Nanoscience
A New World Coming

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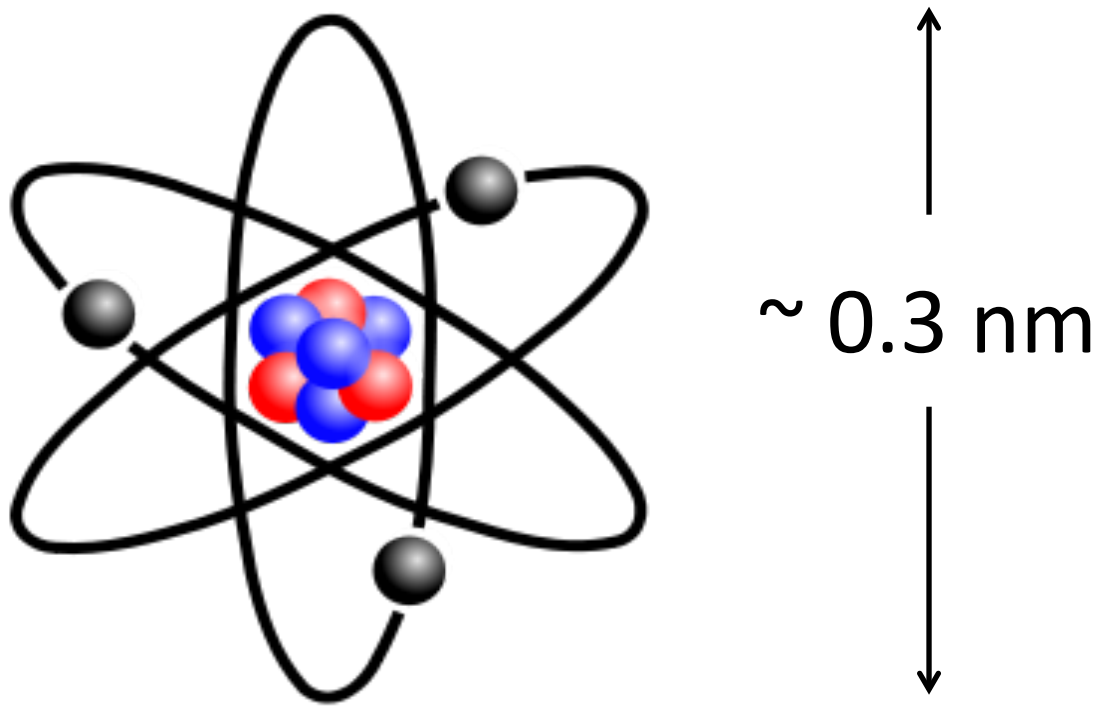
Kansas State University

What if…

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

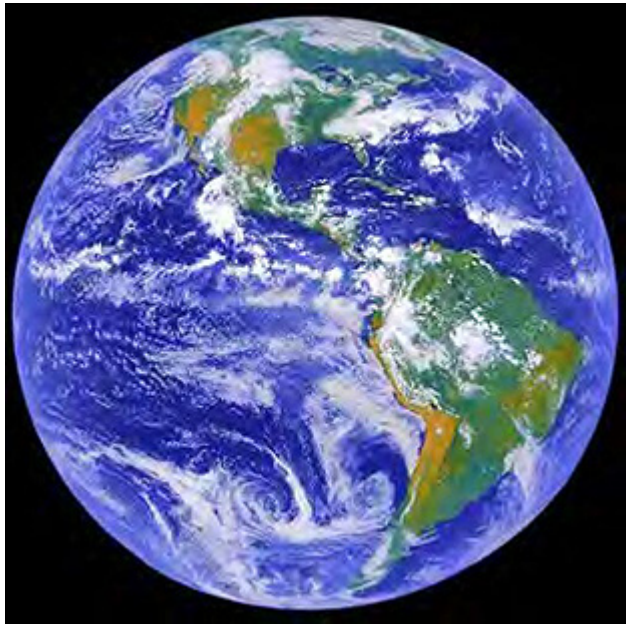
An atom…



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

$$E = h\nu$$

ν is the frequency

h is Planck's constant

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

But why is energy quantized?

Because:

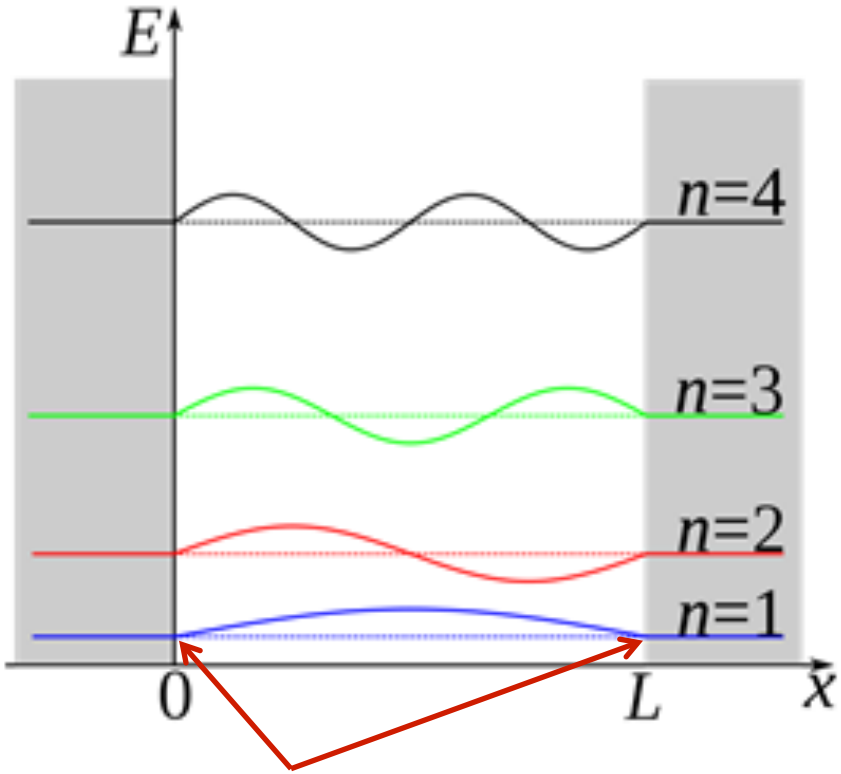
1. everything has a wave nature; de Broglie $\lambda = h/p$
2. confined wave resonate at only specific frequencies

The Particle in a Box

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

The wave/particle duality of Nature

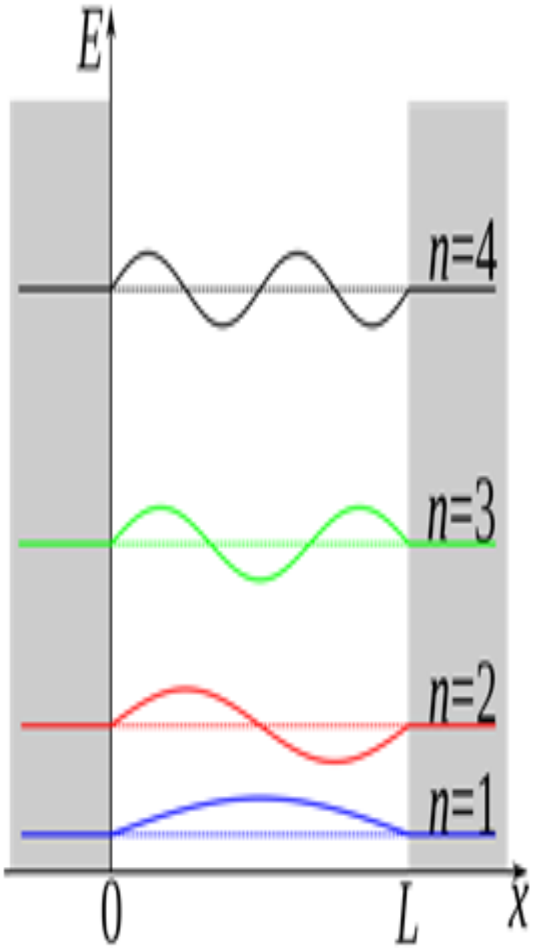
When a particle like an electron is confined to a "box", e.g. an atom or a nanoparticle, it's waves exist in only certain <u>resonances</u> called "eigenstates", as drawn to the right.



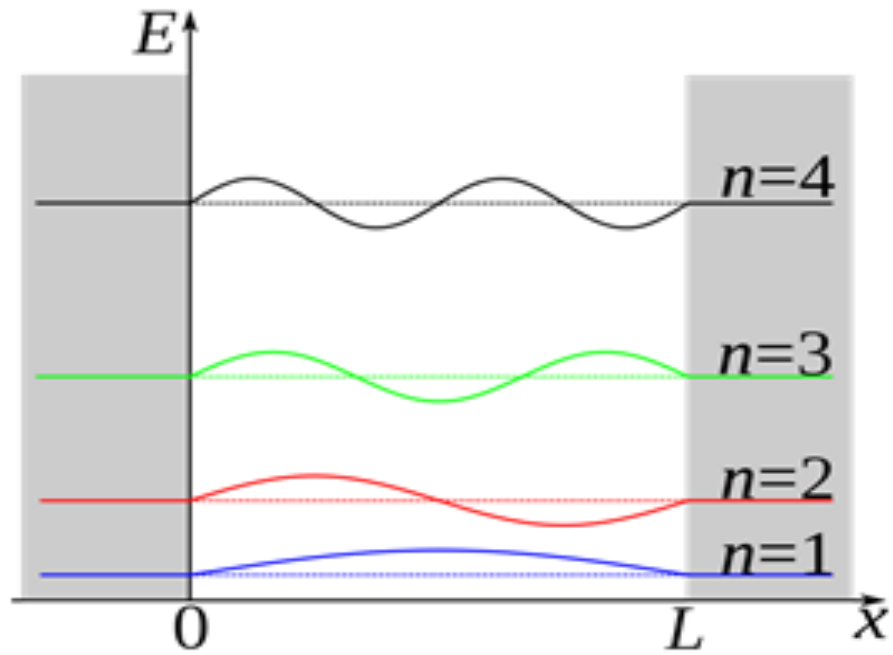
Boundary conditions, wave ψ = 0 at boundaries.

Particles in Different Boxes

Small boxes,
higher frequencies,
bigger energies



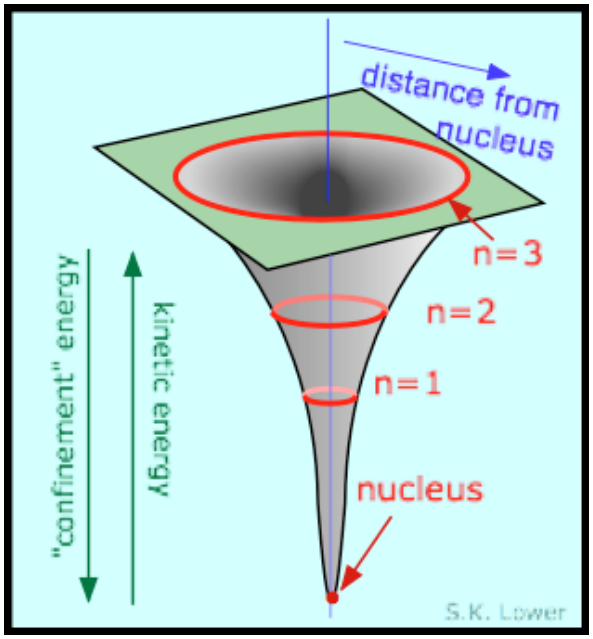
Big boxes,
lower frequencies,
smaller energies



The atomic “box”. Size ~ 0.3 nm.

Confinement of the electron

by the attraction of the nucleus



Energy level spacings of 1 to 10 eV.

<u>Quantum mechanics rules!</u>

Note: green light photon carries 2.5 eV

A penny, size ~ 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.

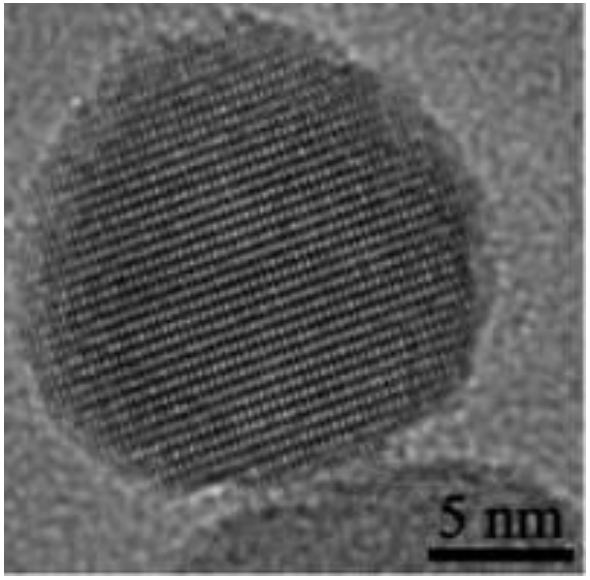
essentially a continuum of energy…

<u>no quantum effects</u>.

A “sea” of electrons!

A nanoparticle box, ~ 10 nm

Confinement of the electrons by the walls of the particle.

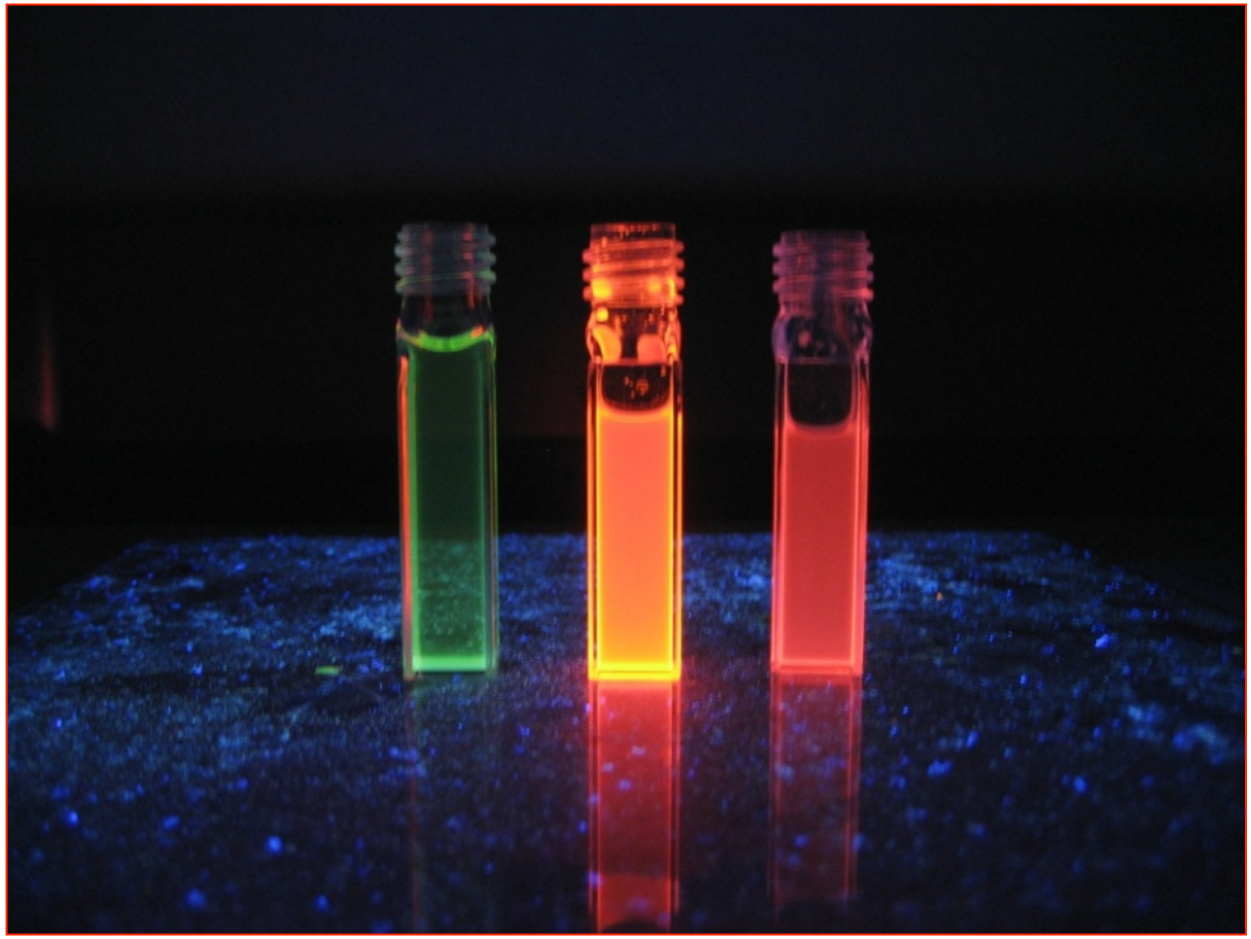


Energy level spacings 0.1 to 1 eV.

<u>Quantum mechanics still important.</u>

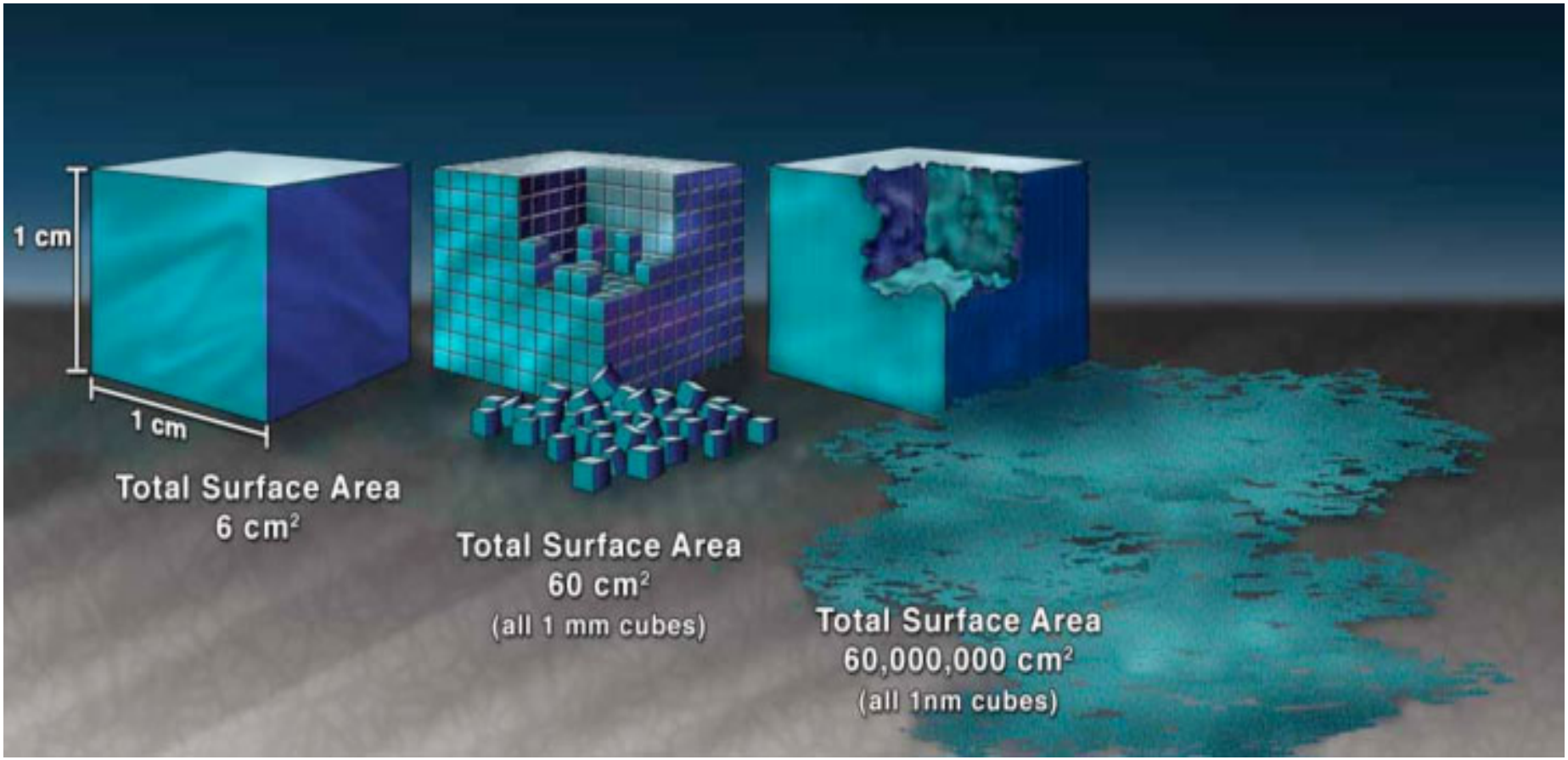
CdTe nanoparticles
Different sizes

UV light(fluorescence)



Small medium large

Nanostuff is surface stuff



Surface Fraction

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

Everyday things are bulk stuff.

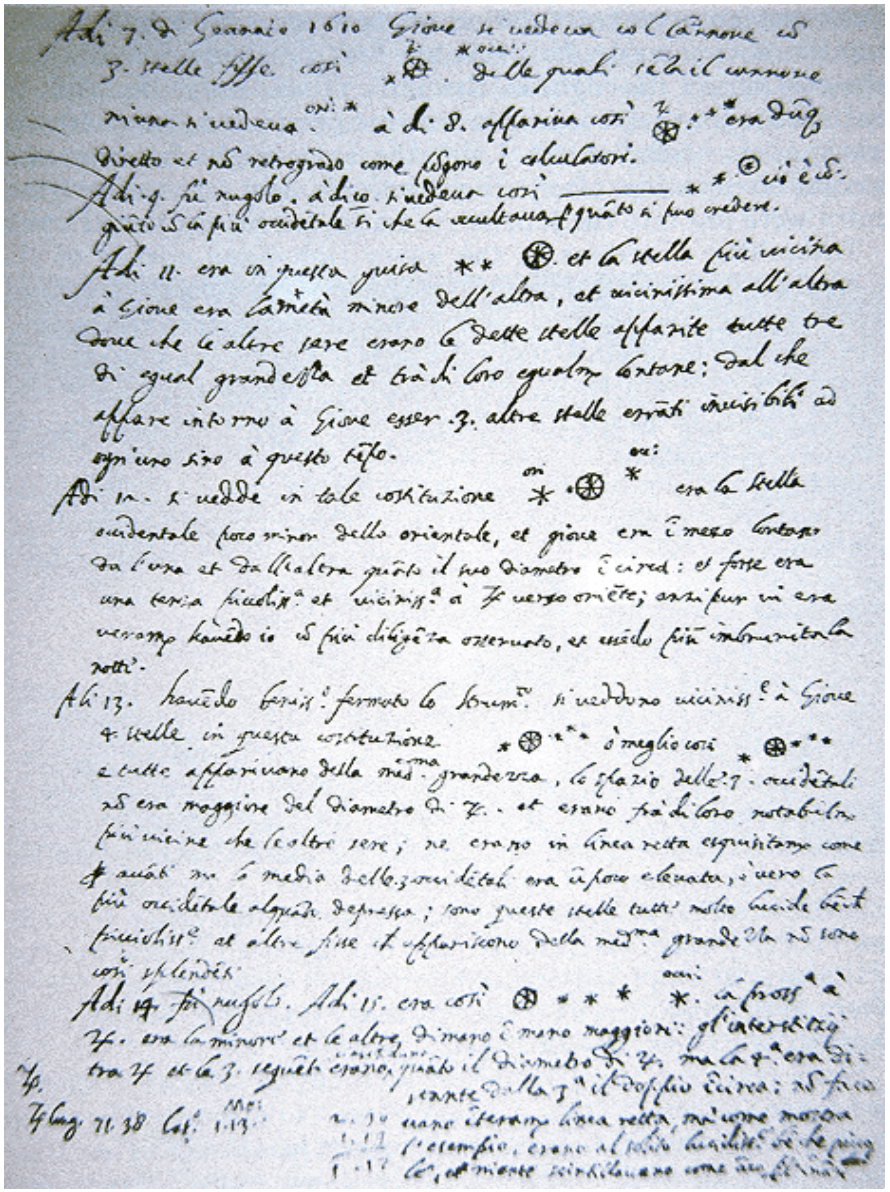
Most of the atoms are hidden beneath the surface.

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

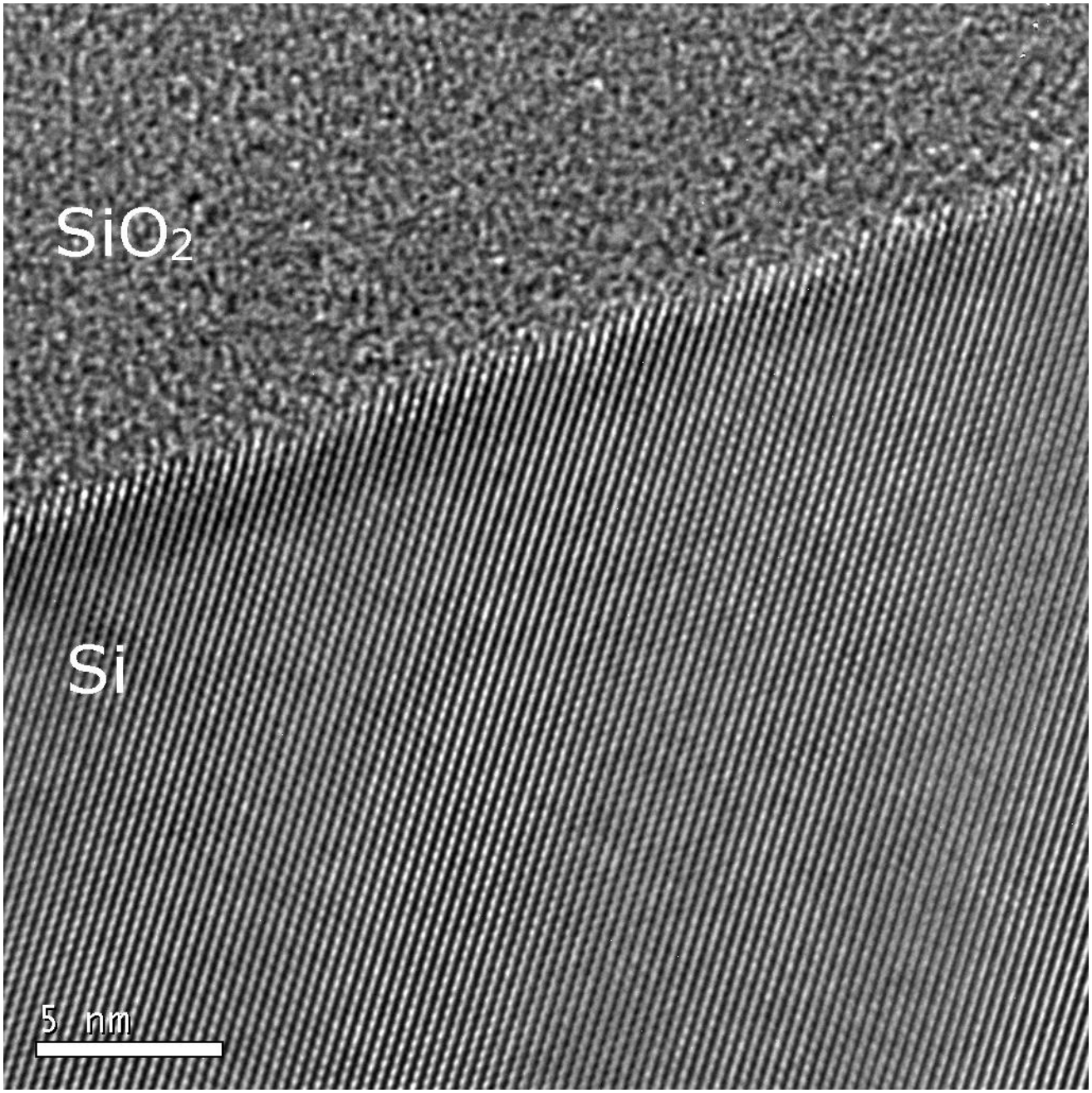


You gotta have the right equipment

Microscopy

The electron microscope

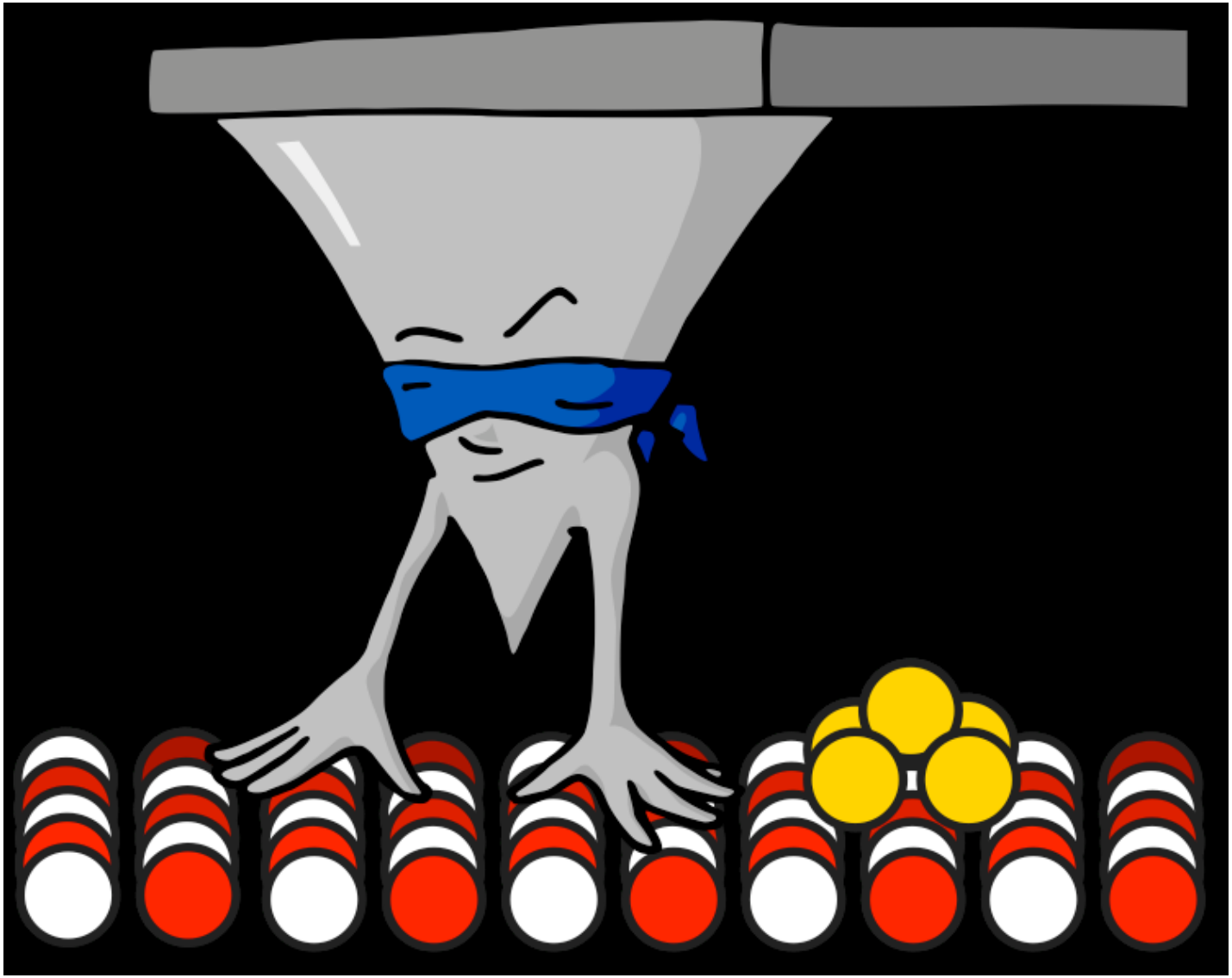
Ernst Ruska



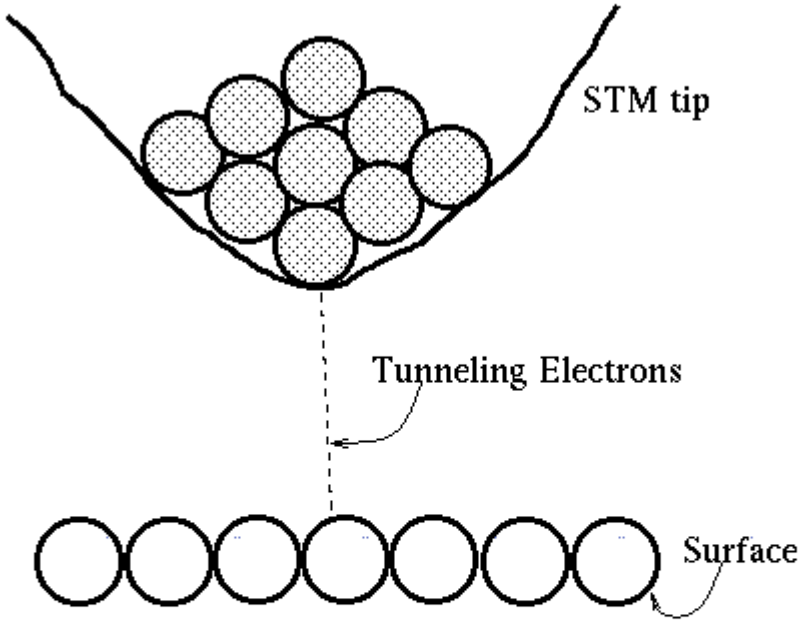
Duc The home page

Feeling is Seeing

Binnig and Rohrer and their scanning tunneling microscope
Nobel prize 1986



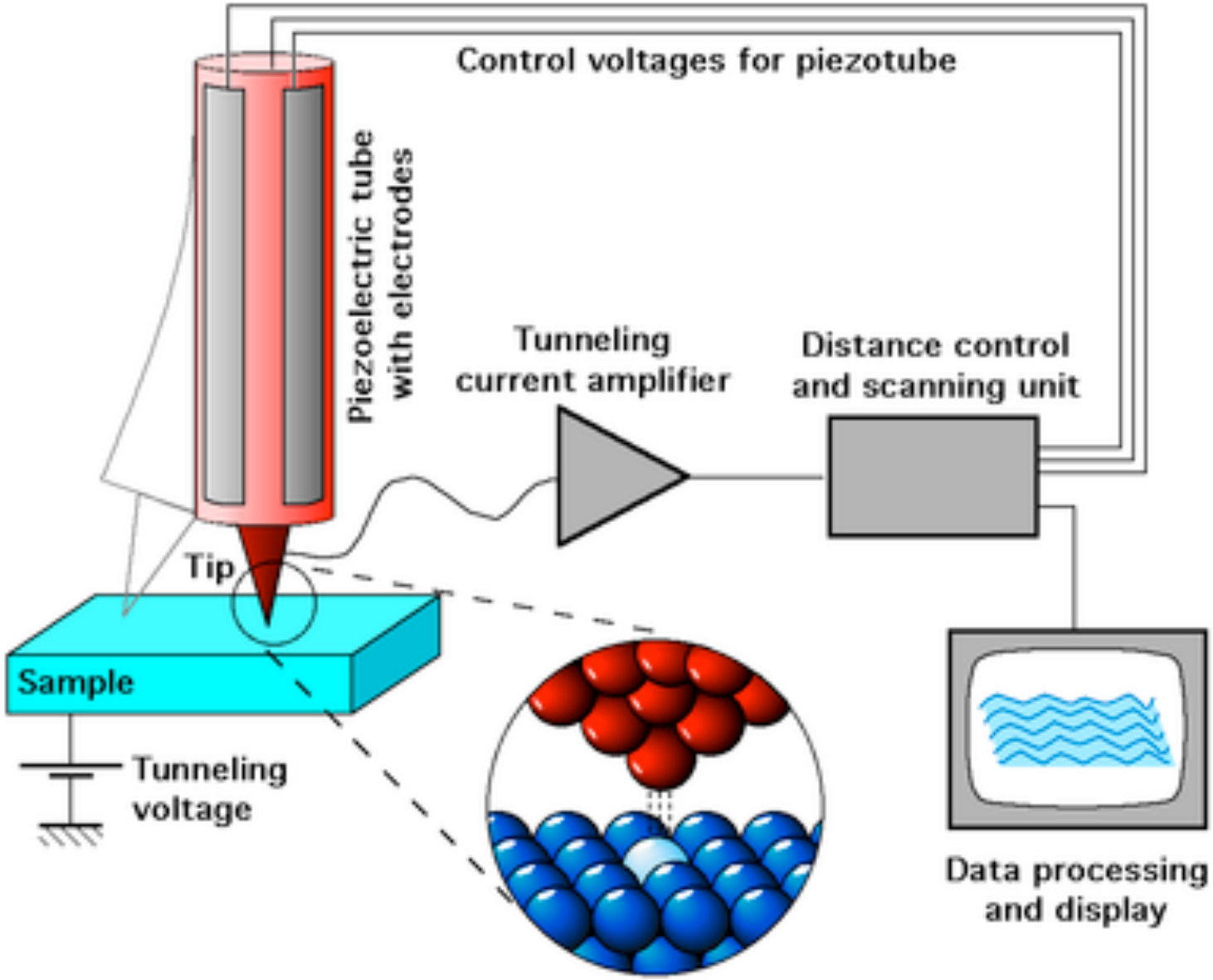
The Scanning Tunneling Microscope



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.

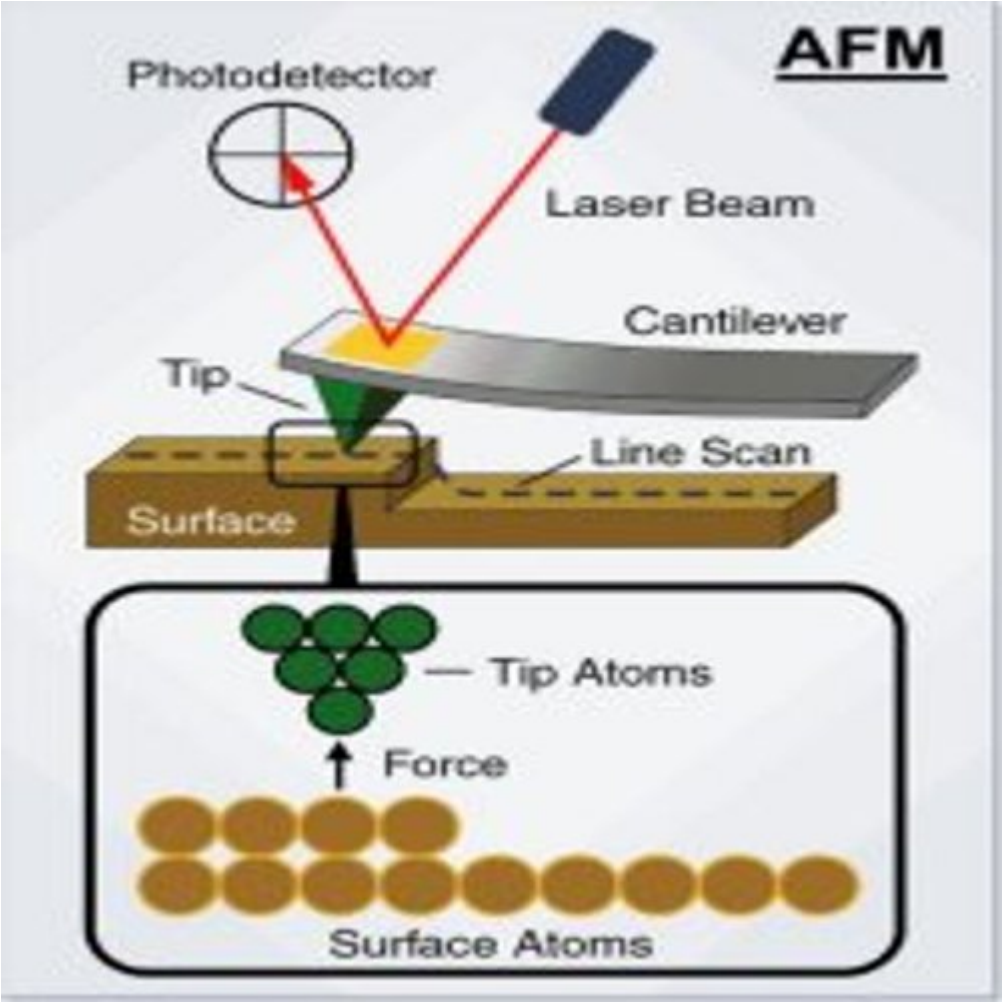
LASSP, Barbara Cooper

STM layout



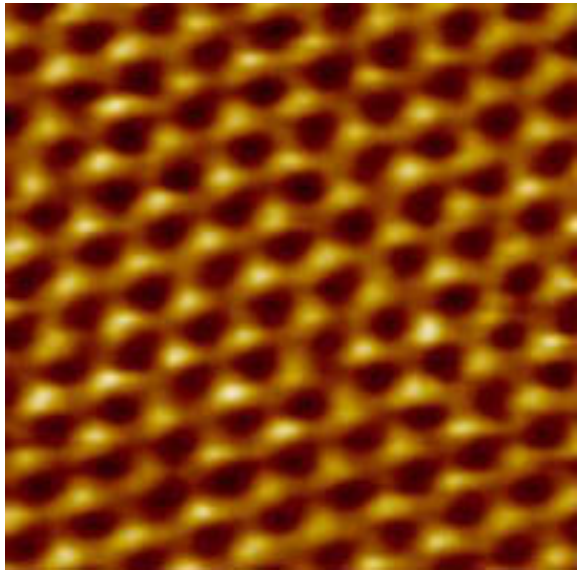
wikipedia

Atomic Force Microscope



Vrije Universiteit Brussel

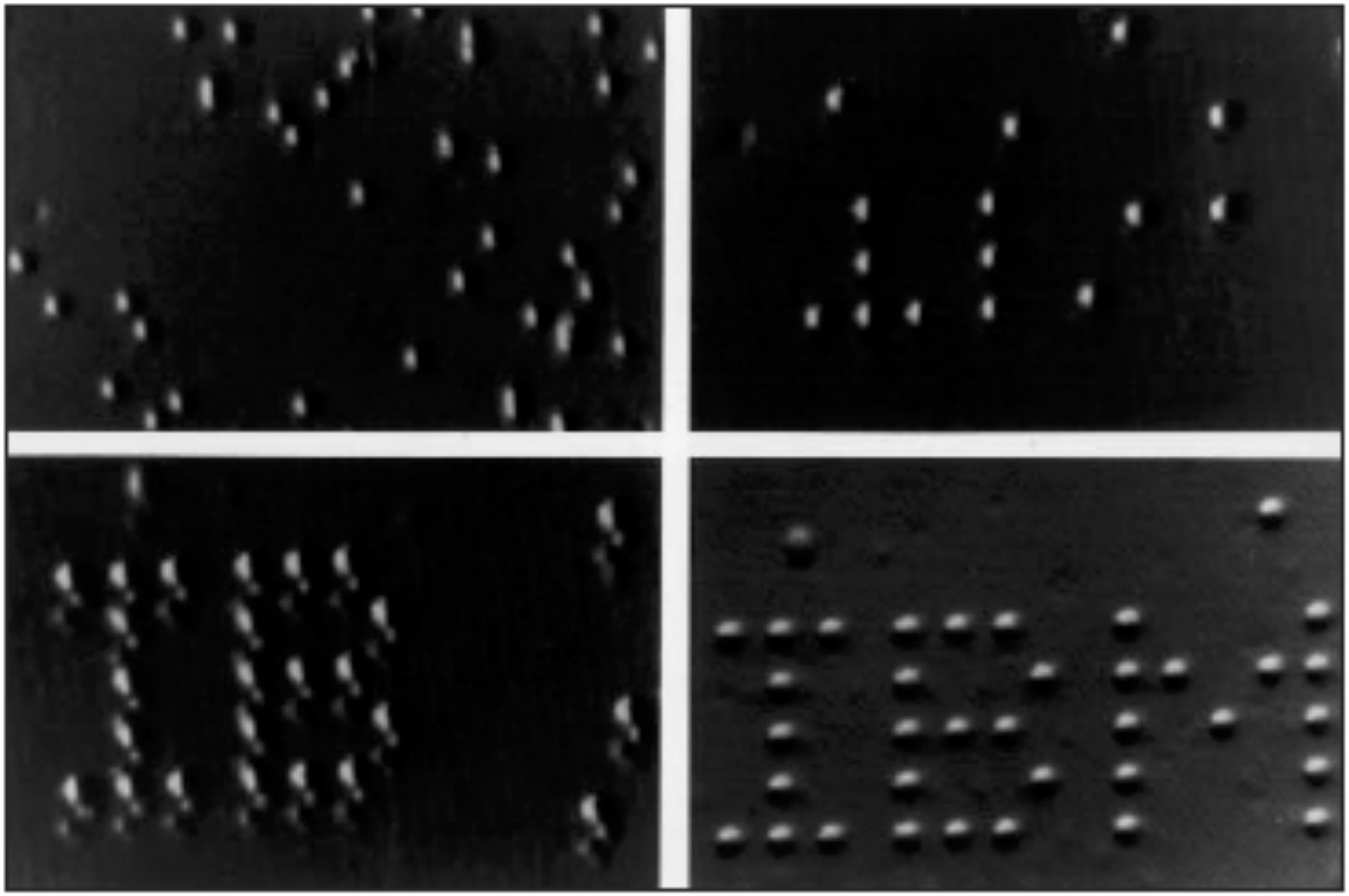
Graphite individual bumps are C atoms.
Overall size is 2 nm by 2 nm.



2 nm

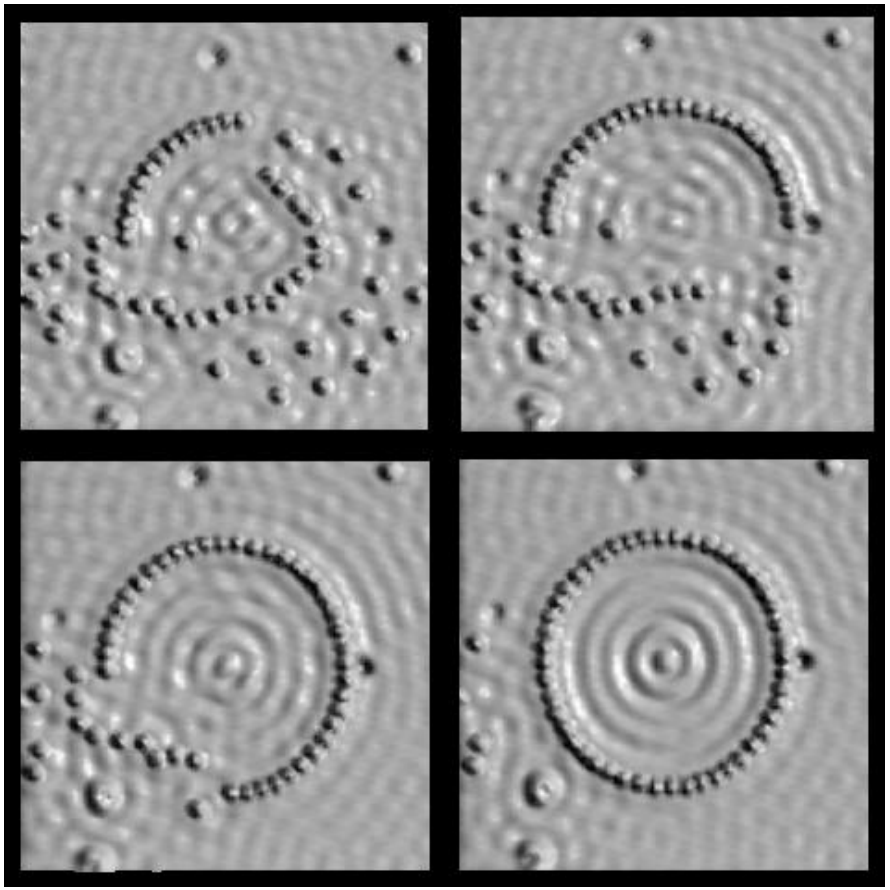
Image is courtesy of Nanosurf Ag

STM manipulation of argon atoms



Construction of a quantum corral

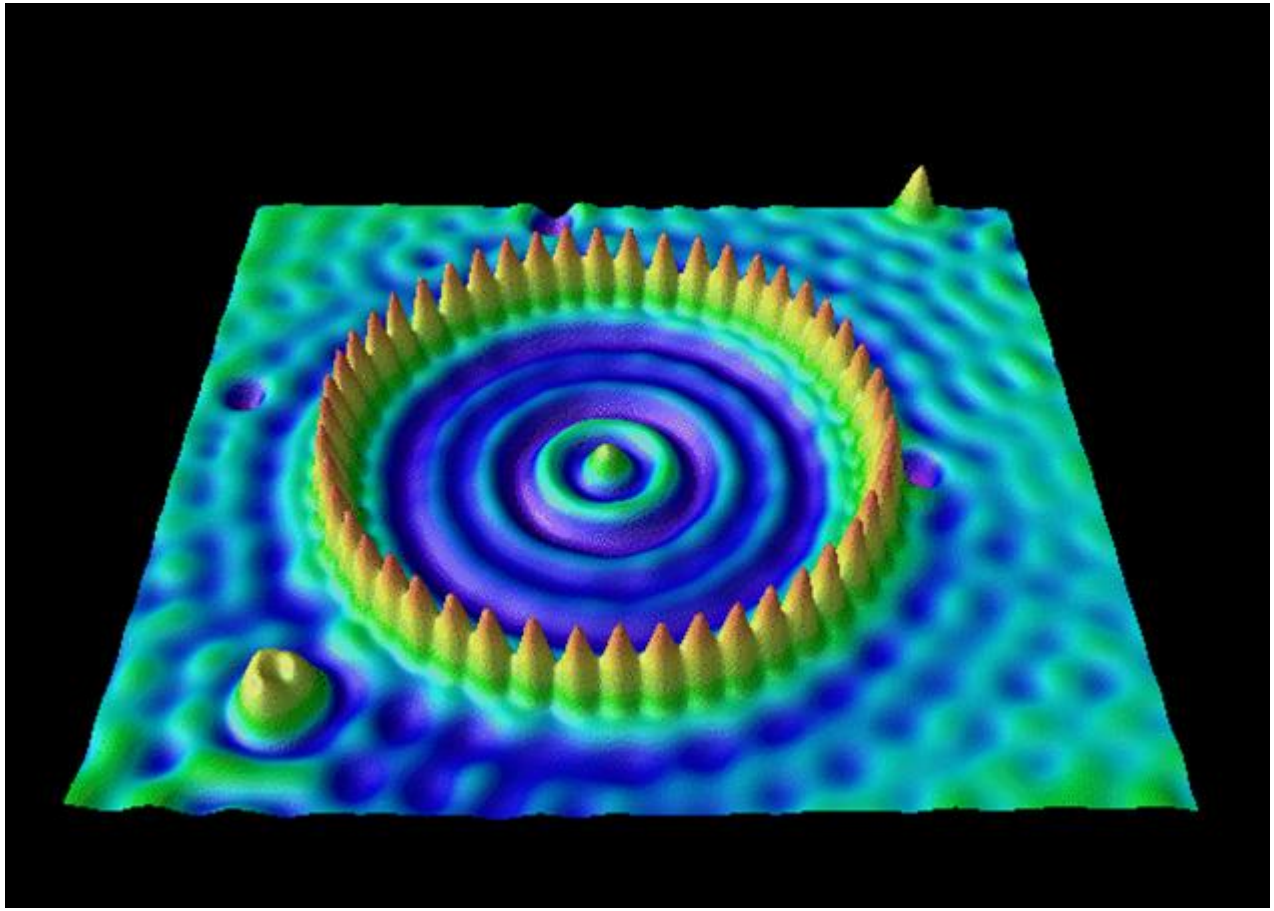
48 iron atoms on a copper surface being pushed around with an STM tip. The diameter of the corral is 7.13 nm



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.

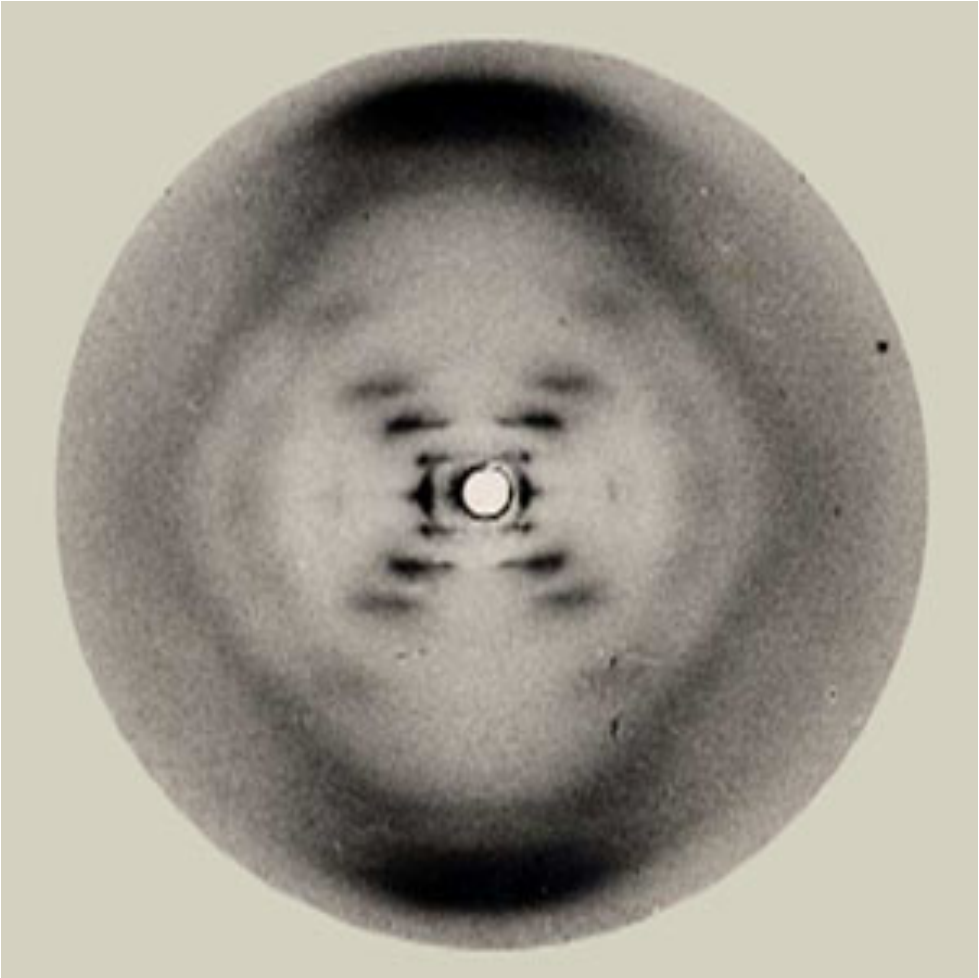
Crommie et al. Science 262, 218 (1993)

The Quantum Corral



Diffraction

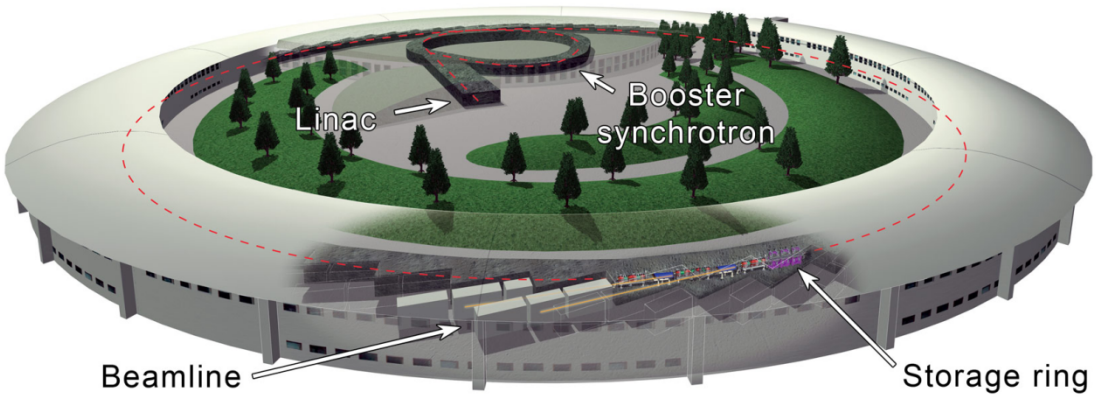
Example: Rosalind Franklin's DNA work



Advanced Photon Source (APS)
Argonne National Laboratory
Argonne, IL

Synchrotron Radiation

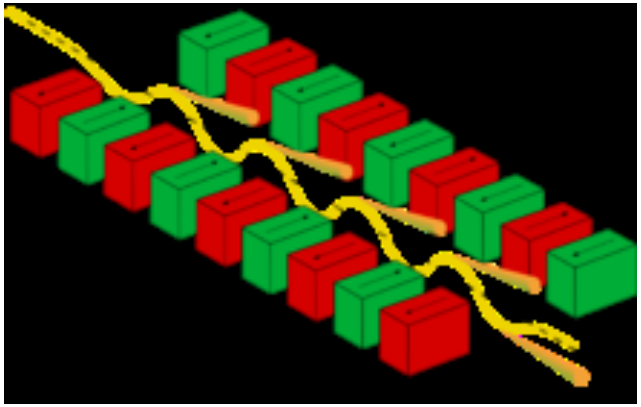
Accelerating charges radiate “light”.



Acceleration around
A curve.

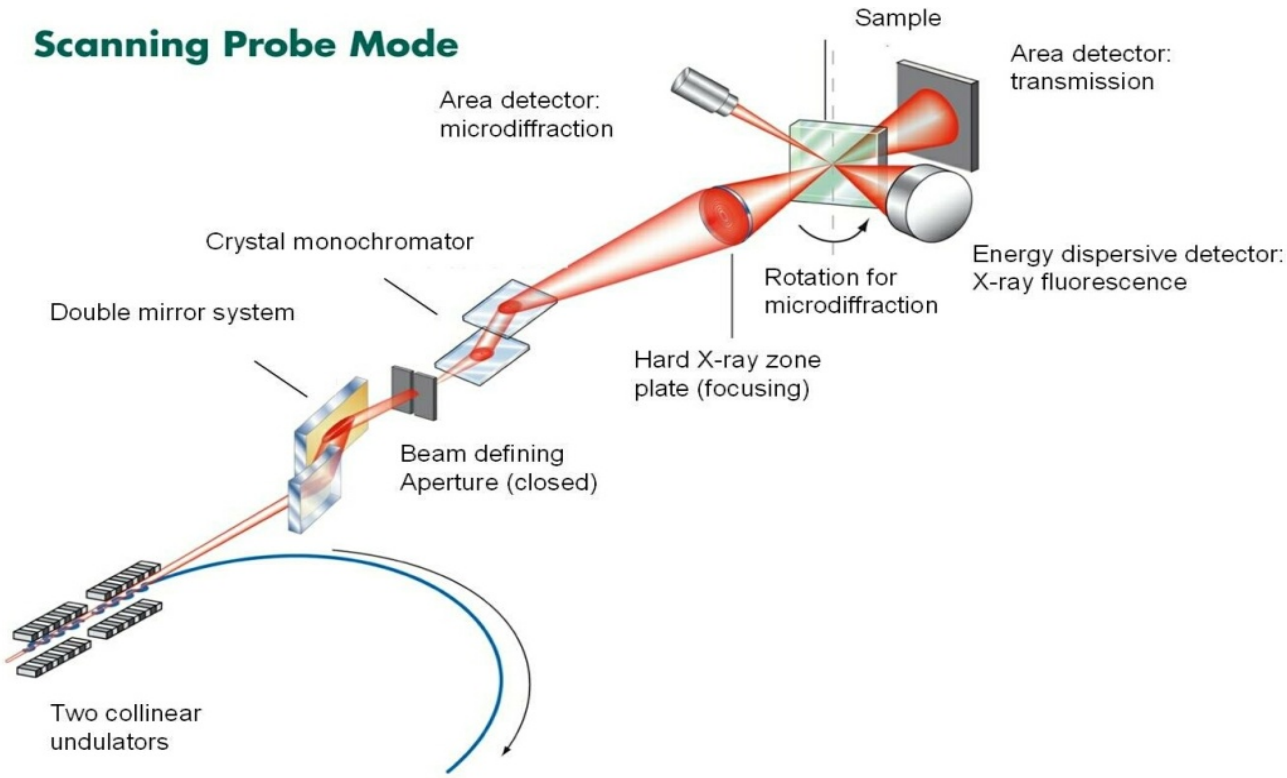
ESRF

Acceleration in
an undulator



Wikipedia

CNM Nanoprobe at the Advanced Photon Source



Nanoparticle Synthesis

The Chemistry

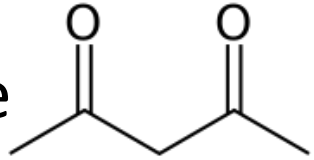
Some examples:

Borohydride reduction

$AuCl_3 + NaBH_4 \longrightarrow Au^0 + \ldots$

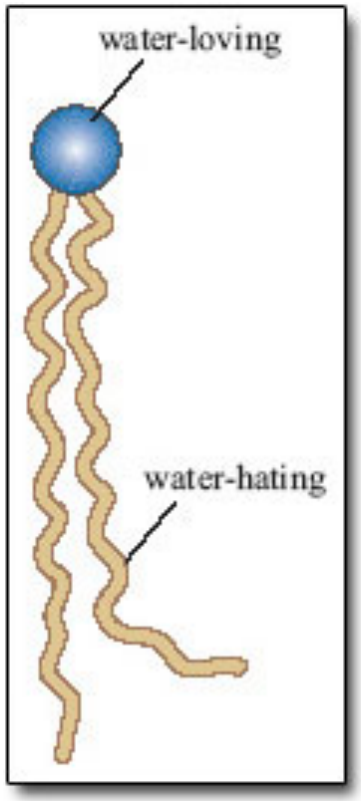
Organo chemistry

$Cd(CH_3)_2 + H_2S \longrightarrow CdS \ldots$

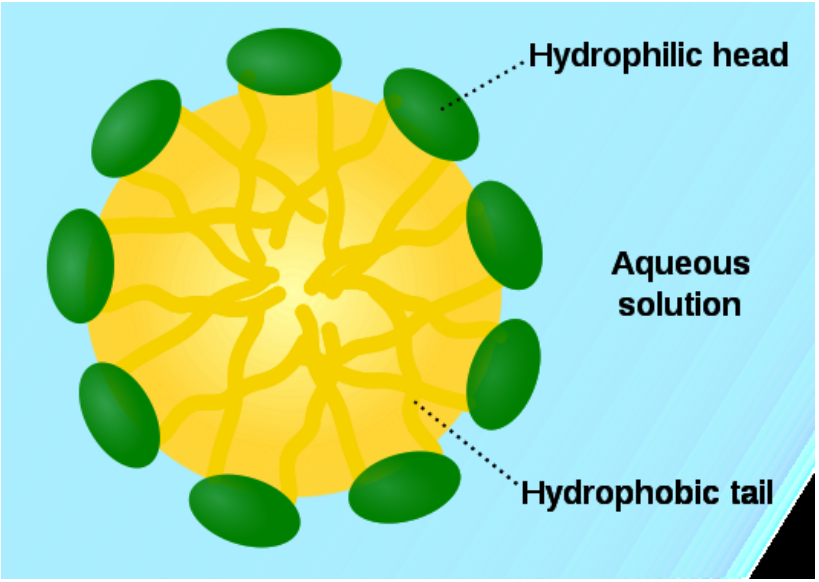
Fe  + Oleylamine $\longrightarrow Fe_3O_4$

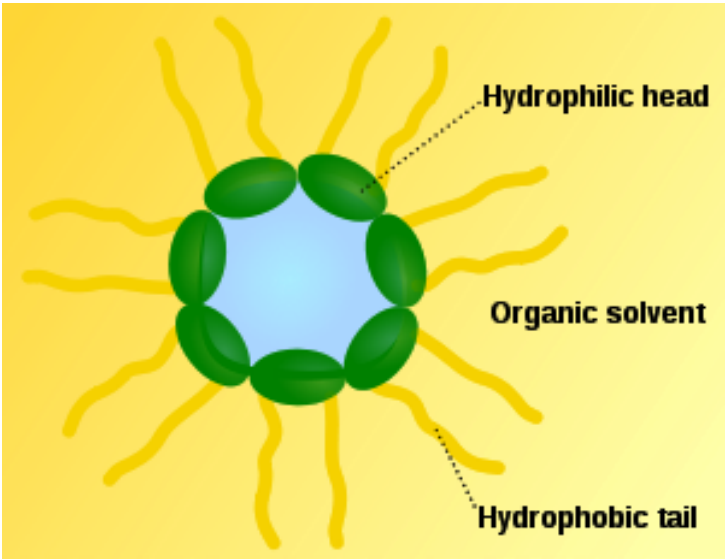
Surface active molecules
Surfactants

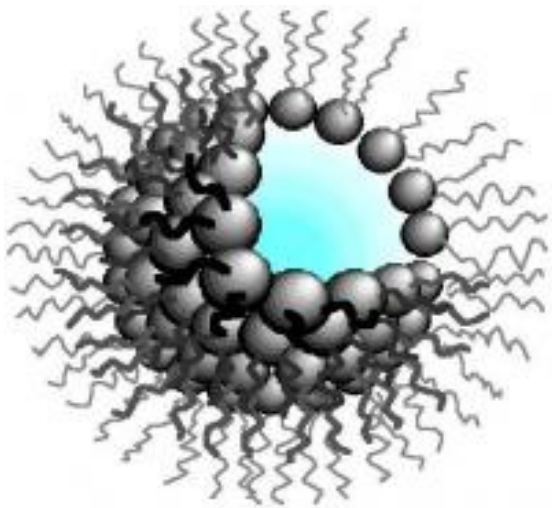
Soaps with hydrophilic (water loving)
e.g. RCOOH, NR_4
and hydrophobic (water hating,
but oil loving) parts, e.g. R = alkanes.



Micelles and Inverse Micelles



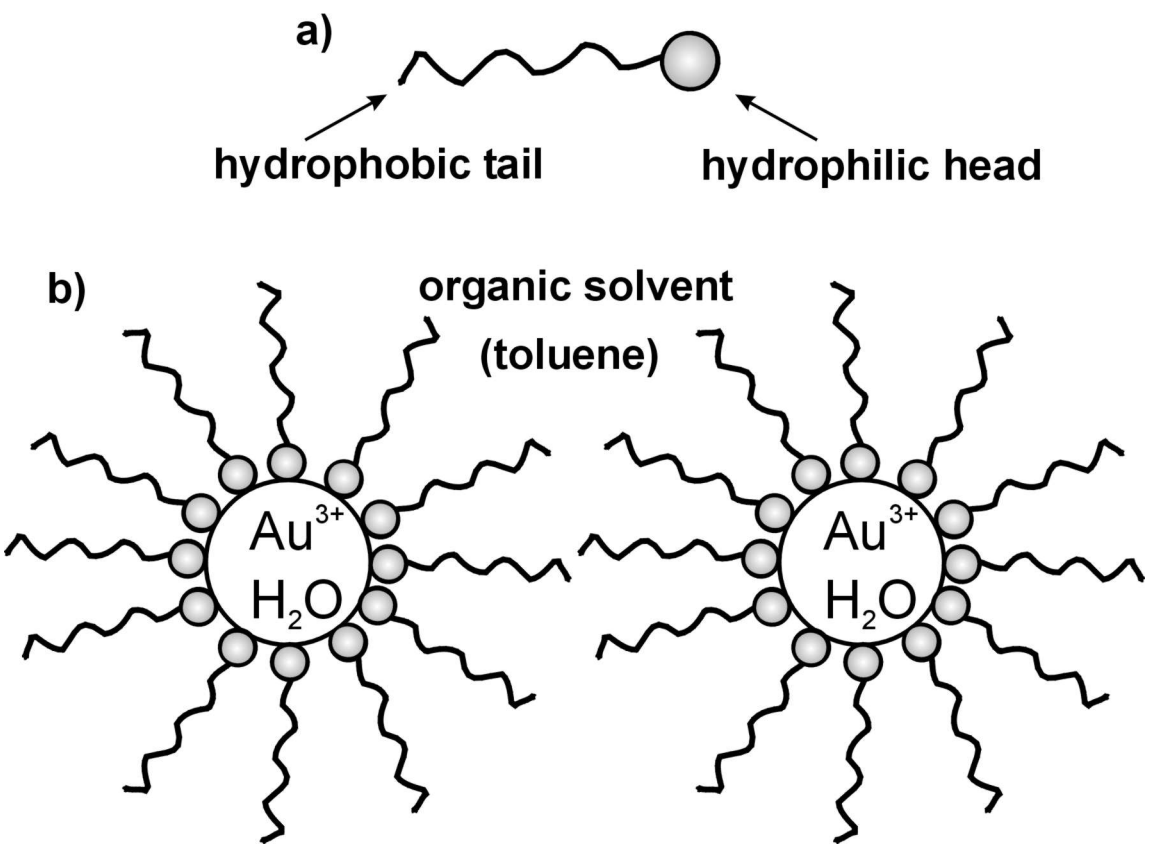




Inverse Micelles

as

Nanoscale reactors



Ultra-Fast Synthesis

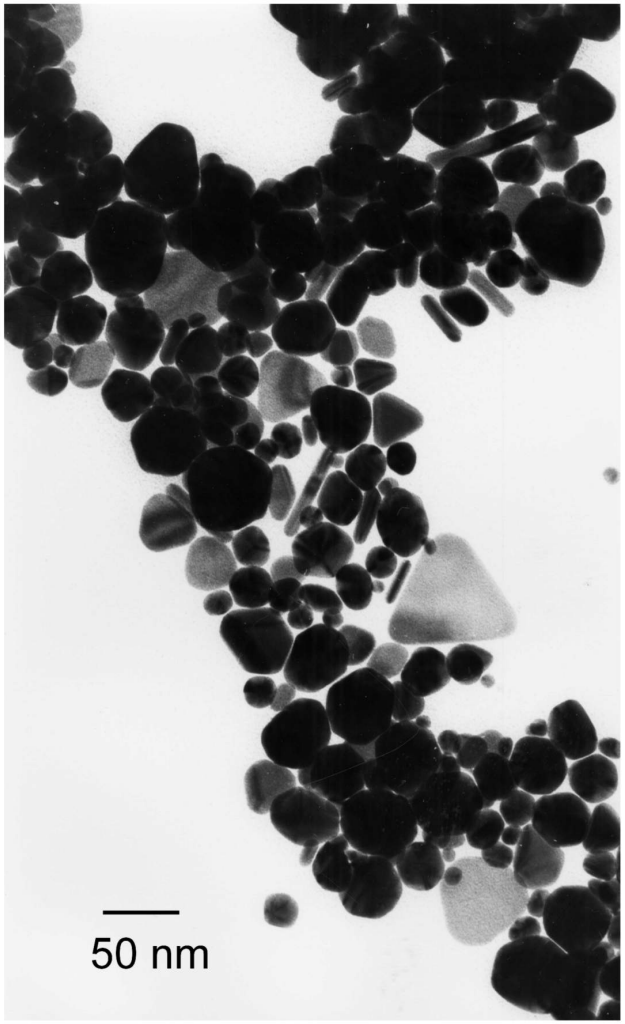
&

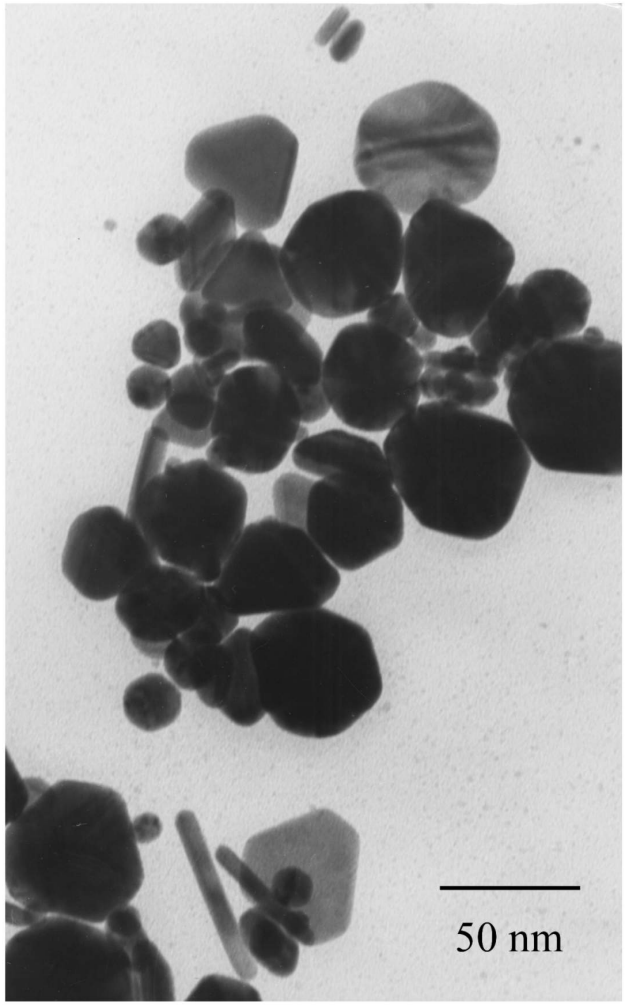
Ultra-Simple 2D Self-Assembly

of

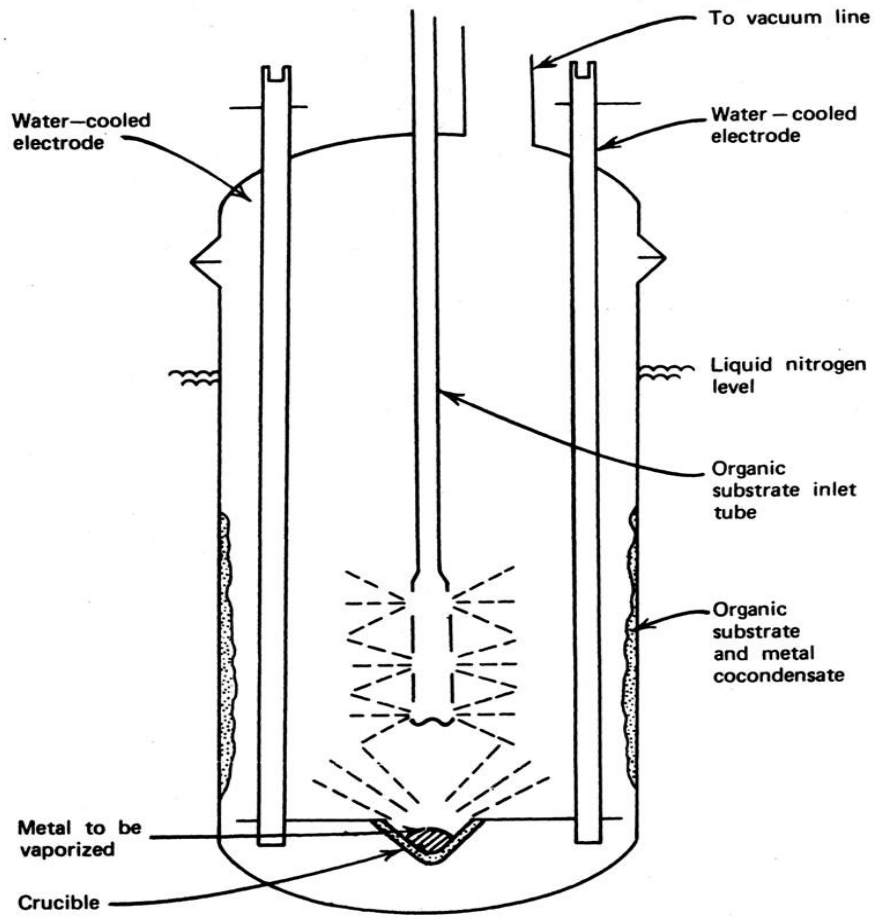
Monolayer-Protected Gold Nanoparticles

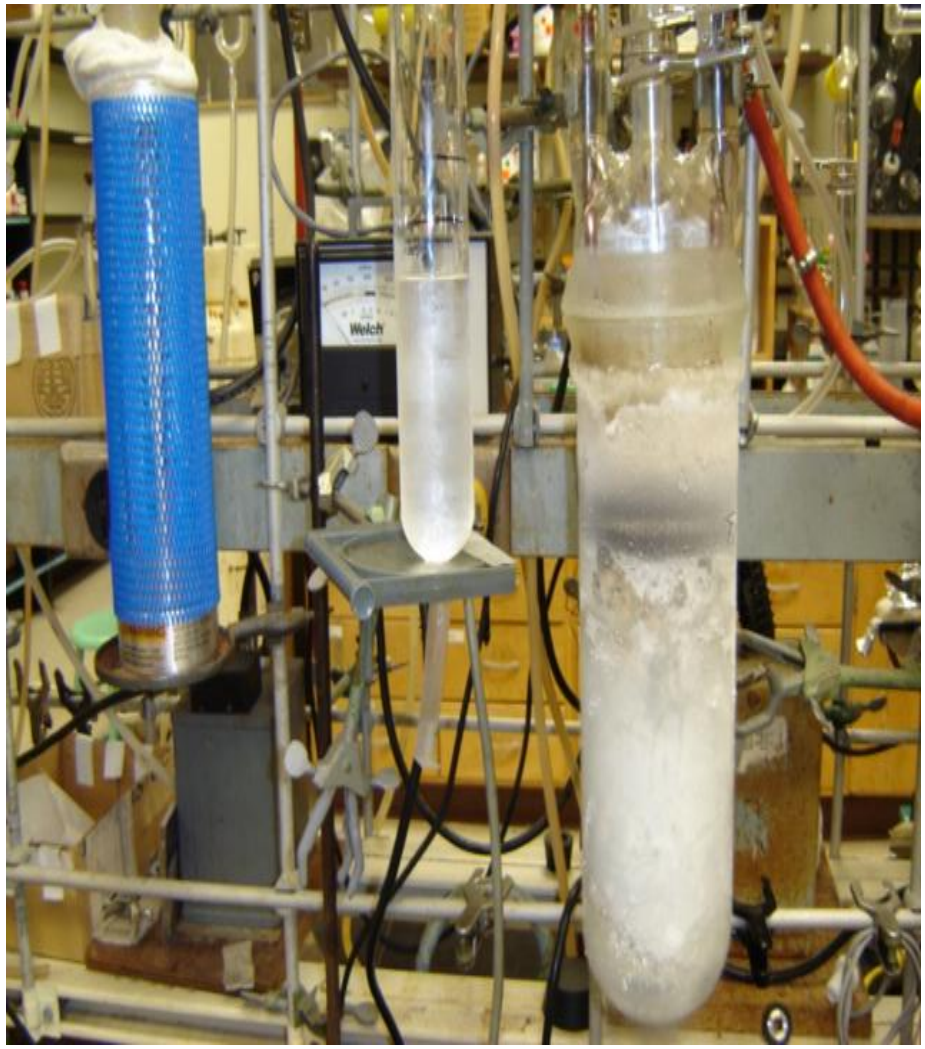
TEM OF AS-PREPARED GOLD COLLOIDS BY THE INVERSE MICELLE METHOD





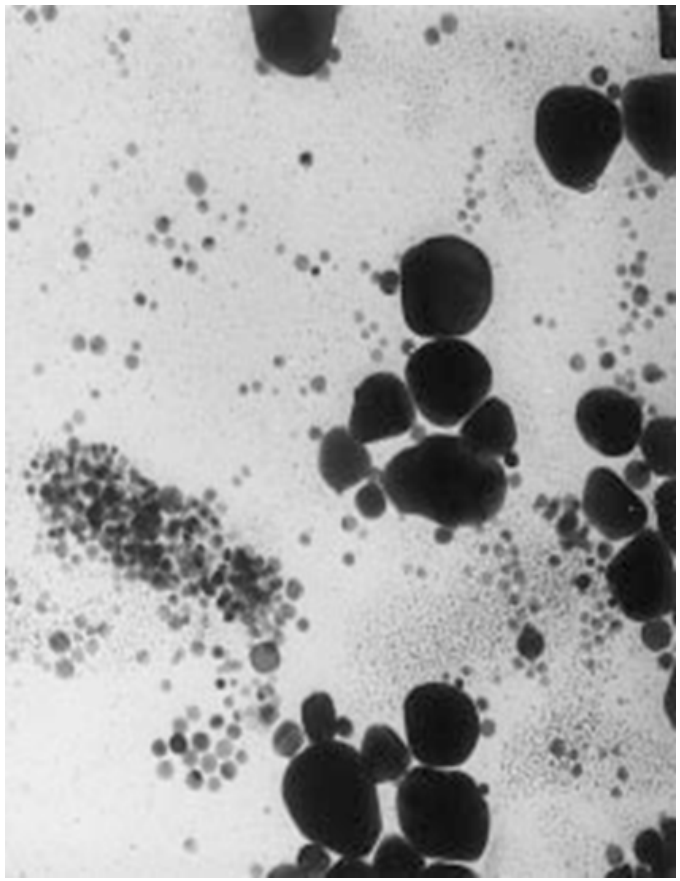
Solvated Metal Atom Dispersion Reactor





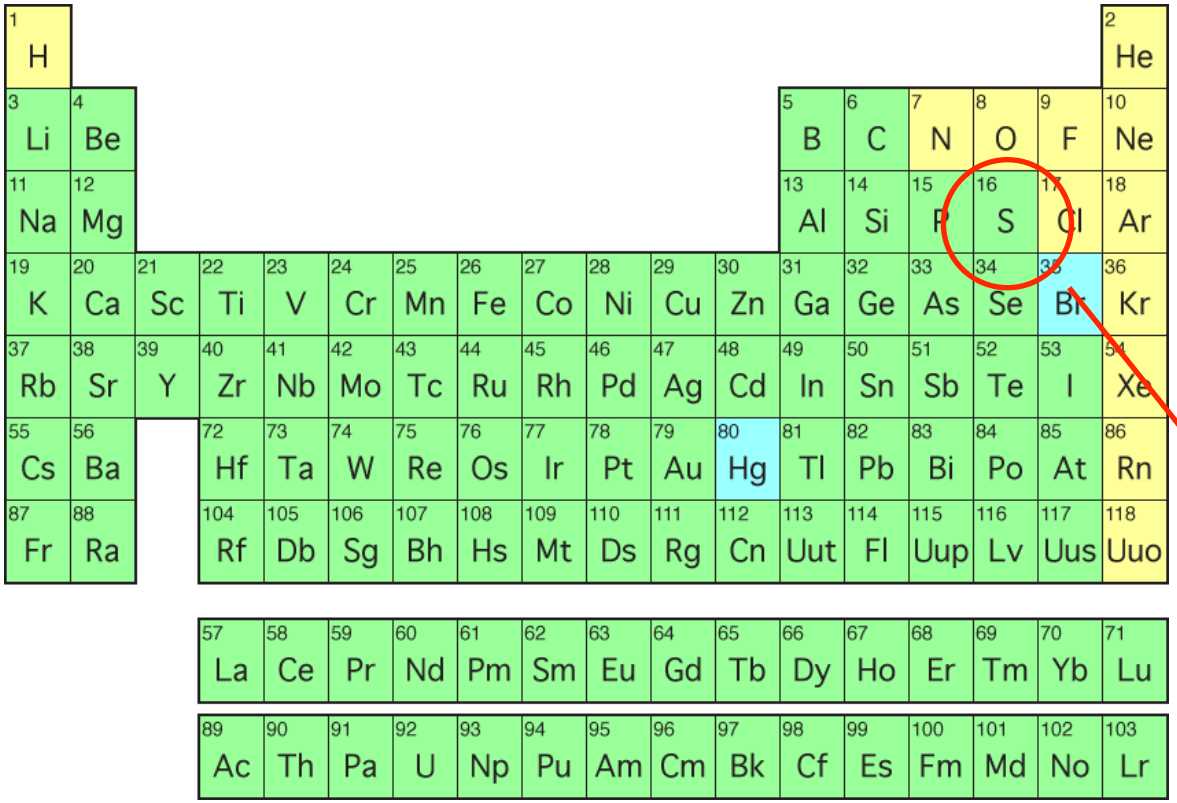
Synthetic Method Developed by Dr. Kenneth J. Klabunde, Kansas State University .

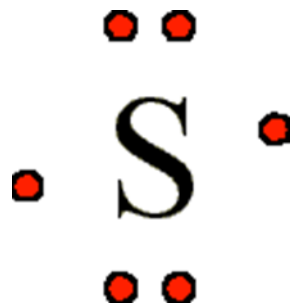
Gold particles made via the SMAD process

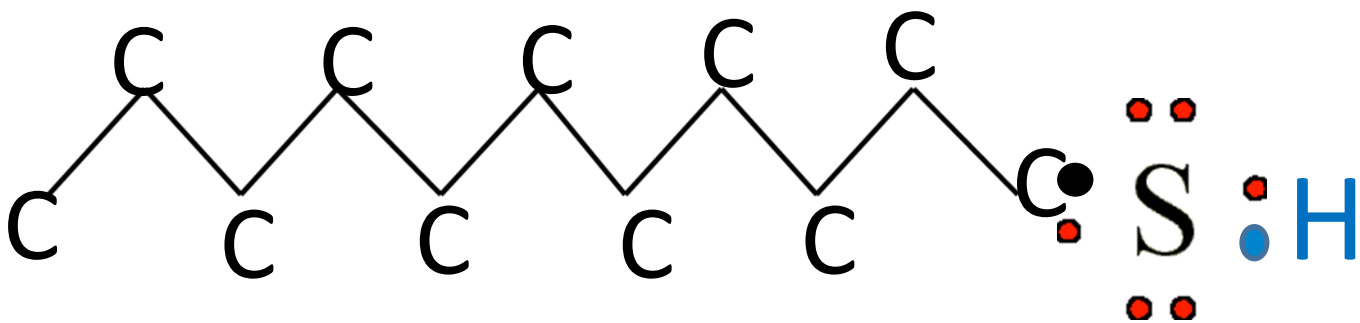


50 nm

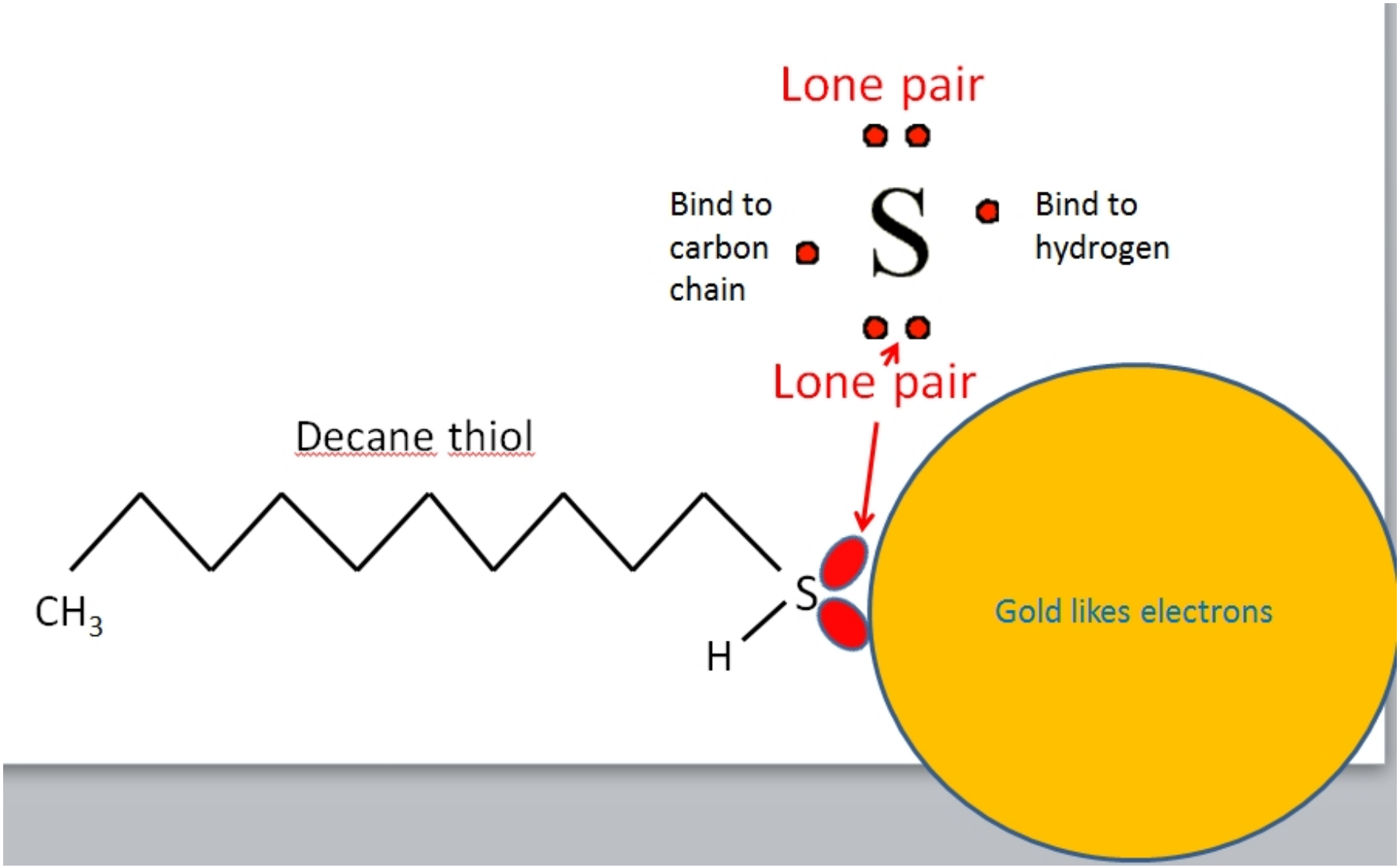
Some chemistry … Thiols





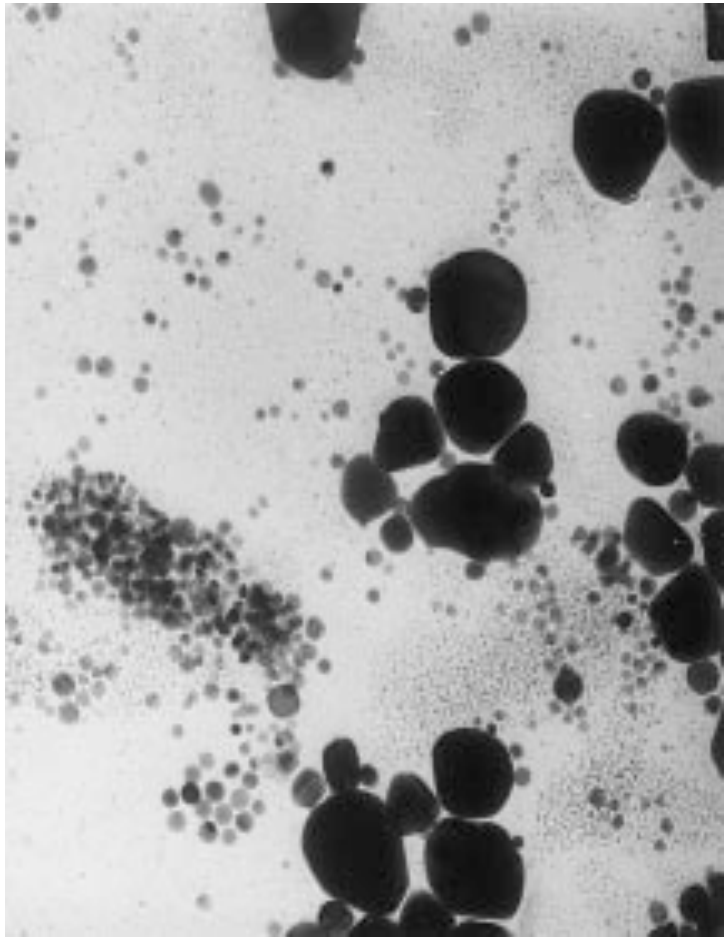


Ligation


Lone pair
Bind to carbon chain
S
Bind to hydrogen
Lone pair
Decane thiol
CH_3
S
H
Gold likes electrons

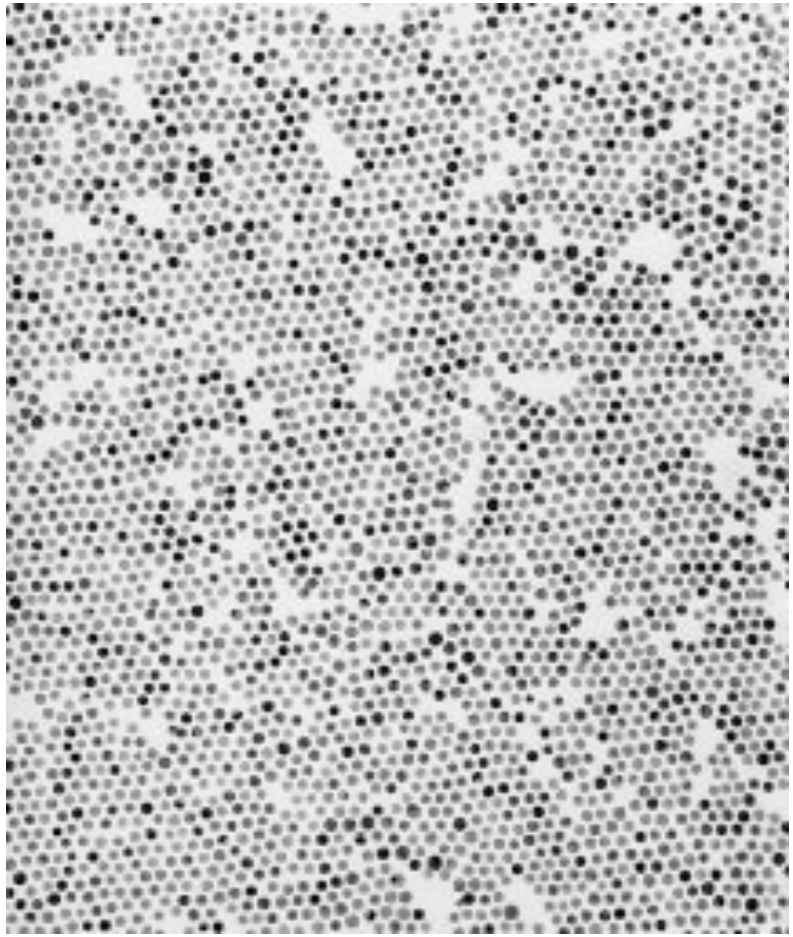
Digestive Ripening:

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



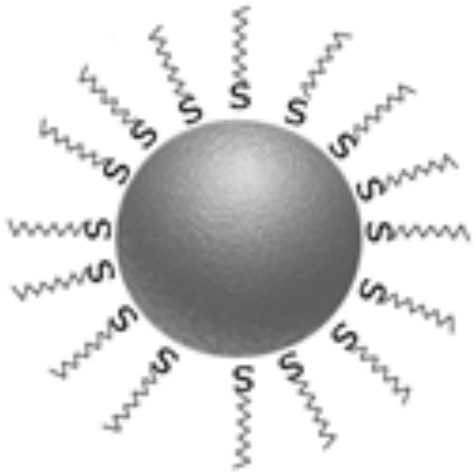
Before

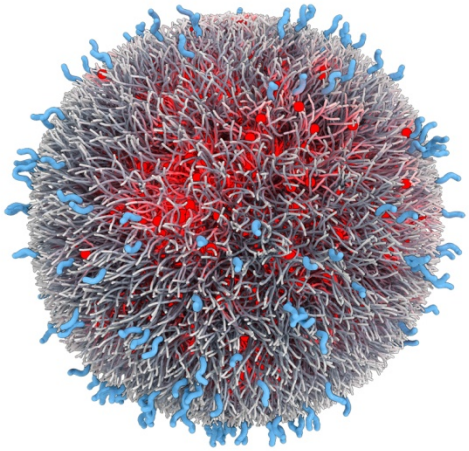
→



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

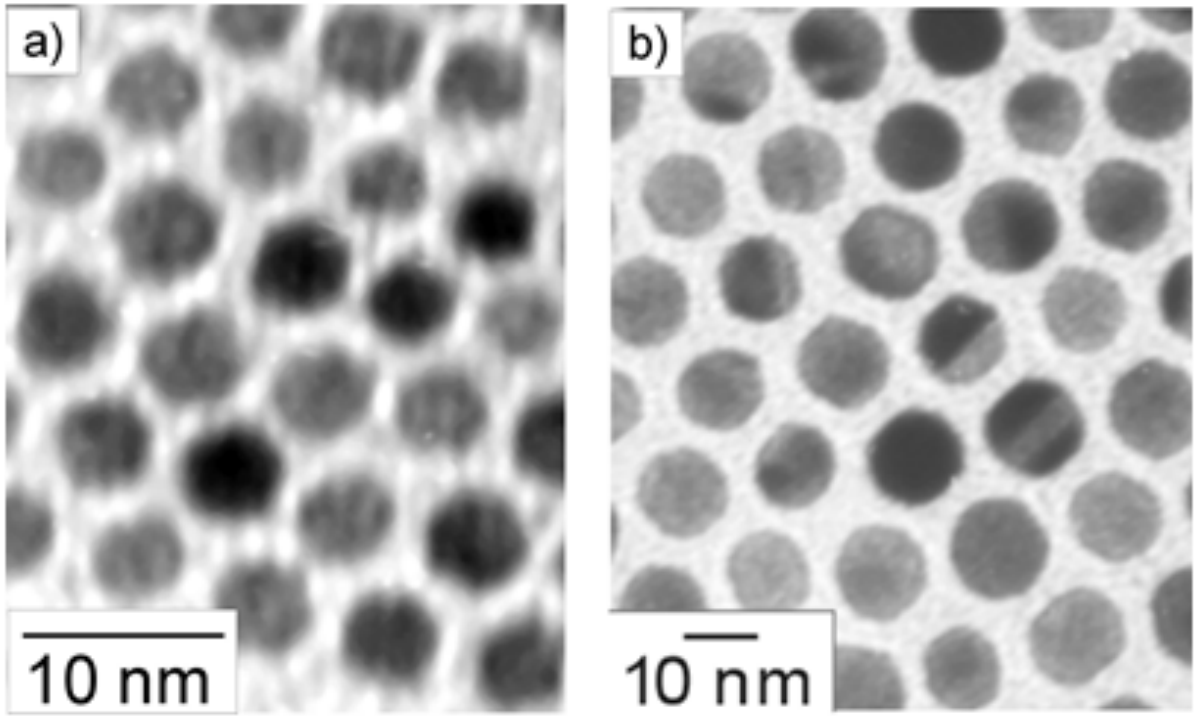
acids RCOOH

Materials that have been Digestively Ripened

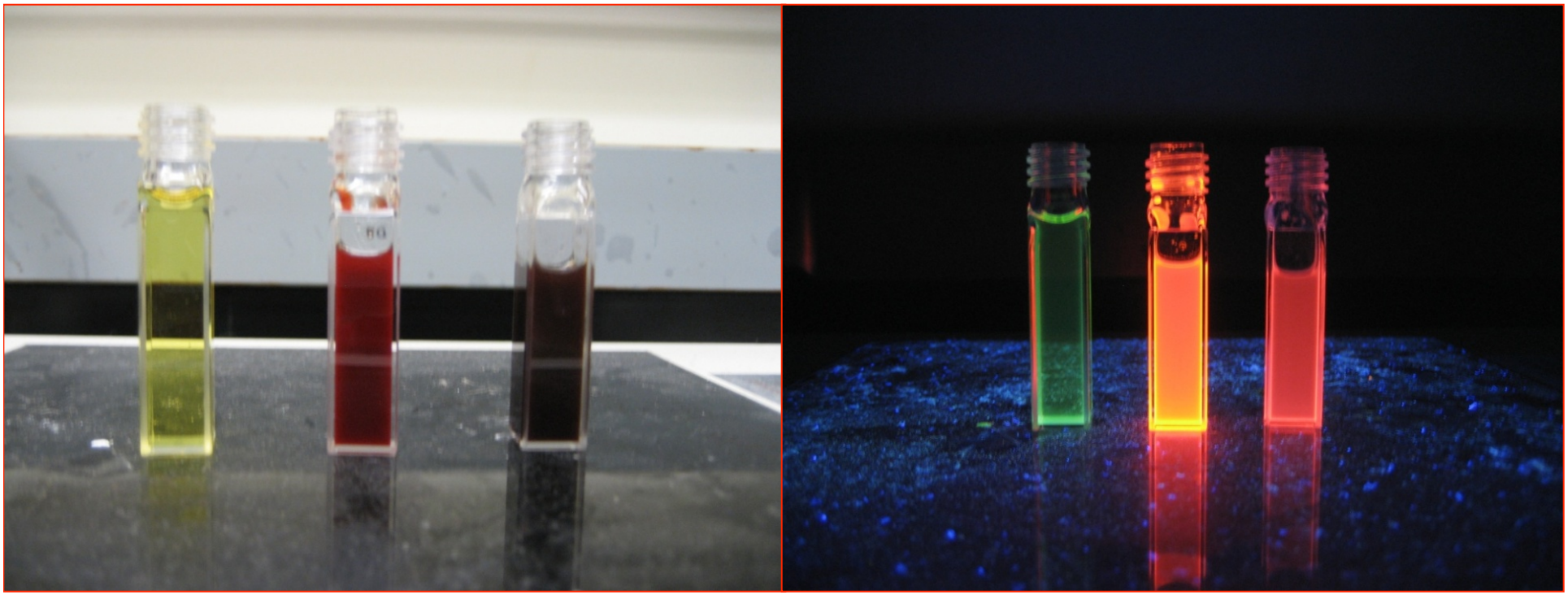
Gold, silver, copper, CdS, CdSe, CdTe, Pd, In, Fe_2O_3, Fe_3O_4

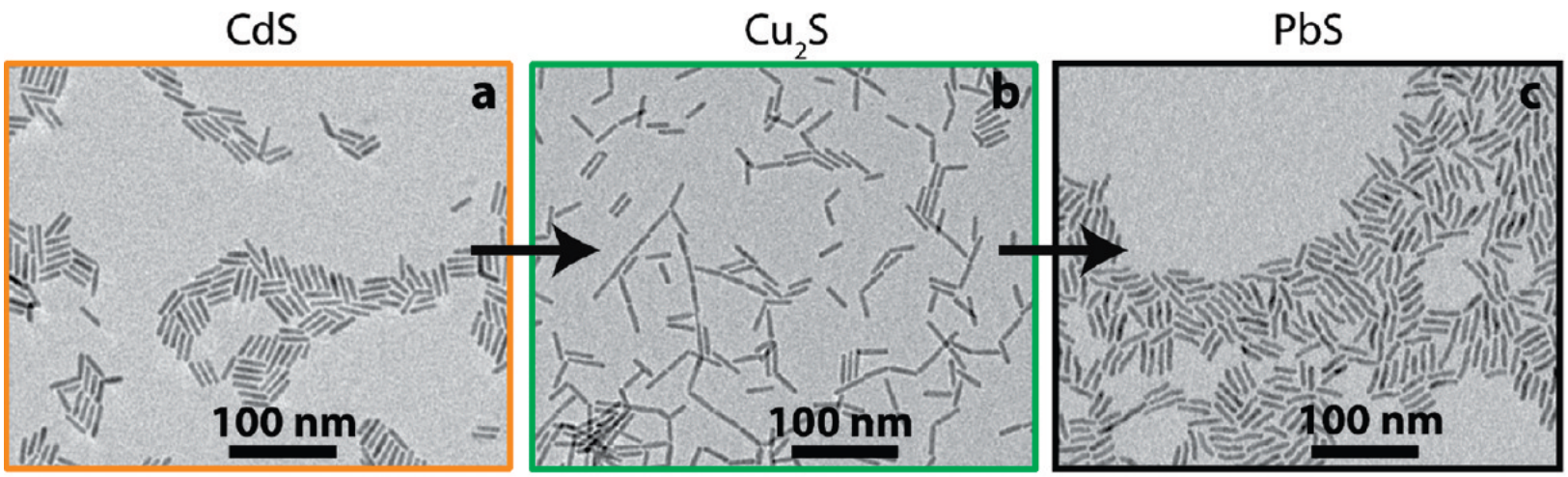
Different ligands --- different sizes

$C_{12}SH$ $C_{12}NH_2$



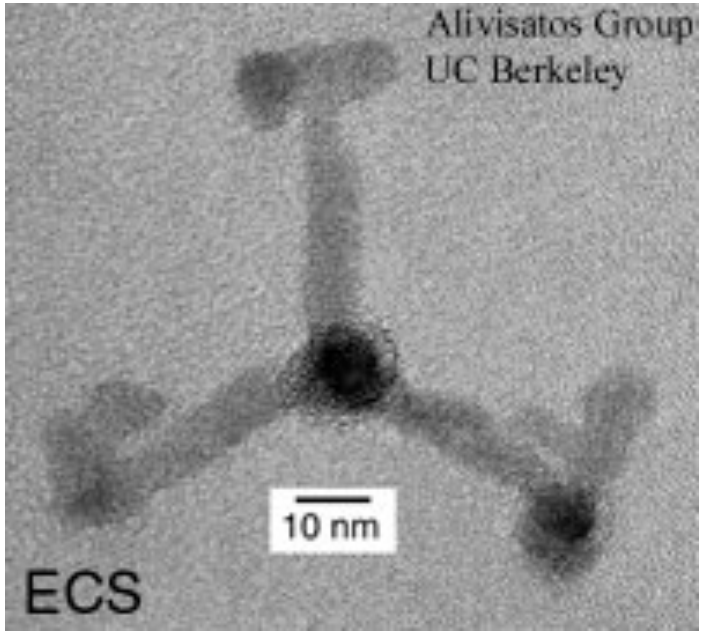
CdTe nanoparticles
Different digestive ripening times
lead to different sizes

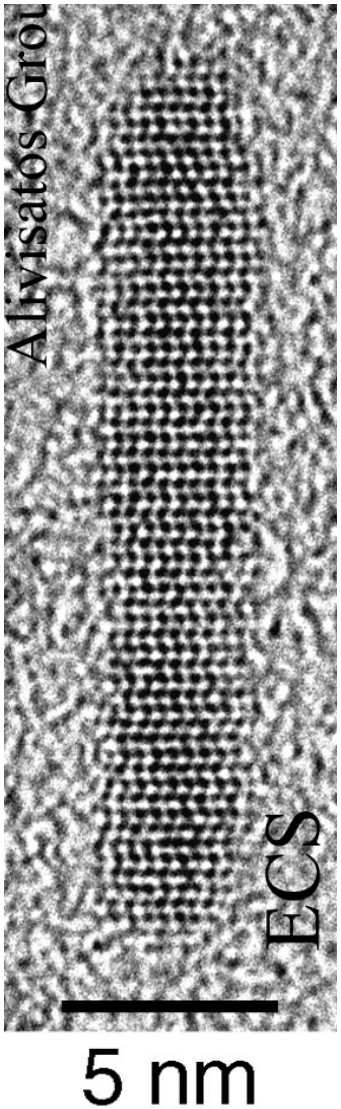


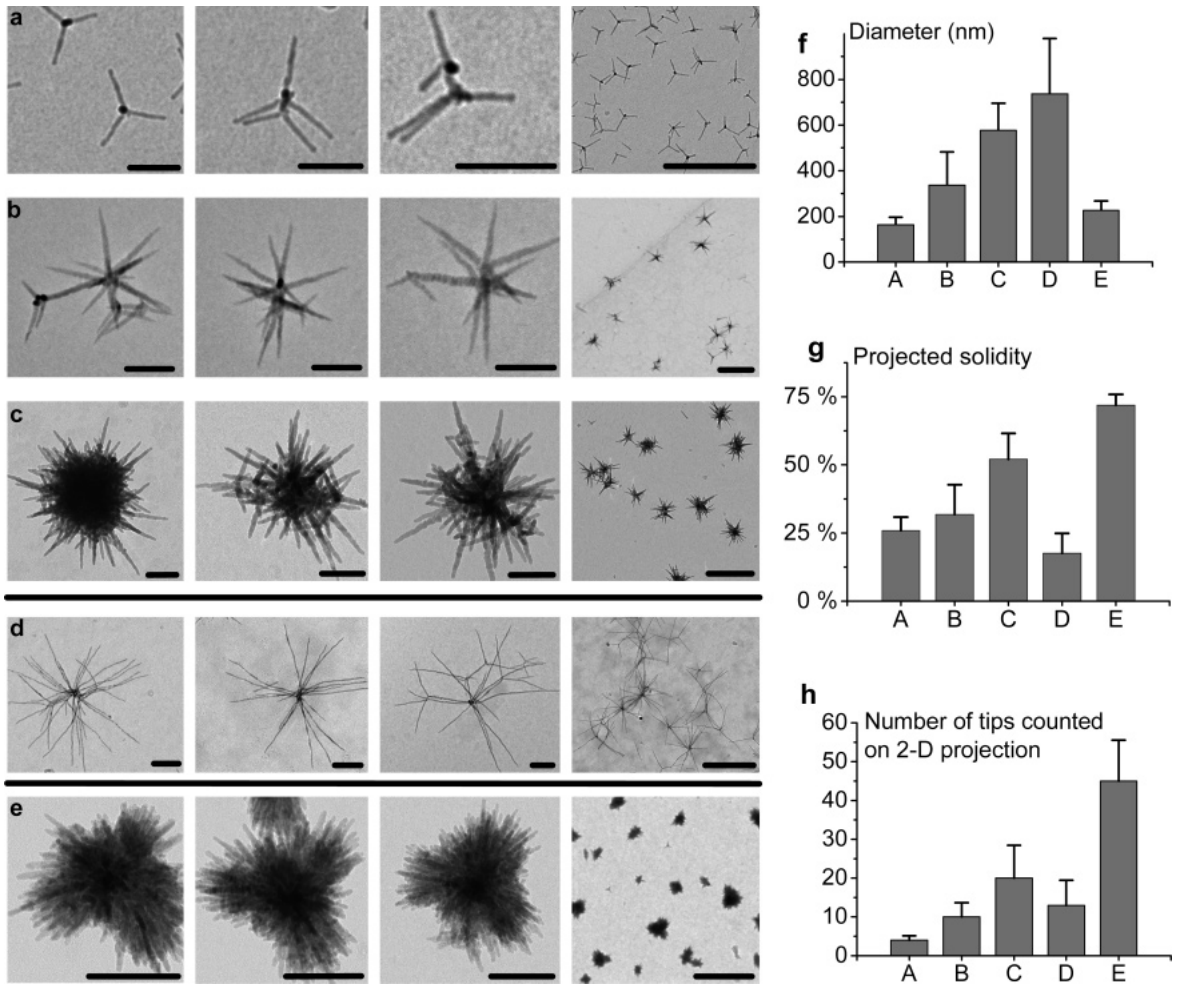


Luther et al. JACS 2009

Tetrapod of CdSe

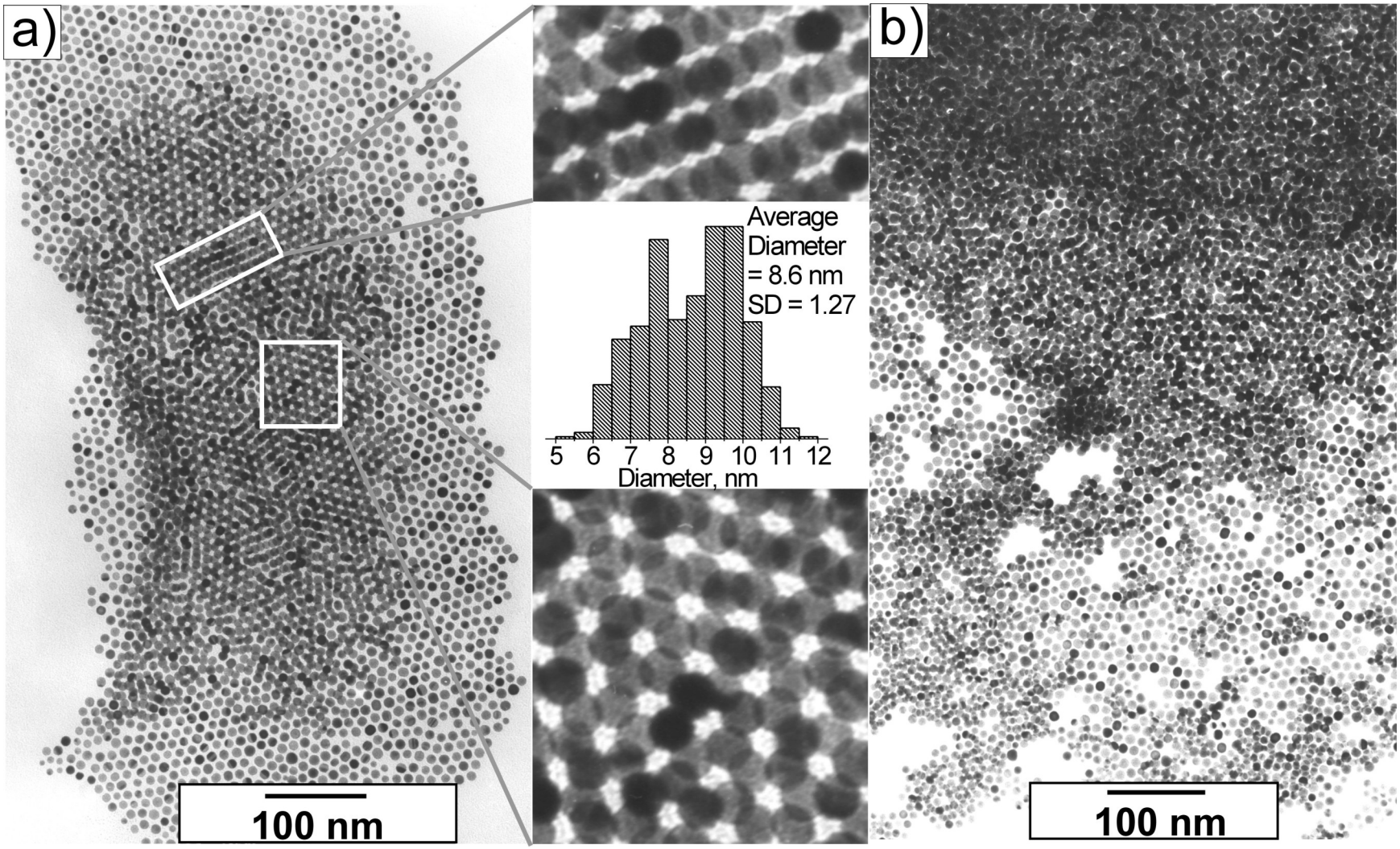






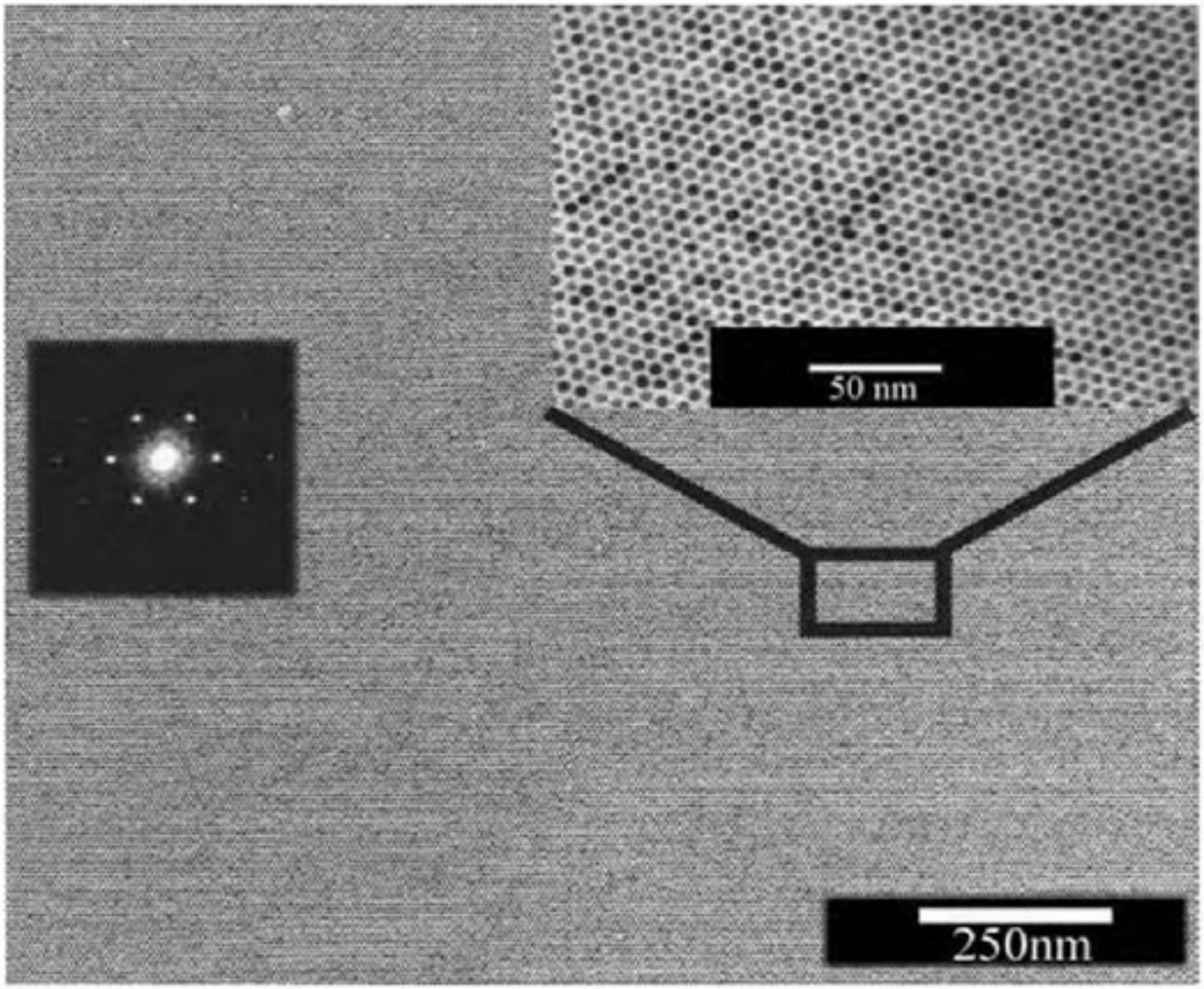
Kanaras et al. Nanoletters 5 (2005)

Inverse Micelle Au/$C_{12}NH_2$



Two-Dimensional Superlattice!

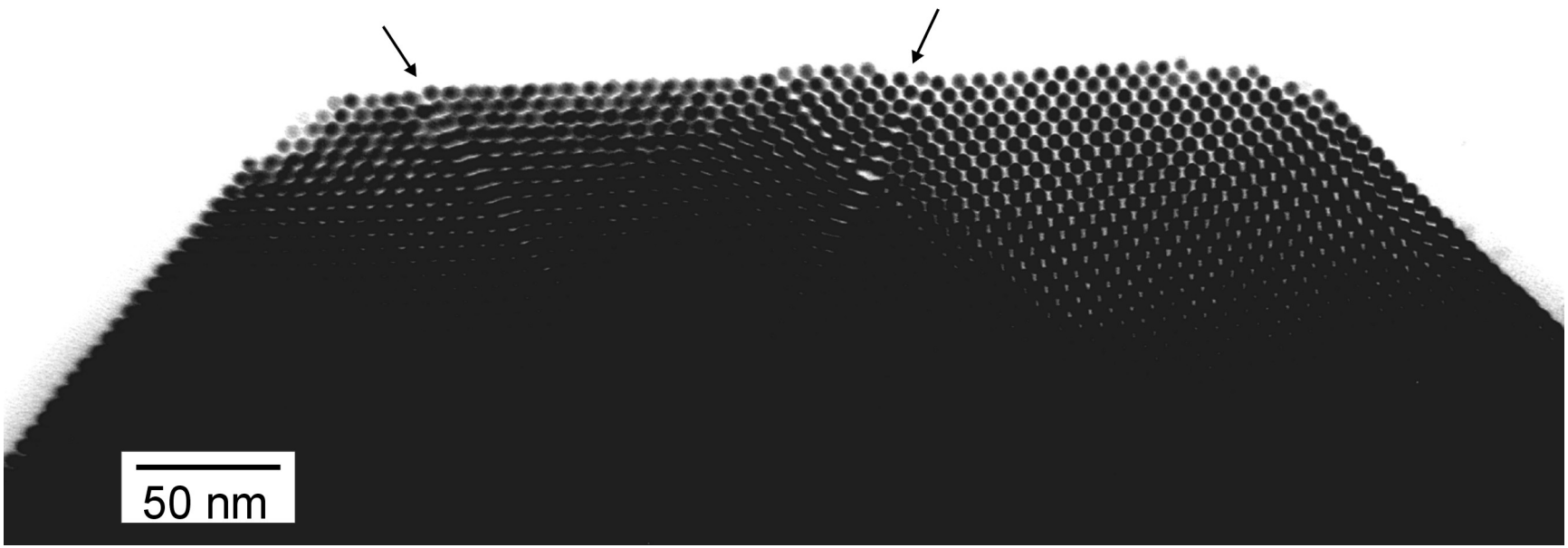
Electron diffraction



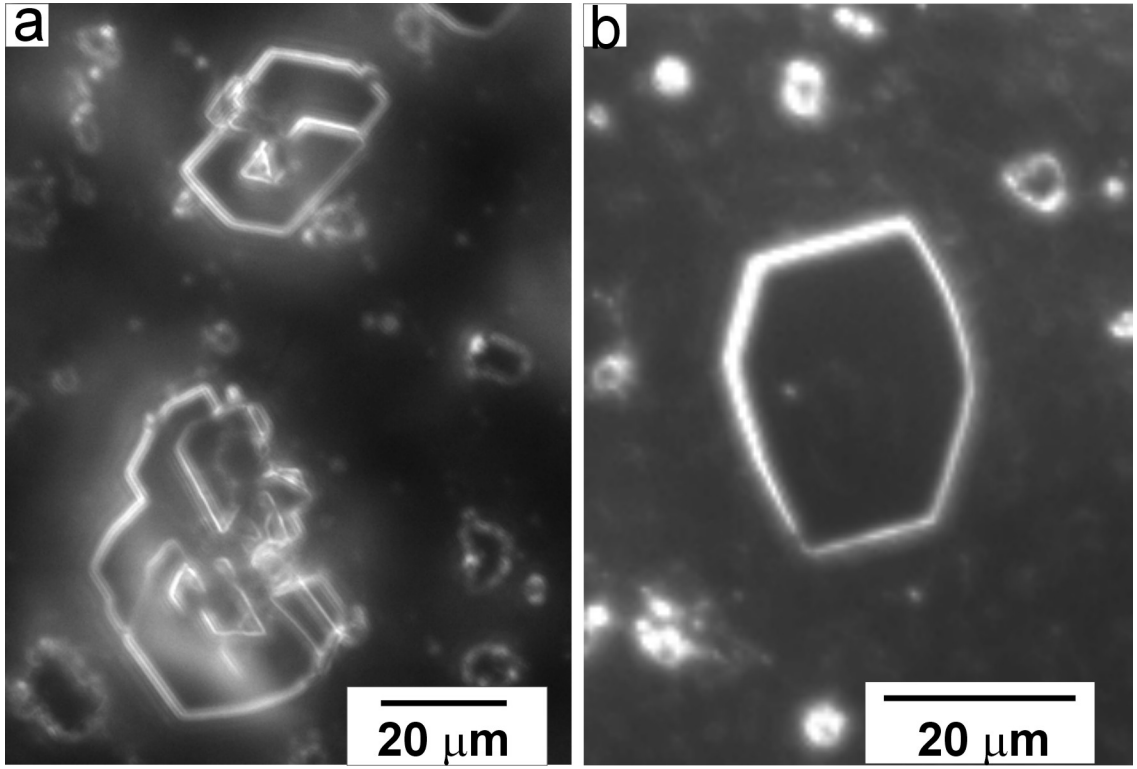
JPC B105, 3353-3357 (2001)

3d Superlattice of Au/C_{12}SH nanoparticles

$[110]_{sL}$ 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?

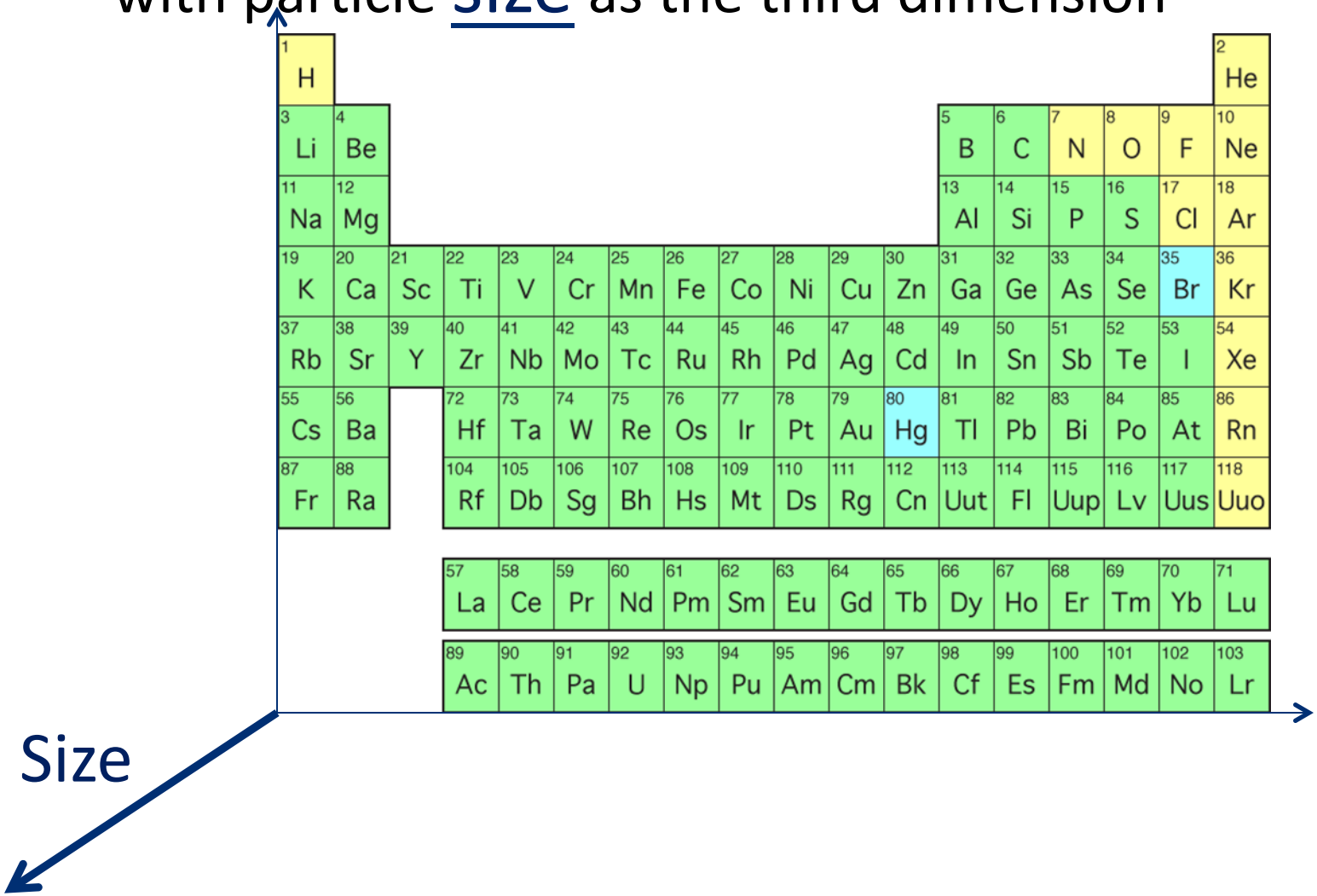
A ligated 5.0 nm Au nanoparticle can be represented by

$$Au_{4000}(C_{12}SH)_{365}$$

with ~10% variation on the numbers.

A three-dimensional Periodic Table

with particle size as the third dimension



Thank You

Particle group