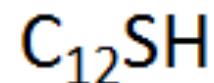
phosphines      e.g. Tri-Octylphosphene

acids       $RCOOH$

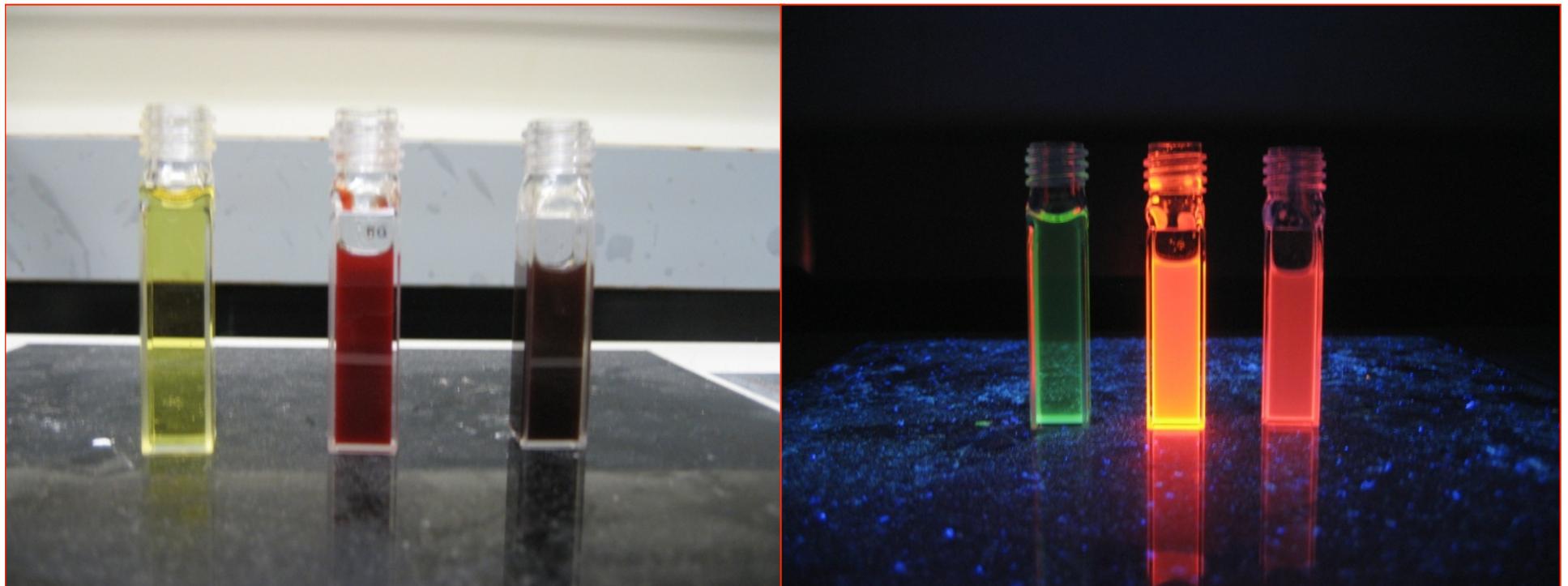
# Materials that have been Digestively Ripened

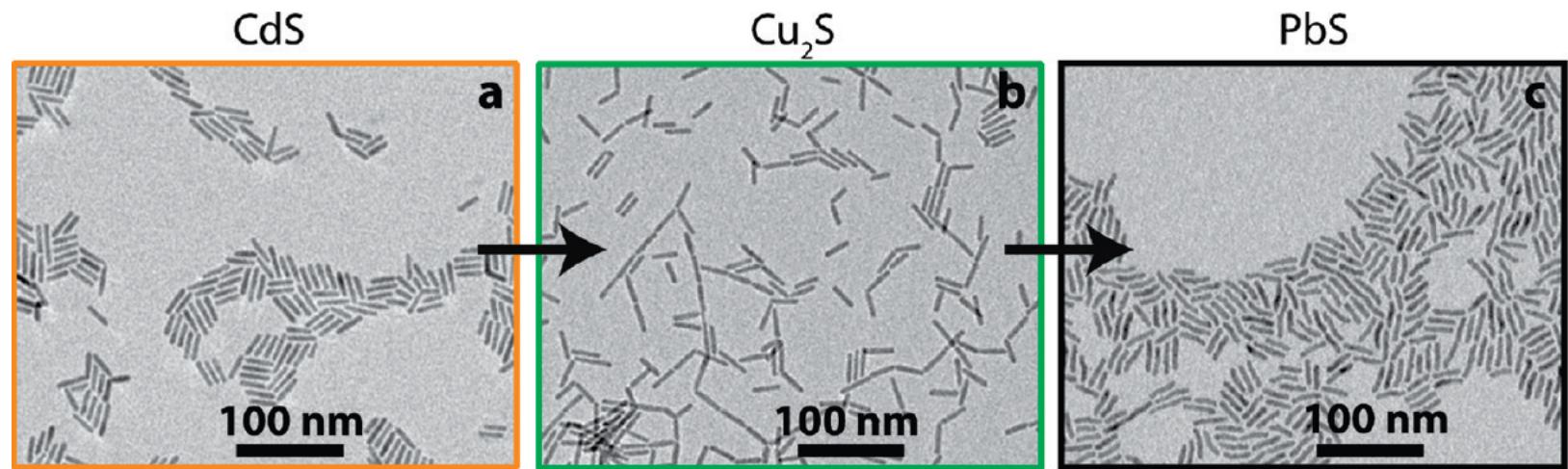
Gold, silver, copper, CdS, CdSe, CdTe, Pd, In,  
 $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$

# Different ligands --- different sizes



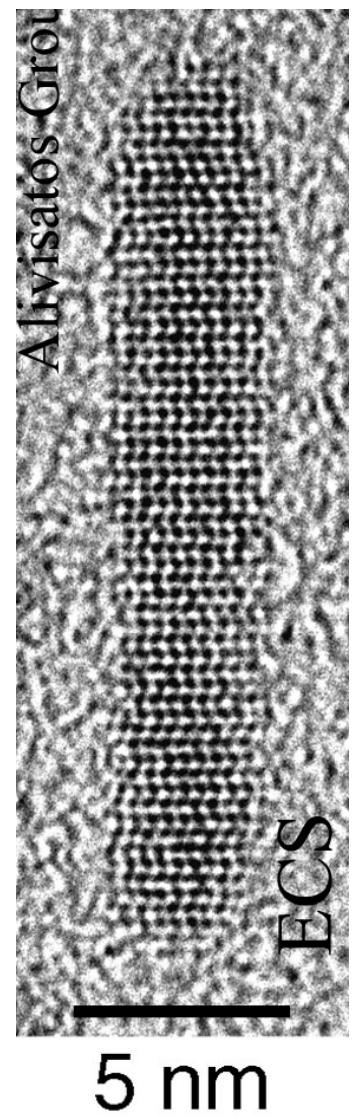
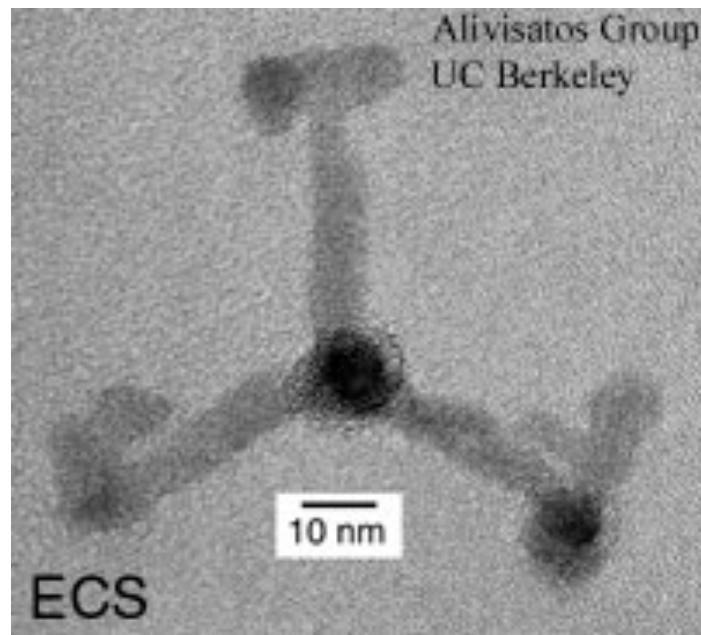
CdTe nanoparticles  
Different digestive ripening times  
lead to different sizes

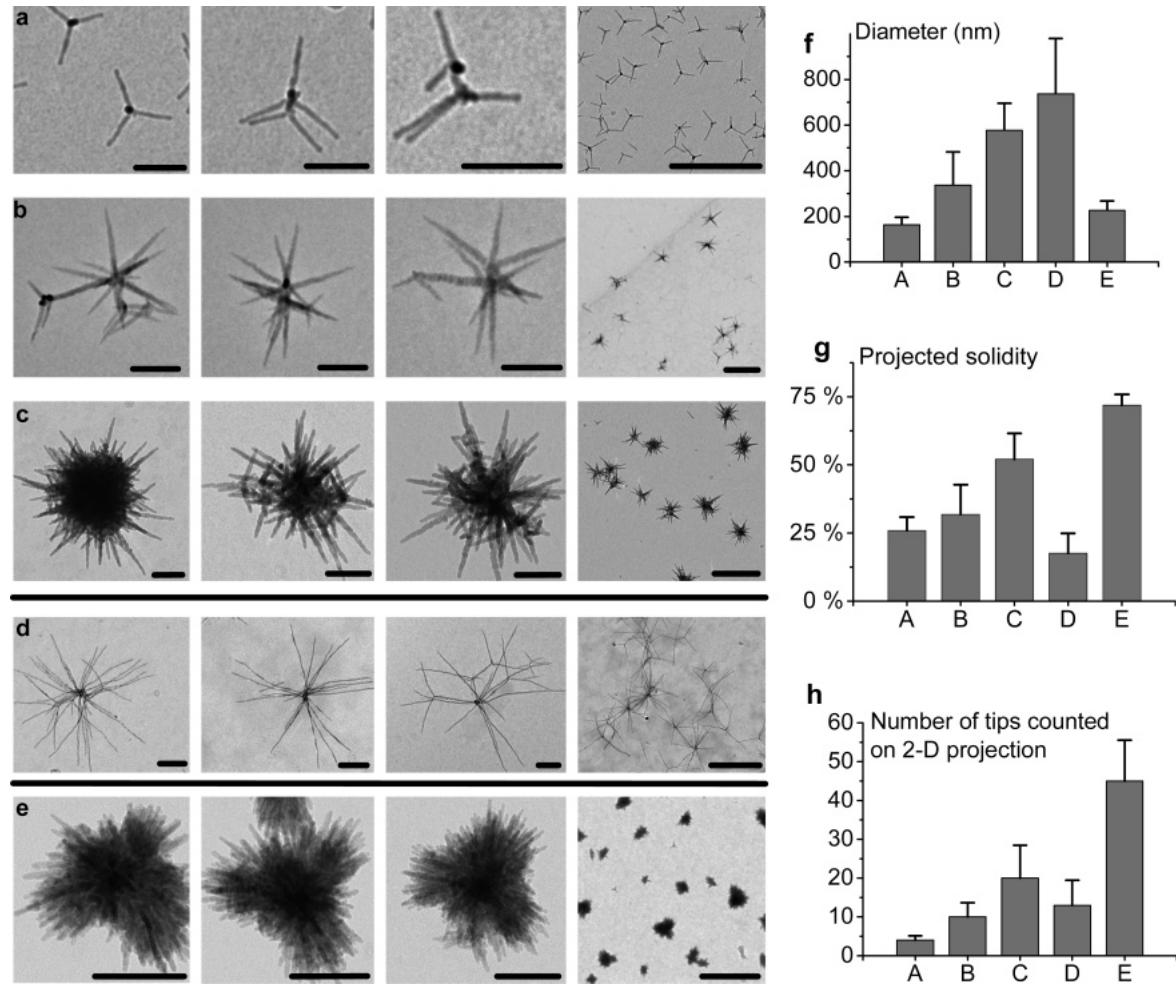




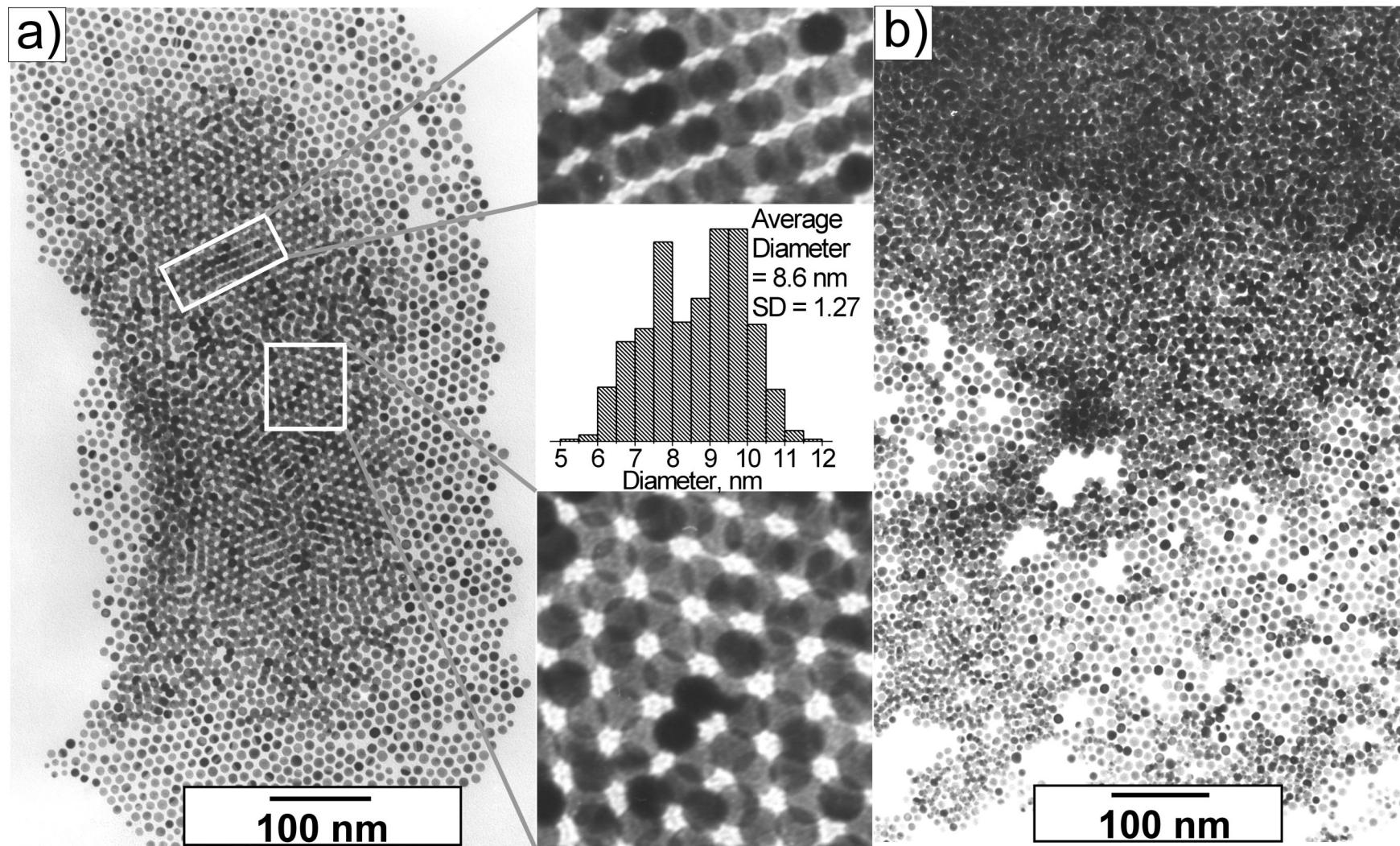
Luther et al. JACS 2009

# Tetrapod of CdSe



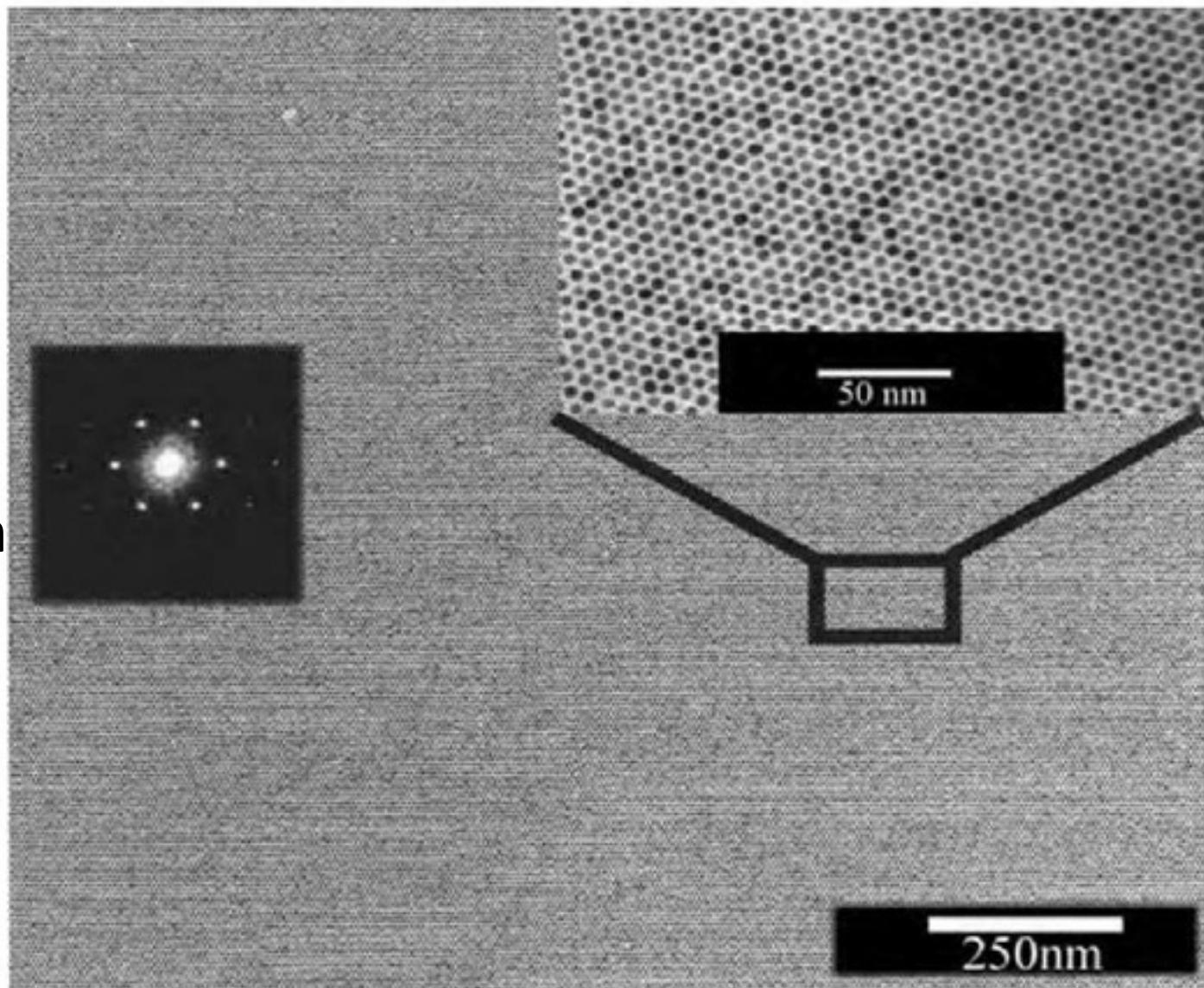


# Inverse Micelle Au/C<sub>12</sub>NH<sub>2</sub>



# Two-Dimensional Superlattice!

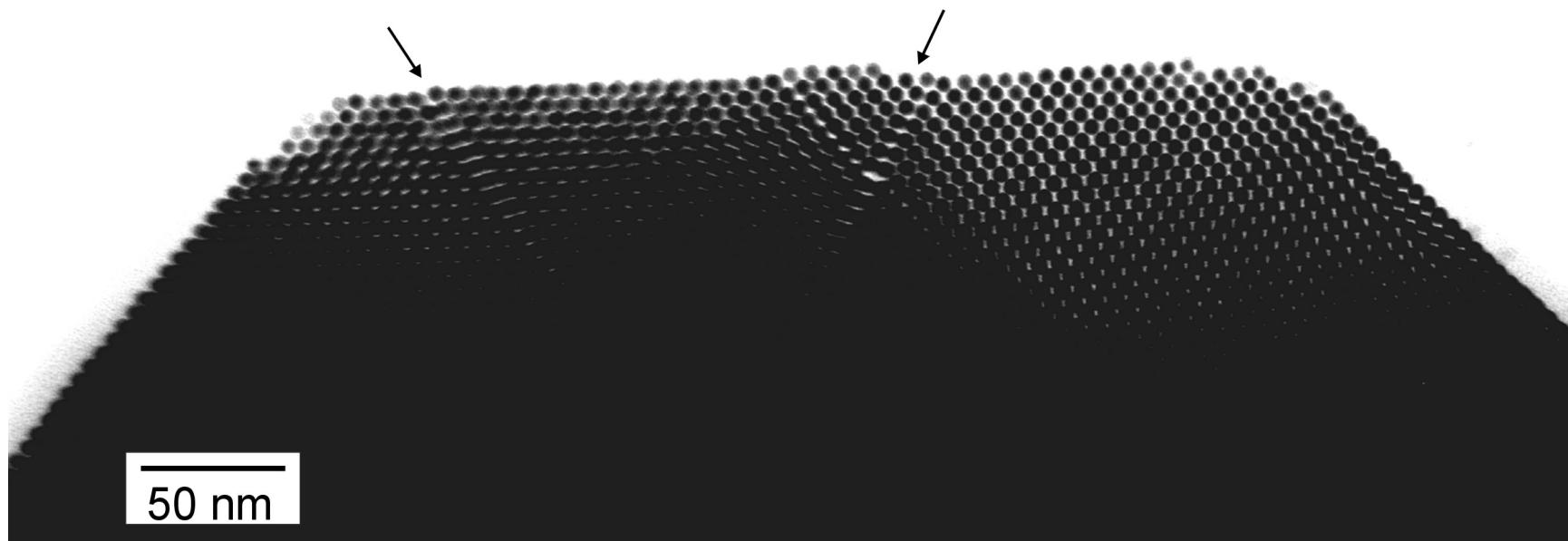
Electron  
diffraction



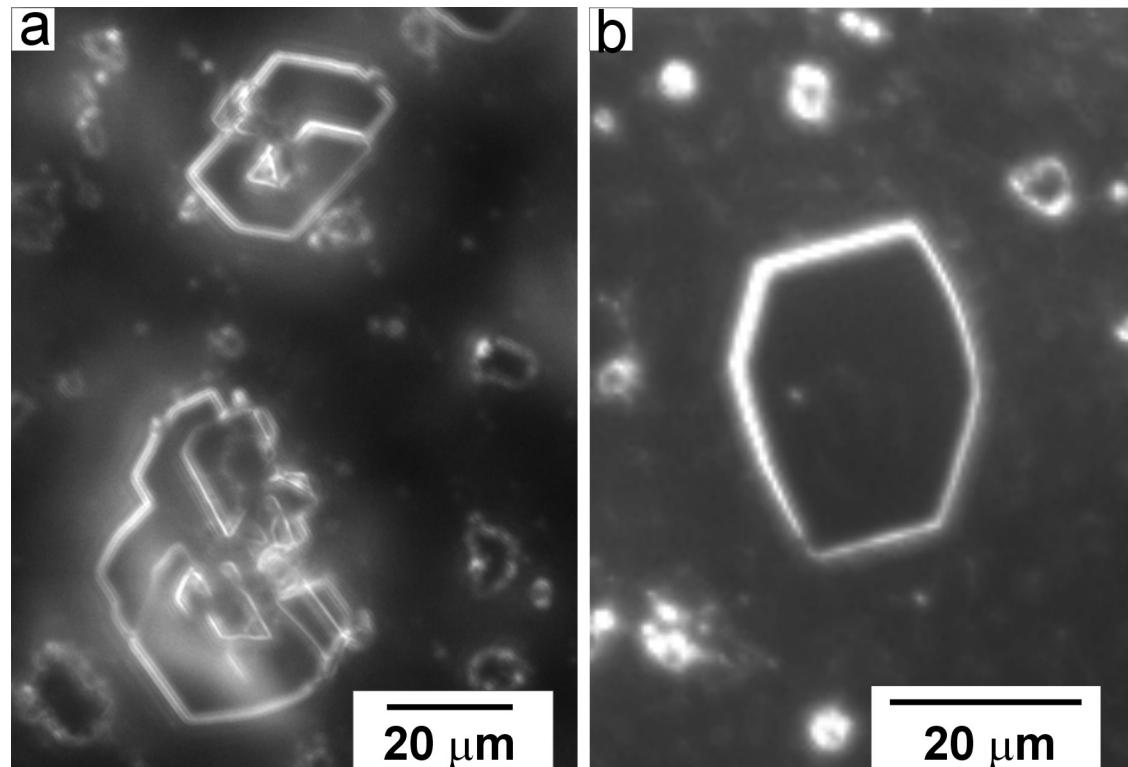
JPC B105, 3353-3357 (2001)

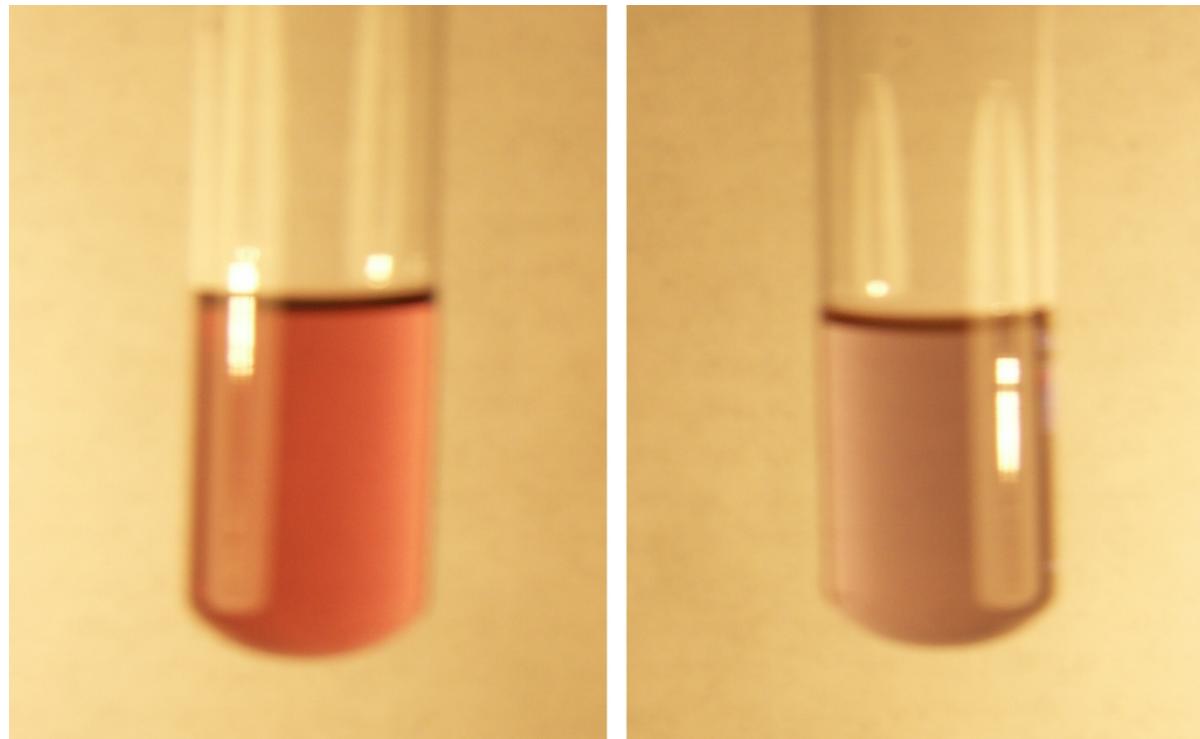
# 3d Superlattice of Au/C<sub>12</sub>SH nanoparticles

[110]<sub>SL</sub> projection



# 3d Superlattice Crystals





75 °C

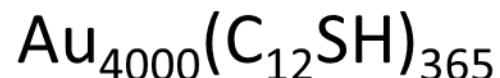
24 °C

↔ Reversible →

The particles all have about the same size,  
their suspensions act like solutions,  
they form crystalline superlattices  
so can we view them as ...

## Stoichiometric Particle Compounds?

A ligated 5.0 nm Au nanoparticle can be represented by



with ~10% variation on the numbers.

# A three-dimensional Periodic Table with particle size as the third dimension

1	H																									2	He
3		4	Be																								
11		12	Mg																								
19	20	21	22	23	24	25	26	27	28	29	29	30															
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn																
37	38	39	40	41	42	43	44	45	46	47	48																
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I											
55	56			72	73	74	75	76	77	78	79	80															
Cs	Ba			Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At										
87	88			104	105	106	107	108	109	110	111	112	Cn	Uut	Fl	Uup	Lv	Uus	Uuo								
				57	58	59	60	61	62	63	64	65	66	67	68	69	70	71									
				La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu									
				89	90	91	92	93	94	95	96	97	98	99	100	101	102	103									
				Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr									

Size



Thank You

# Particle group



