Practical Theory of Nano- Materials

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Lecture notes and supplementary materials at;

http://www.ch.ic.ac.uk/harrison

Aims:

Provide the ability to critically assess theoretical studies.

Background for theoretical projects

Plan…

Properties at the nano-scale : quantum theory

Classical Methods (Free Energy and Mol. Dynamics)

Practical quantum mechanics – density functional theory

Implementations

- Plane waves and pseudopotentials
- Local basis sets – all electron calculations

Approximate quantum methods

Some recent progress…

- Spin transport and quantum computing
- New solar cells: quantum dots & wells
- Chemistry at interfaces
- Magnetic carbon polymorphs

The Scale of Nanotechnology

Institute of Nanotechnology Figures (**estimates**):

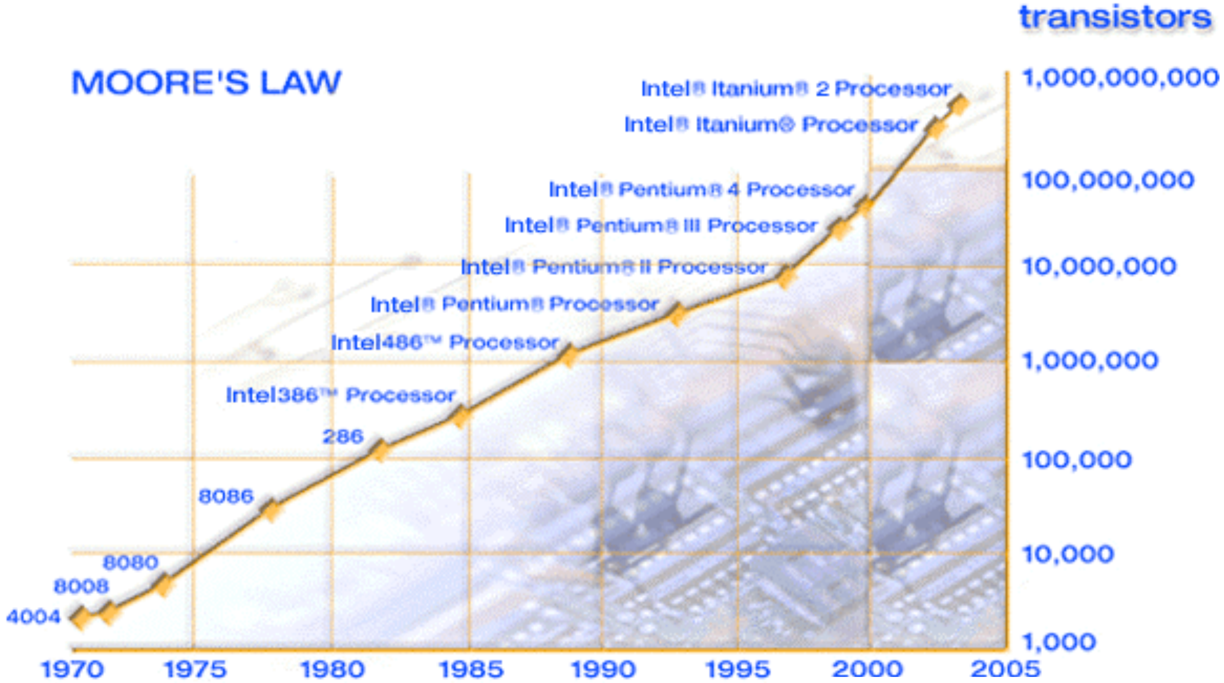
New Materials -> Products : ~£1 trillion / year by 2010-2015
- Materials beyond chemistry : £210B/year over 10 years (materials and processing)
- Electronics in 10-15years : £200B/year for semiconductor industry, integrated circuits
- Pharmaceuticals in 10-15years : (£100 B /year)
  about half of production will depend on nanotechnology,
- Aerospace(about £40B/y in 10years)
- Tools (measurement, simulations) :~£12B/year in 10year

~2million new nanotech workers required worldwide

Improved healthcare : extend life-span, its quality, human physical capabilities(~£20B in tools for healthcare in 10years)

Sustainability : agriculture, water, energy (~£30B/year in 10 years), materials, environment ; ex : lighting energy reduction ~10% or £60B/year

Technical Drivers ? Eg: Computing



Pentium 4

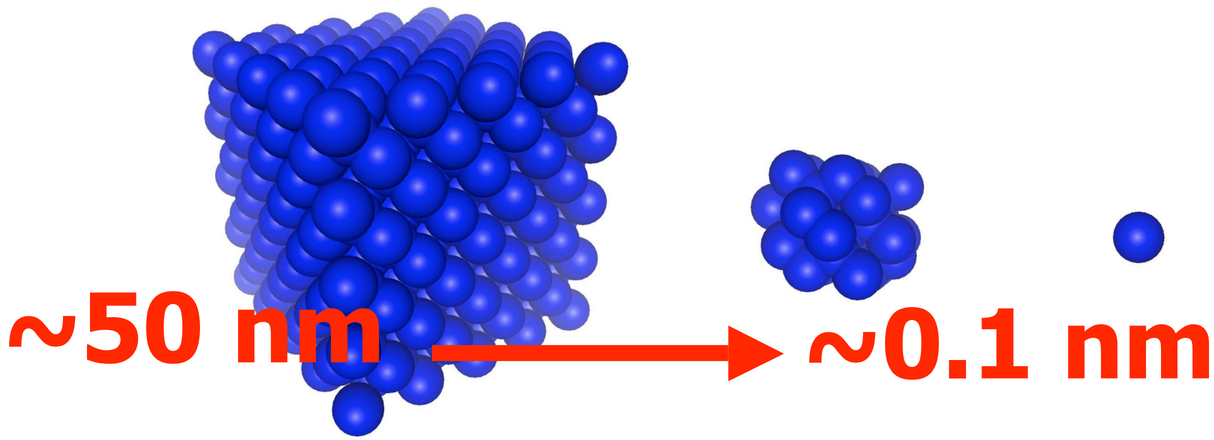
gate length ~50nm

Quantum Limit ?

~5nm

Spintronics

~1nm..



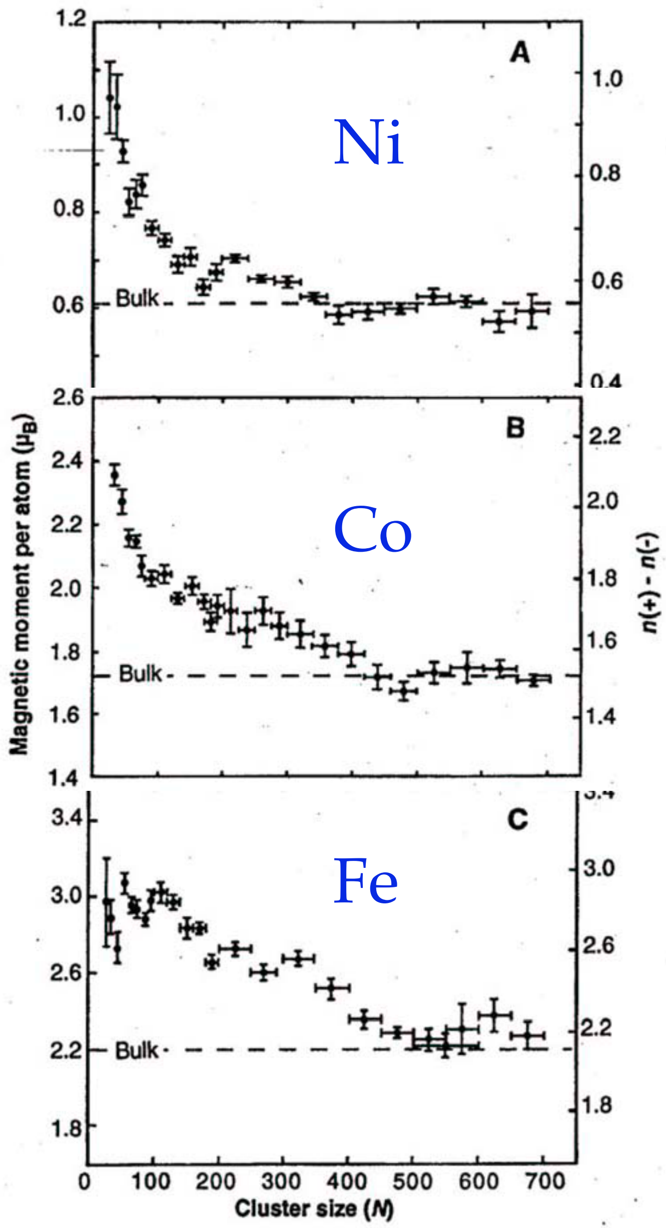
http://www.popularmechanics.com/technology/computers/2001/9/small_wonder/print.phtml

Magnetic Moment vs Cluster Size

Ferromagnetic metals

Bulk moment recovered for clusters of ~500 atoms

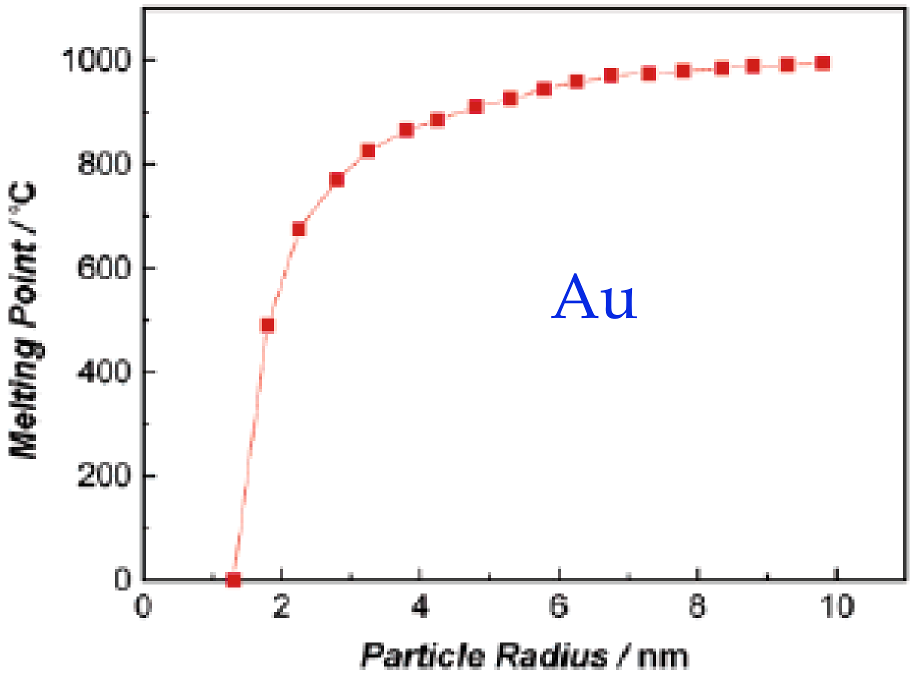
Surprising ?



Gillas, Chatelain, De Heer, *Science* (1994)

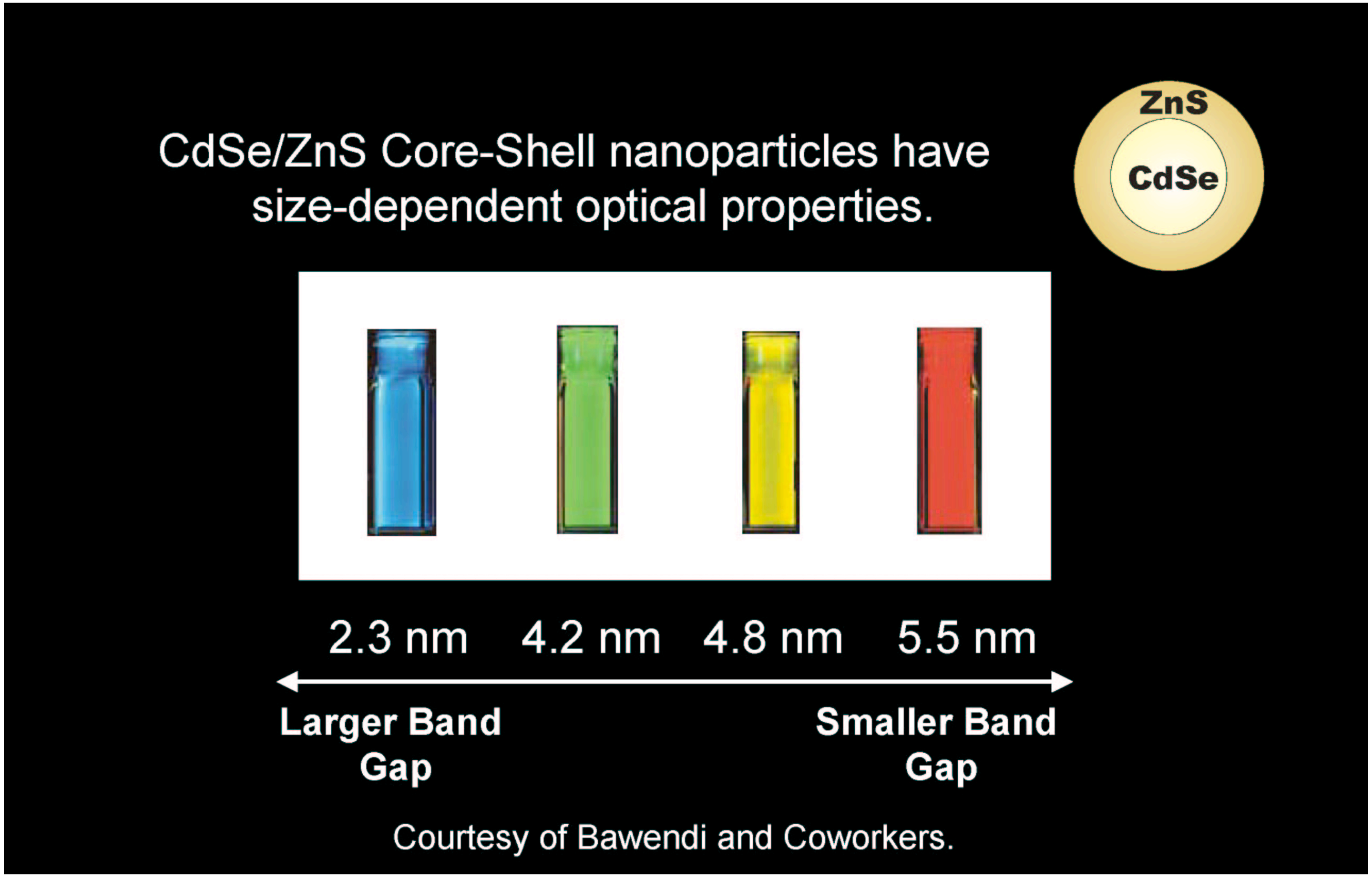
Melting Point

The thermodynamic stability of different phases & the dynamics of phase transitions depend on size.



Shmid, in *Nanoscale Materials in Chemistry*, Ed Klabunde, Wiley, NY 2001

Core Shell Structures



Early Uses of Gold Nanoparticles I

The *Labours of the Months*, Norwich *ca*. 1480.

The dark red colour is probably due to the embedded gold nanoparticles

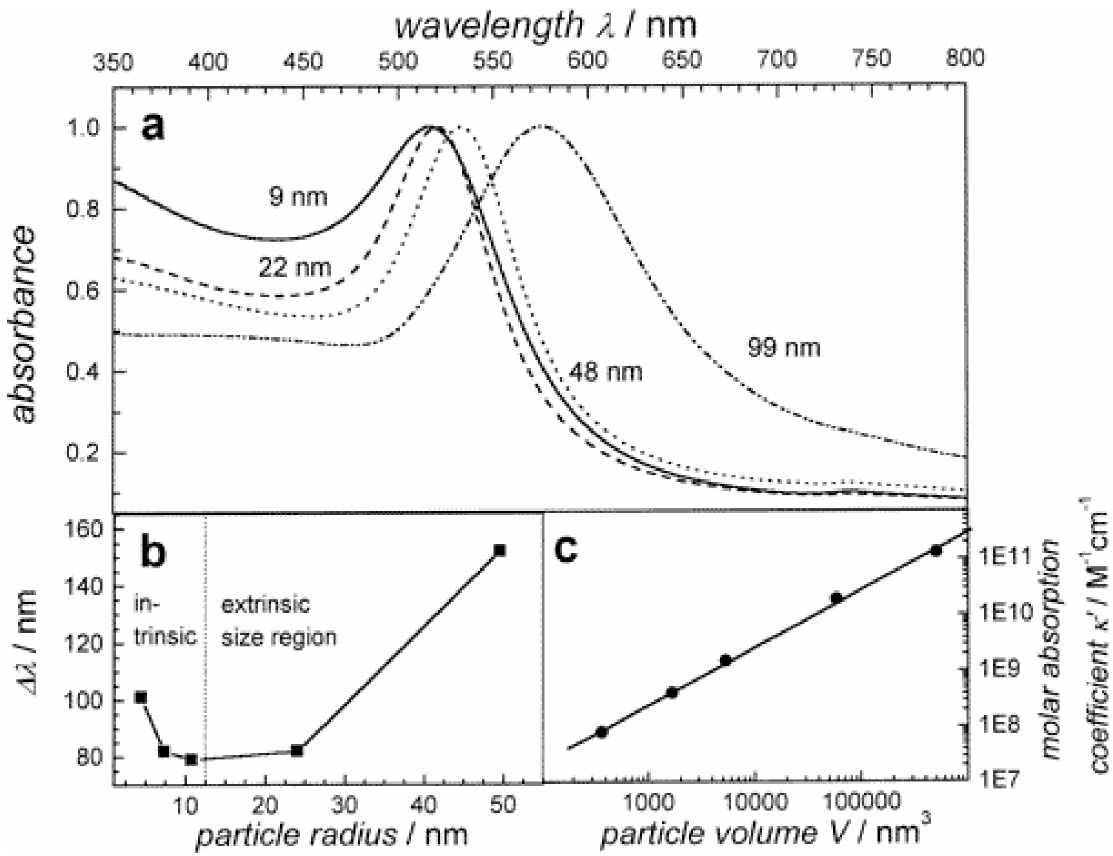
Early Uses of Gold Nanoparticles II

The Lycurgus Cup (British Museum, 4th century AD)

When lit from the outside it appears green, lit from within it glows red - due to the embedded gold nanoparticles (adsorbtion at λ~520 nm)

Optical-UV Adsorption (Colour)

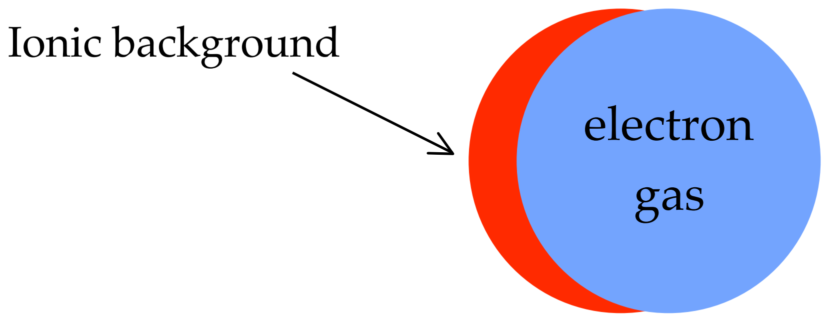
Au: As the particle size increases red shift of the surface plasmon (a) and bandwidth decreases then increases (b)



Link, El-Sayed, *J. Phys. Chem.* B **103** 8410 (1999)

Surface Plasmons

Collective vibrations of the electron gas within the nanoparticle in the confining potential of the ion cores - usually confined to the surfaces of solids but nanoparticles are ‘all surface’.



Frequencies of plasmons depend on the size and shape of the nanoparticle as well as its dielectric function.

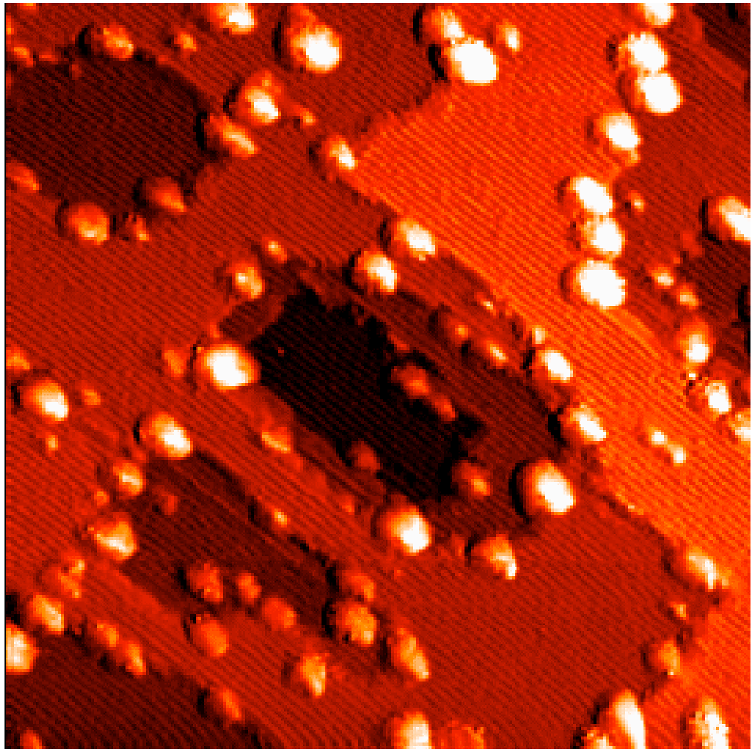
We’ll come back to a quantitative theory in a later lecture

Metal Clusters on an Oxide Surface

0.25 monolayers of gold on $TiO_2(110)$

Scanning Tunelling Microscope

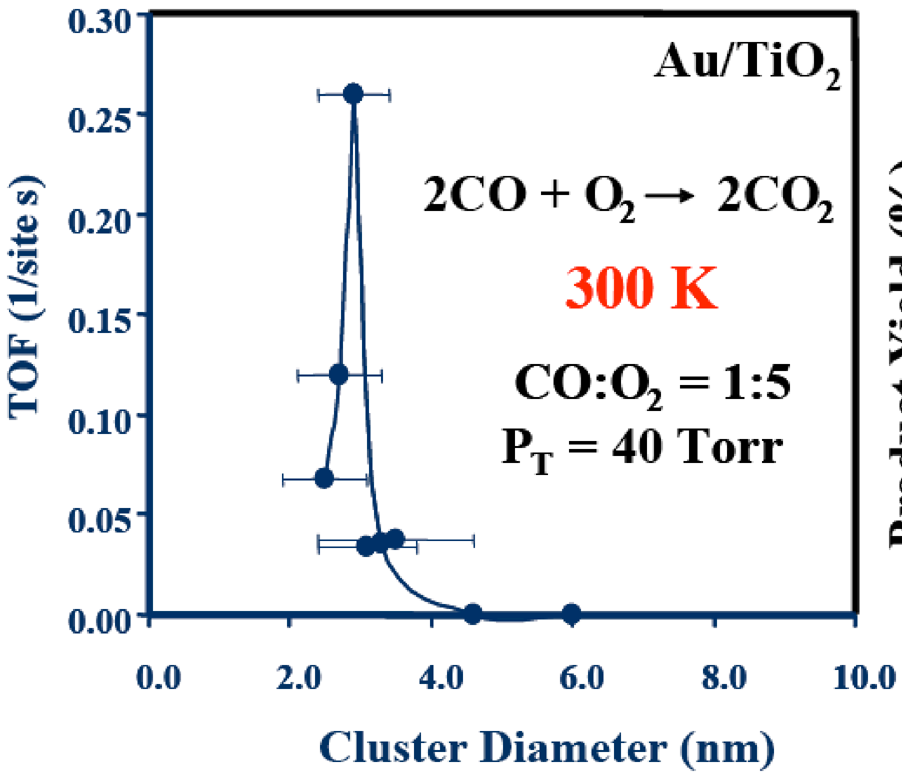
STM



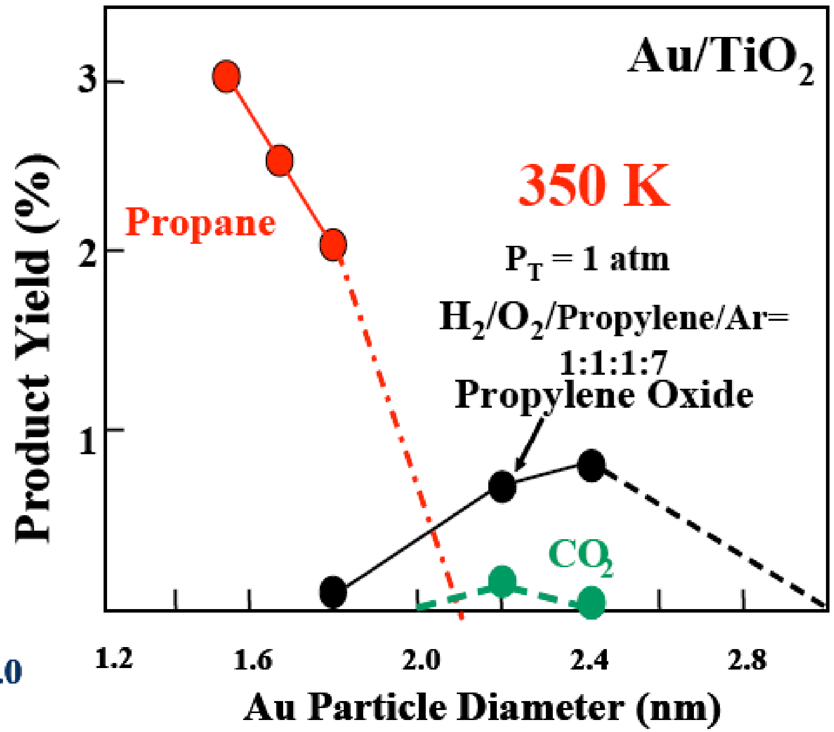
50nm

Catalytic Activity of Gold Nanoparticles

Gold 2-4nm nanoparticles on TiO_2 are an excellent oxidation catalyst !!!

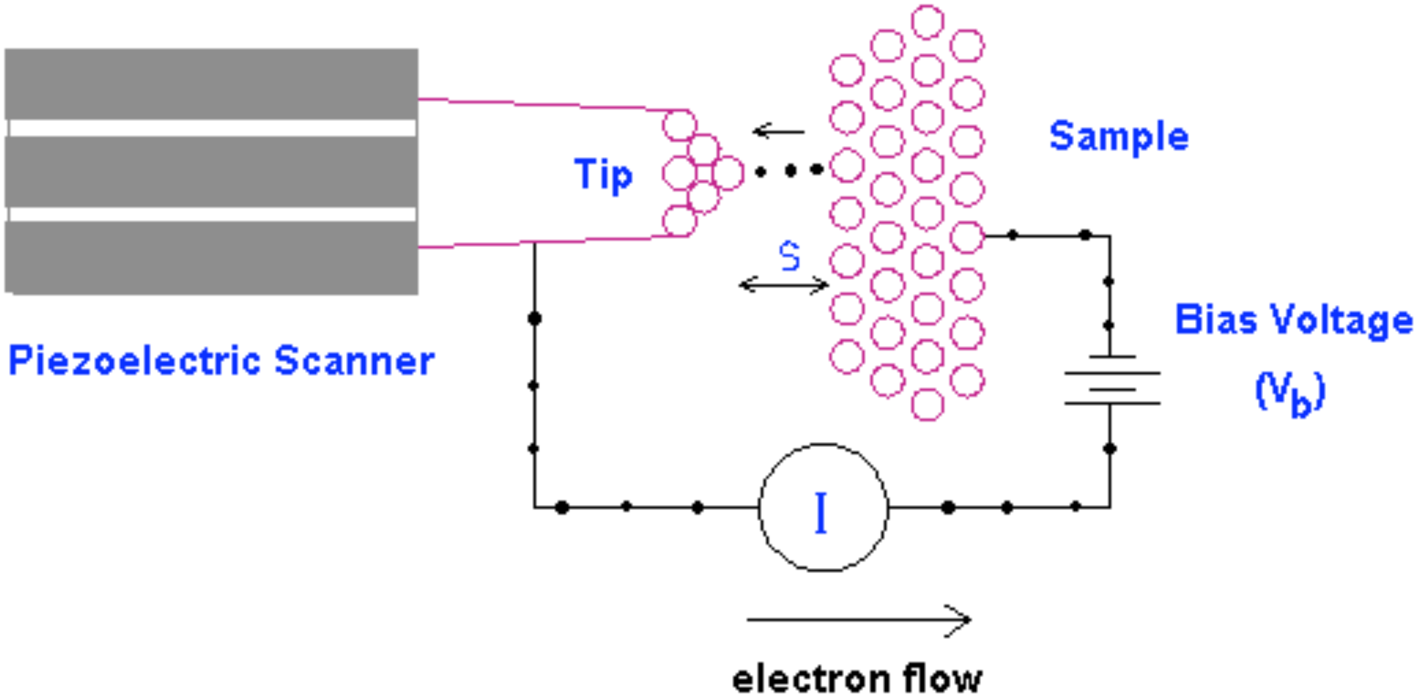


from Haruta, et al., <u>Catalysis Letters</u> (1997)



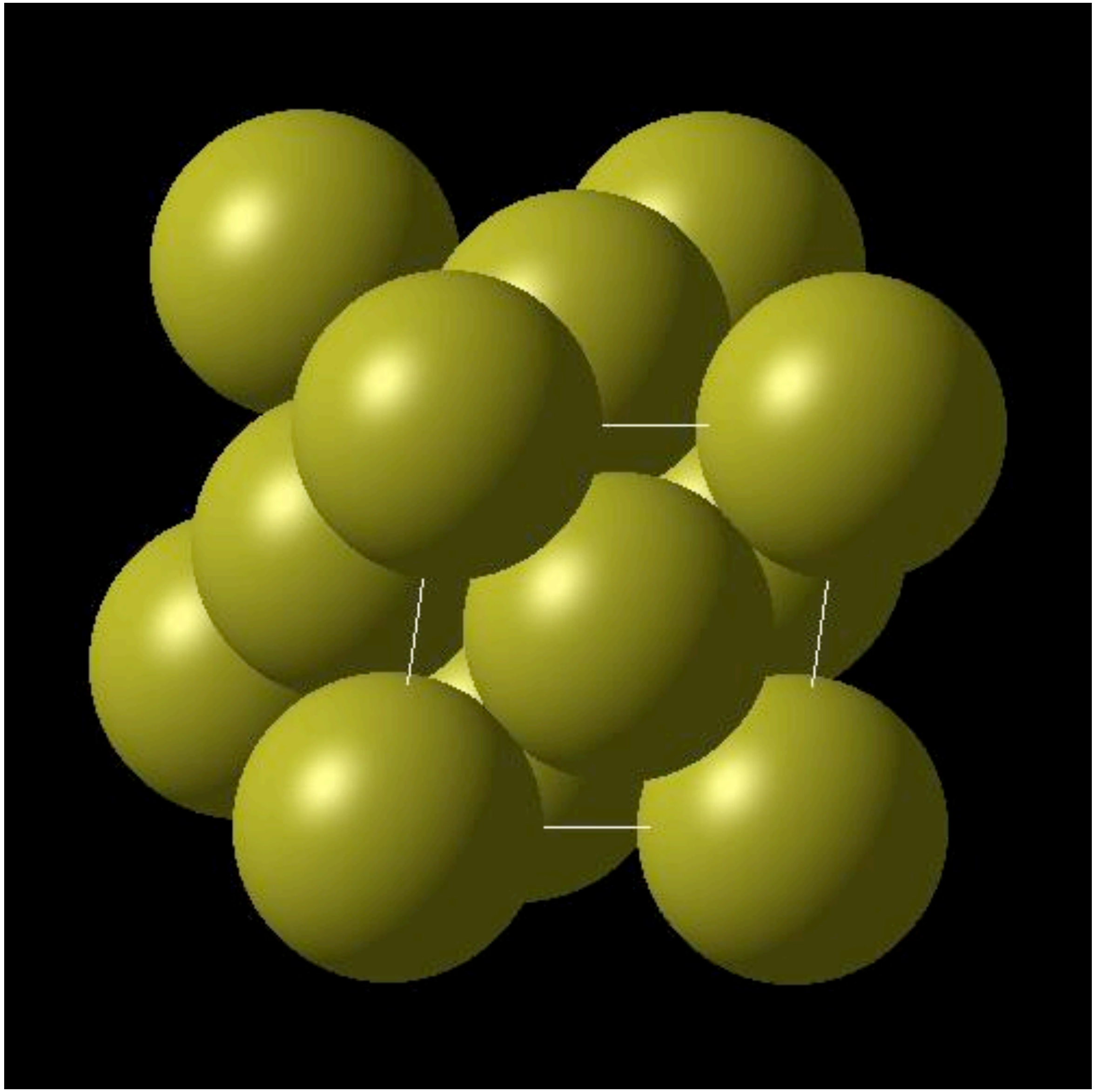
from Haruta, et al., <u>Shokubai, Catalysts and Catalysis</u> (1995)

Scanning Tunneling Microscopy

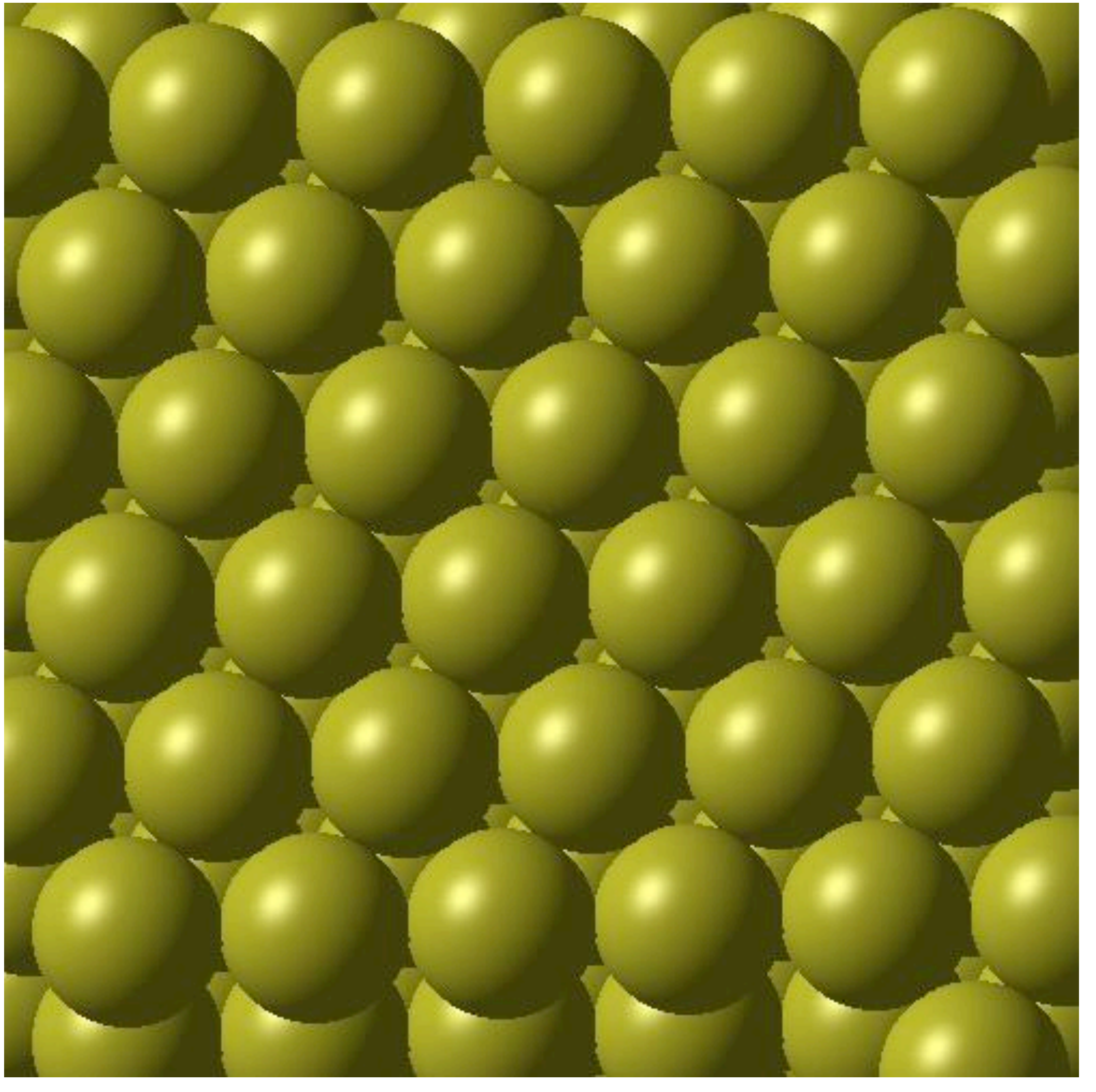


Binnig and Rohrer ~1982

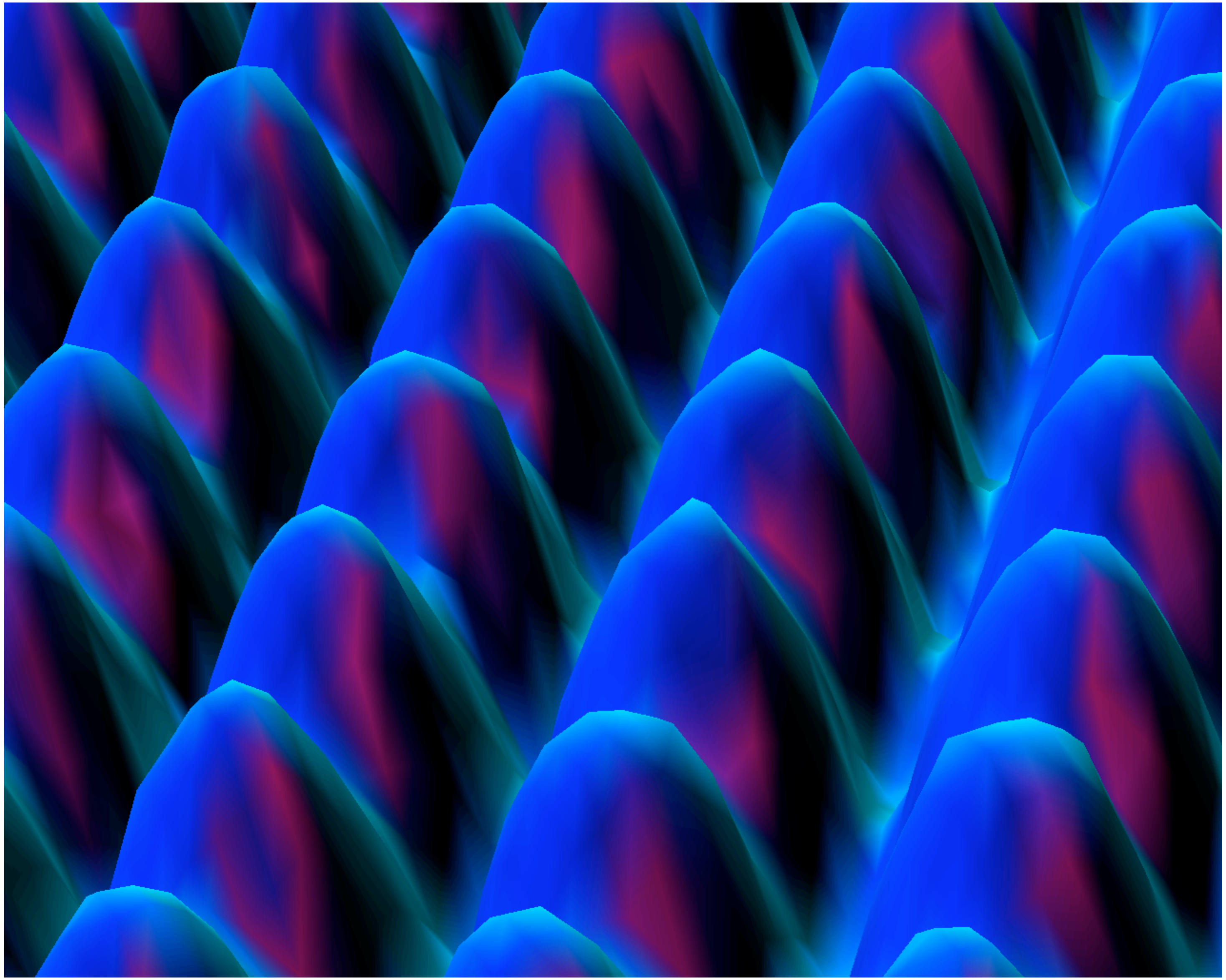
Bulk Copper



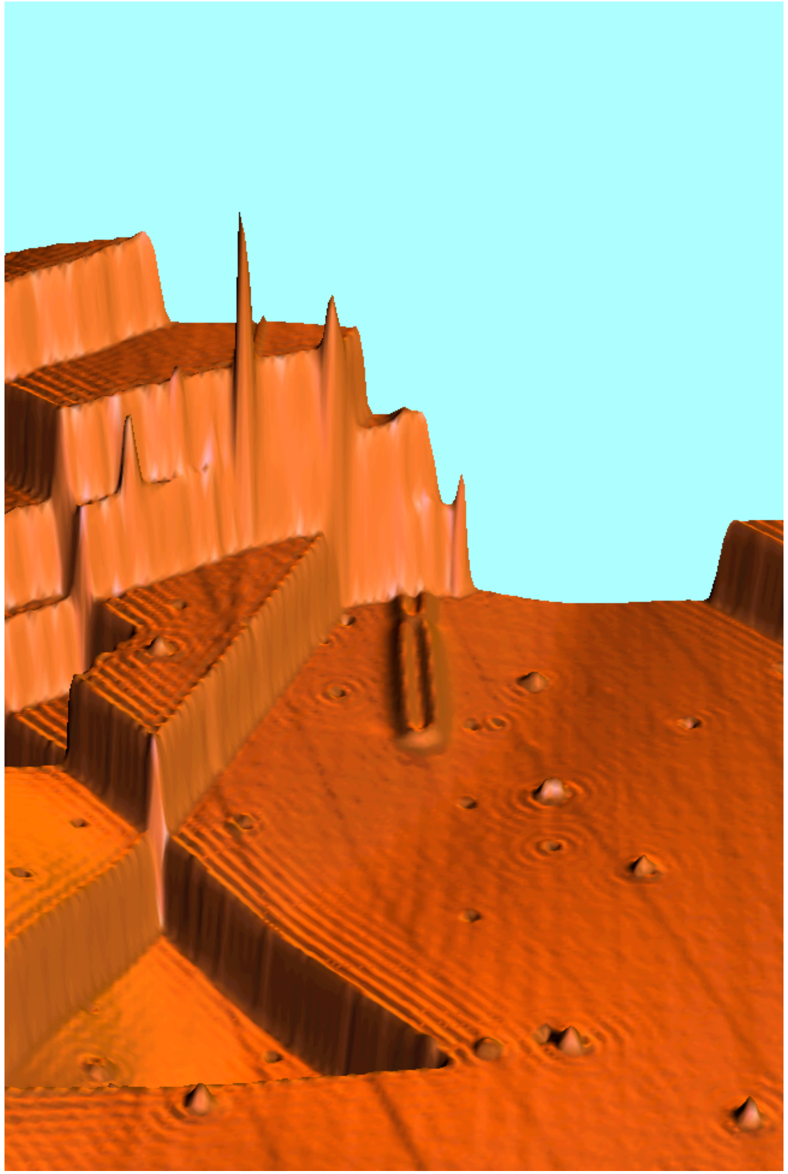
Copper (111) Surface



Nickel (110) – STM Current Map



Copper (111) Surface

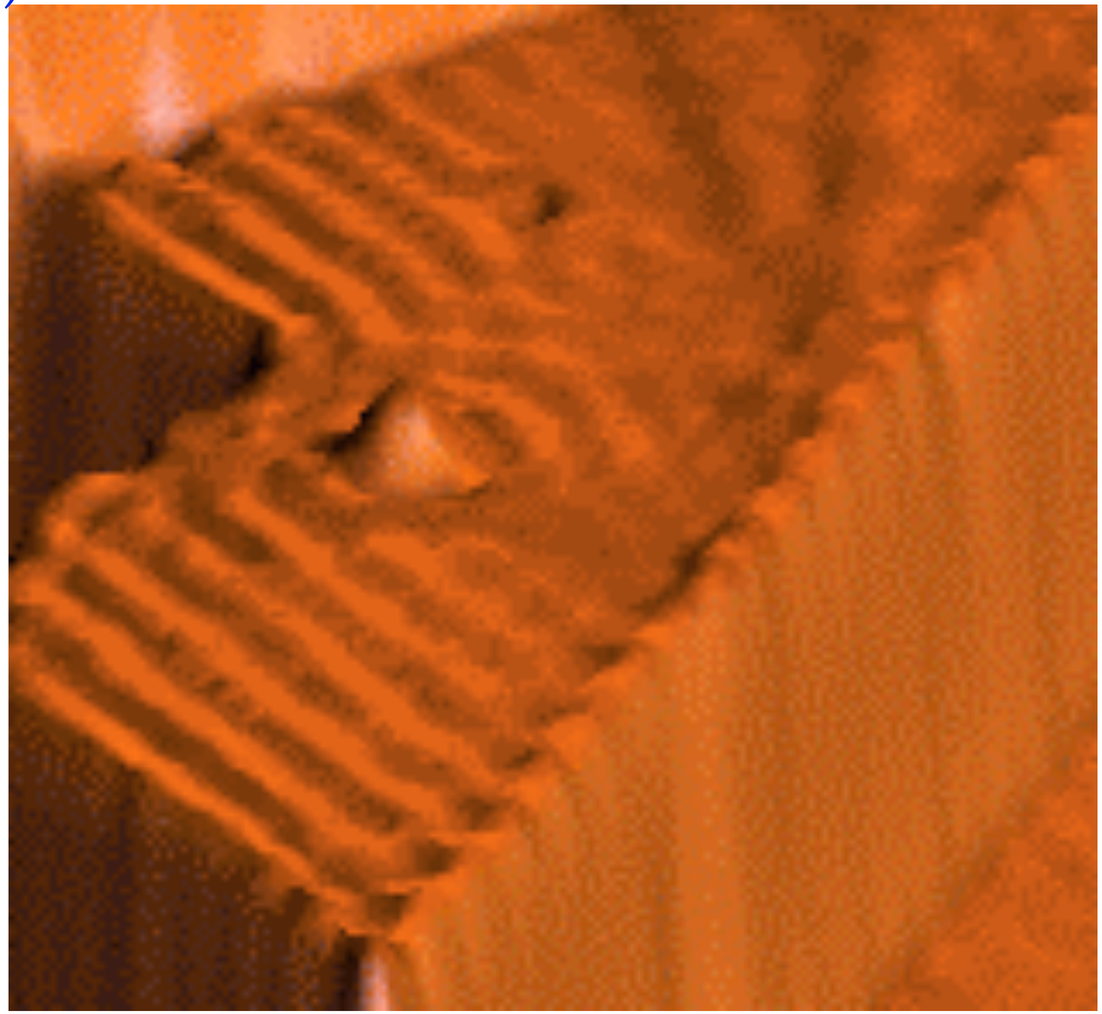


Standing waves of surface states pinned by defects and step edges.

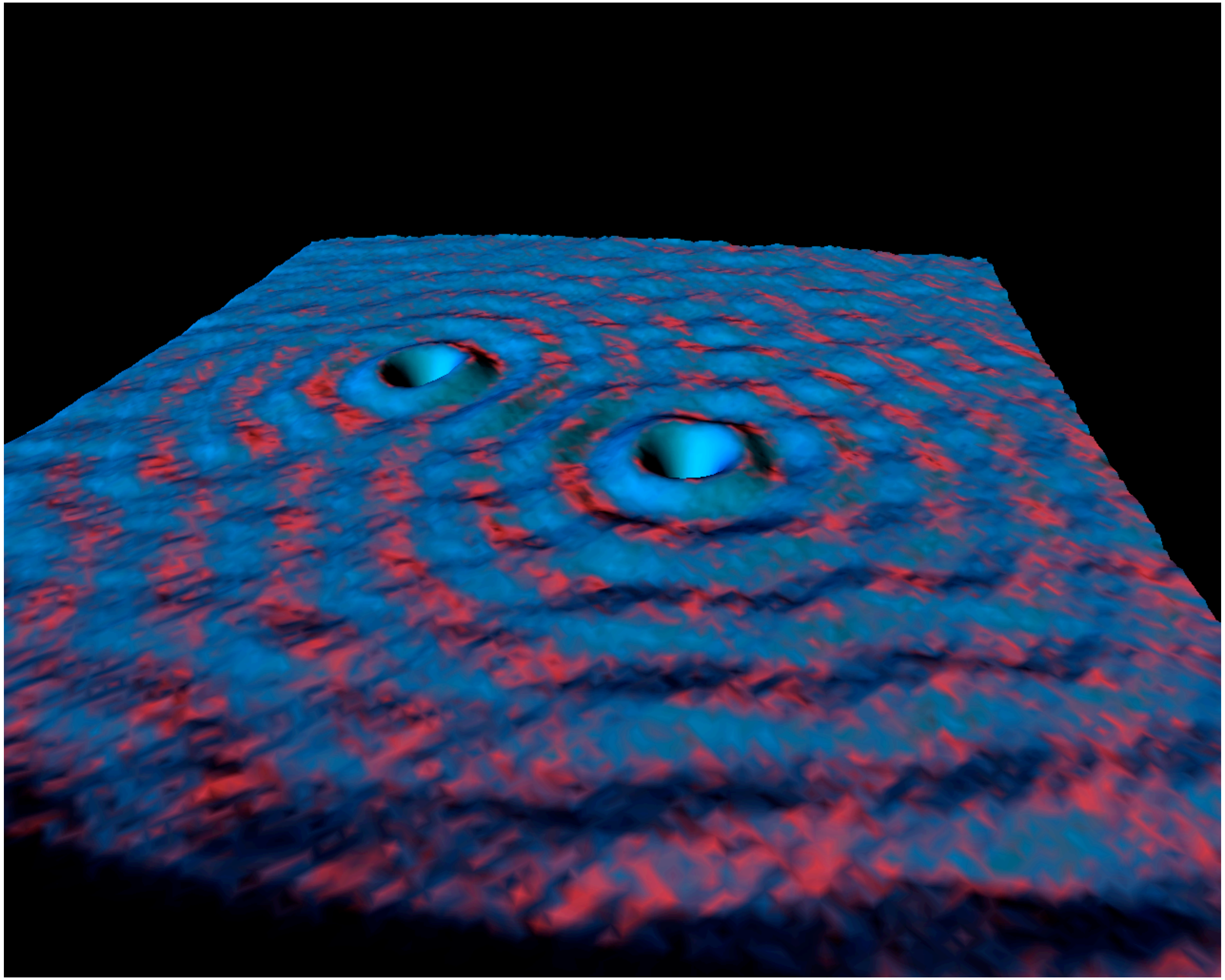
$\lambda = 15$ Å (10 bonds or so)

Cu(111) a defect

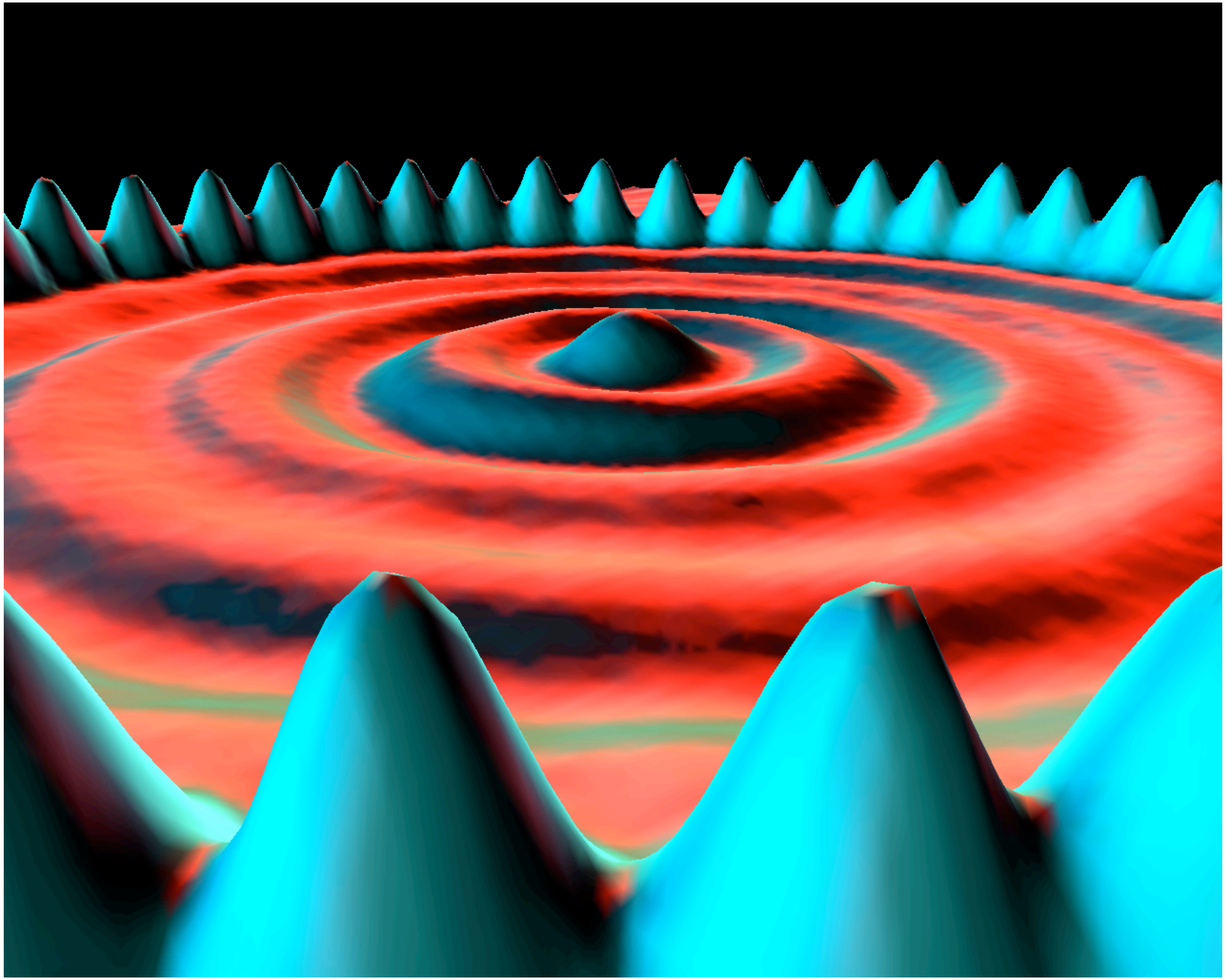
λ = 15 Å   (10 bonds or so)



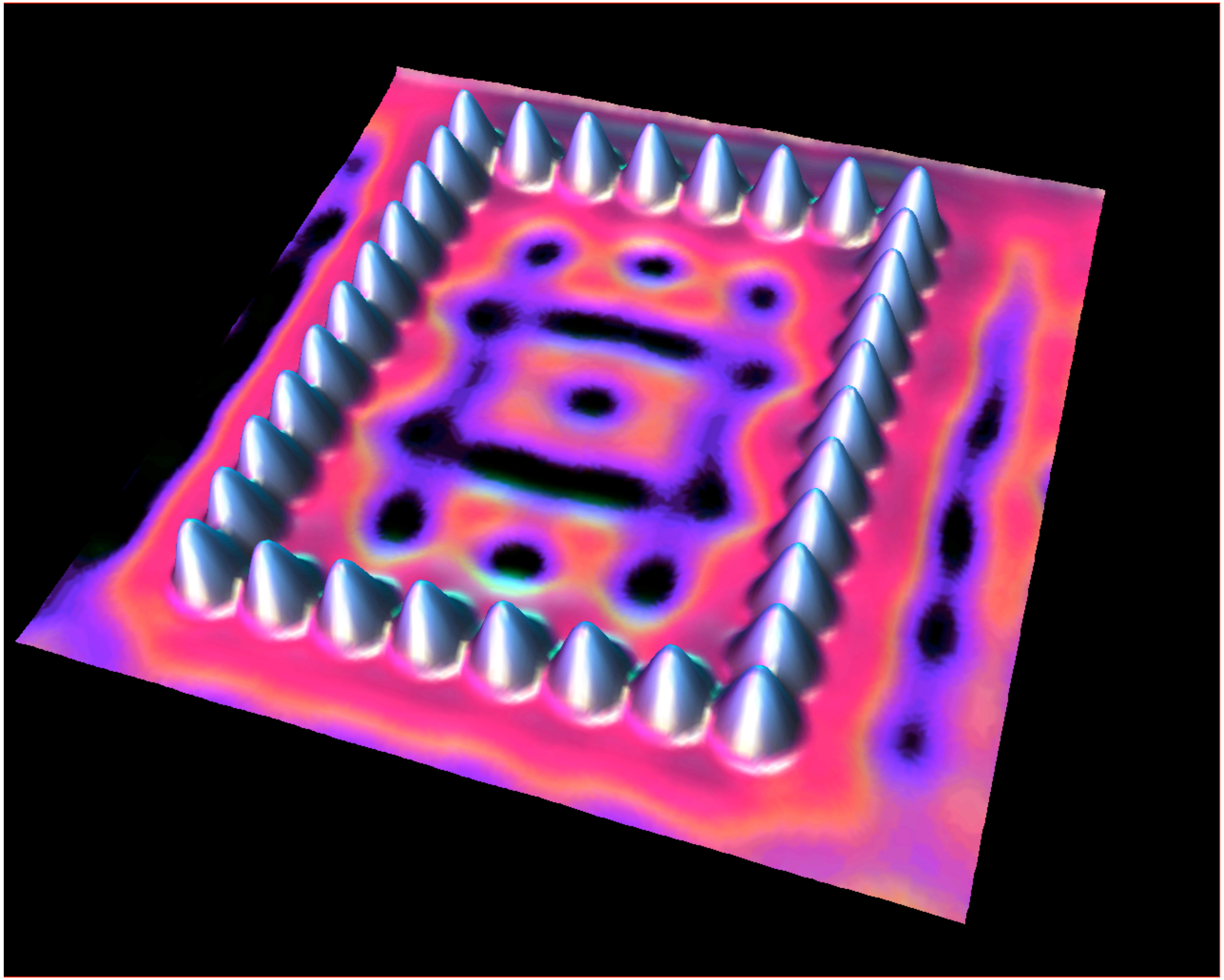
Cu(111) – "flat" surface with 2 defects



48 Fe atoms in a ring…



A Rectangular Corral



Electron Waves

To the first approximation the wavefunction of the metal is a plane wave;

By confining the waves in the coral, or pinning them using a defect you force them to become standing waves – cf: vibrations of a guitar string or the surface of a drum…

Note: The STM images wavefunctions not atoms – this is often forgotten in the literature.

Nano and Quantum !

Many of the properties of nanostructured systems are dominated by quantum mechanical effects

Practical quantum mechanics for nanostructures is **not easy**

In some cases and for some properties classical methods are appropriate (we'll come back to this)

About 1/3 of the top cited articles on nanoscience are theoretically based – to do this kind of work or to understand this literature you need some background… that is the purpose of this course.