Self-Assembled Monolayers Protecting Metal Nanoparticles

3-D SAMs

Outline

- **Introduction to nanoparticles**

- **Monolayer-Protectected Metal nanoparticles**
  synthesis, characterizations
  properties and packing of the monolayer

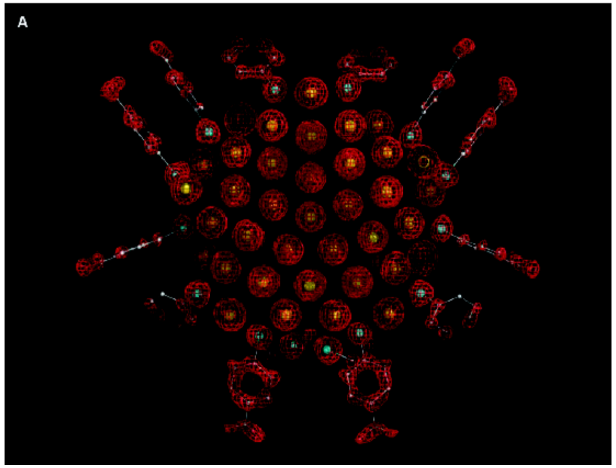
- **Functional Nanoparticles**
  Methods of synthesis. Mixed-monolayers
  Monovalent- and divalent metal nanoparicles

- **Nanoparticles of different size and shape**

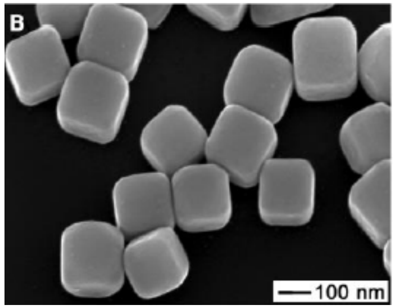
- **Applications of nanoparticles in different fields**

wich nanoparticles?

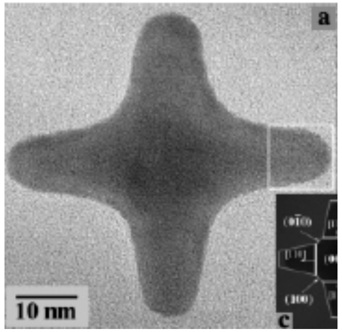
hard nanoparticles: *metal nanoparticles*
semiconductor nanoparticles
magnetic nanoparticles
silica nanoparticles



X-Ray crystal structure determination of the $Au_{102}(SR)_{44}$ *nanoparticle.*

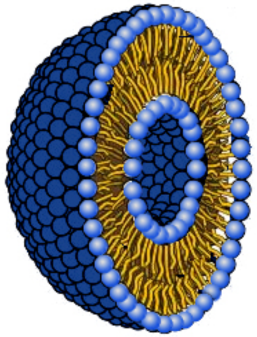


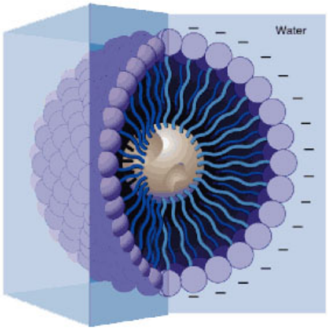
SEM image of Silver Nanocubes.

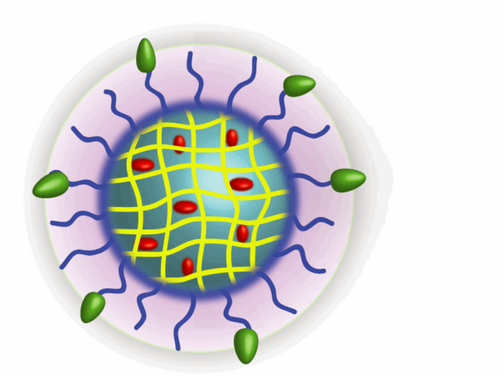


TEM image of a tetrapod nanocrystal.

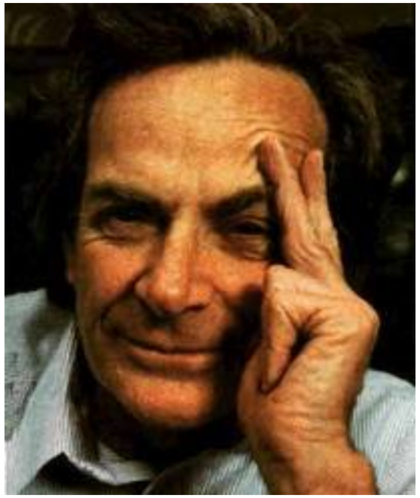
soft nanoparticles: *liposomes (100-200 nm in diameter)*
polymeric micelles (10-100 nm)
polymeric nanogels







Nano — The Interdisciplinary Science



*In December of **1959**, the eminent physicist **Richard Feynman** (1965 Physics Nobel Prize) described the future*

*in a groundbreaking talk entitled “**Plenty of Room at the Bottom** ” about the physical possibilities for*

“making, manipulating, visualizing and controlling things on a small scale,” and imaging that in decades to come, it might

be possible to arrange atoms “ the way we want.”

“Why cannot we write the entire 24 volumes of the Encyclopaedia Brittanica on the head of a pin? ”
“..... and there is no question that there is enough room on the head of a pin to put all of the Encyclopaedia Brittanica.”

What is nano?

***nano** deriva dal greco $\nu\alpha\nu o$*

***Nanoscience** refers to the science and manipulation of chemical and biological structures with dimensions in the range from 1-100 nanometers.*

Nanoscience building blocks may consist of anywhere from a few hundred atoms to millions of atoms. On this scale, new properties (electrical, mechanical, optical, chemical, and biological) that are fundamentally different from bulk or molecular properties can emerge.

Nanoscience is about creating new chemical and biological nanostructures, uncovering and understanding their novel properties, and ultimately about learning how to organize these new nanostructures into larger and more complex functional structures and devices.

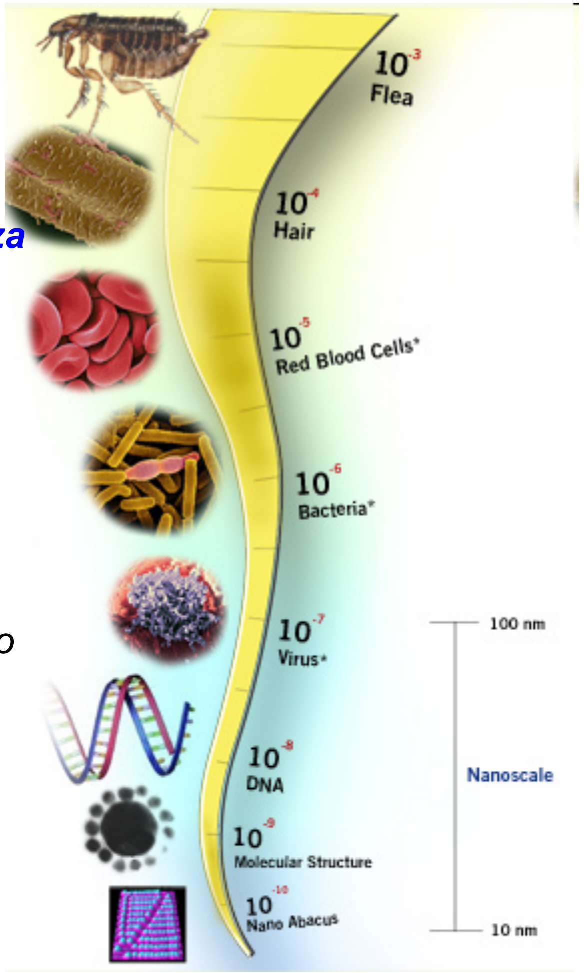
Nanoscience is a new way of thinking about building up complex materials and devices by exquisite control of the functionality of matter and its assembly at the nanometer-length scale.

Nanoscience inherently bridges disciplinary boundaries. The "nano" length scale requires the involvement of chemical concepts at the atomic and molecular level.

Nanoscale

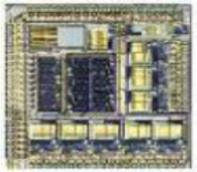
Nanoscale objects have at least one dimension (height, length, depth) that measures between 1 and 999 nanometers (1-999 nm).

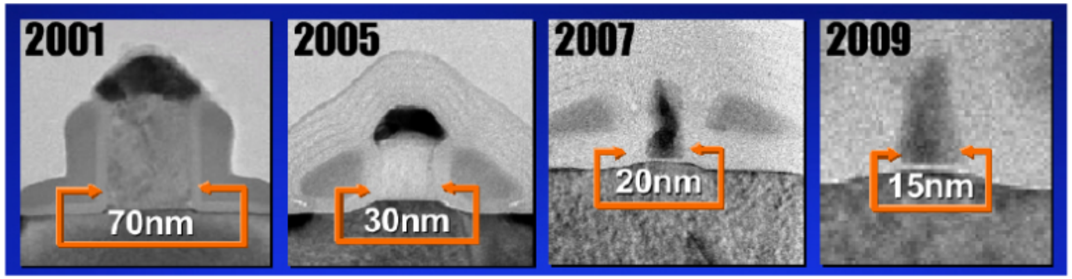
unità di misura	***abbreviazione***	***descrizione***
metro	***m***	***unità base SI della lunghezza***
centimetro	*cm*	*1×10^{-2} m (0.01 m)*
millimetro	*mm*	*1×10^{-3} m (0.001 m)*
micrometro	*μm*	*1×10^{-6} m*
nanometro	*nm*	*1×10^{-9} m la billionesima parte di 1 metro o 10 Å*



Why Nano?

Much of the motivating force and technology for nanotechnology came from integrated circuit industry





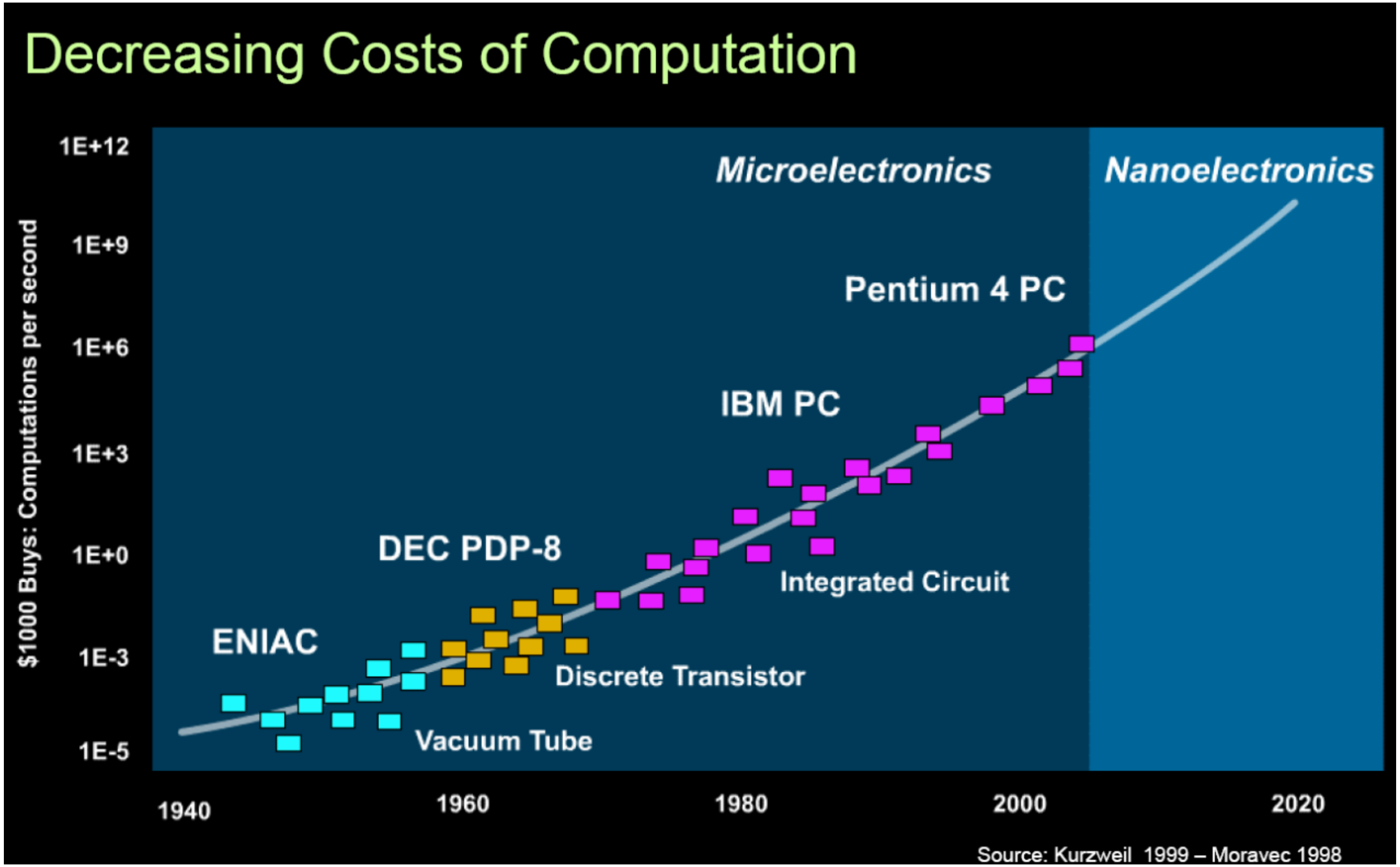
Intel's transistors

As with the fabrication of integrated circuits, nanotechnology is based on building structures and systems at very small sizes

- to enhance performance and produce new properties and applications

- for many types of systems (mechanical, biological, chemical, optical) in addition to electronic

Why Nano?



Source: Kurzweil 1999 – Moravec 1998

Why Nano?

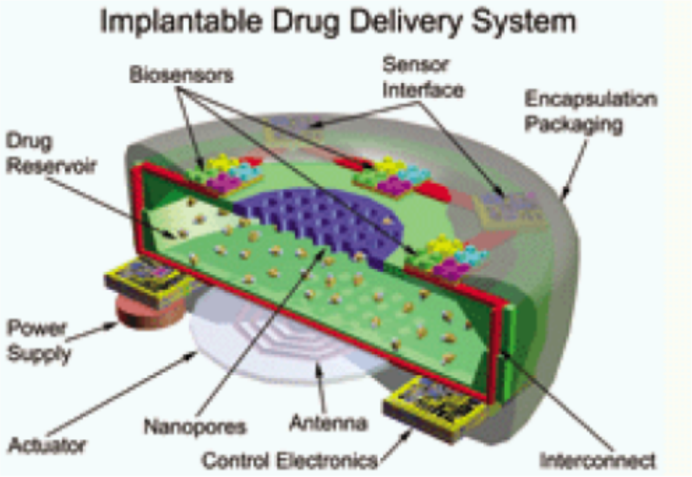
Examples of Nanotechnology Applications

- Supercomputer in your palm, perhaps made from silicon nanowires, carbon nanotubes, or organic materials such as DNA

- Very tiny motors, pumps, gyroscopes, and accelerometers; helicopters the size of flies or smaller

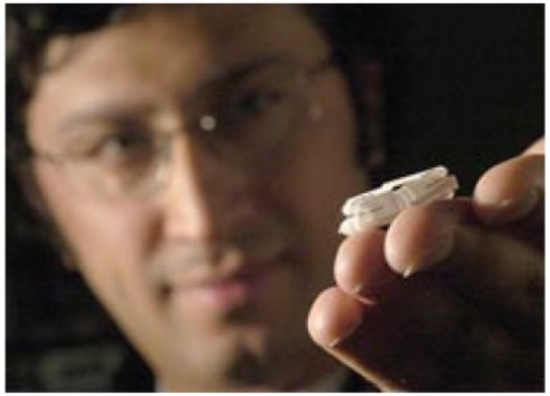
- Tiny bio- and chemical-sensors; nanoparticles that track and destroy cancer cells; artificial body parts and implantable drug delivery systems

- Nano-whiskers, nanoparticles, and nanotubes for stain and wrinkle resistant clothes, transparent zinc oxide sunscreen, fast-absorbing drugs and nutrients, extra-strong tennis racquets, and scratch-resistant paint

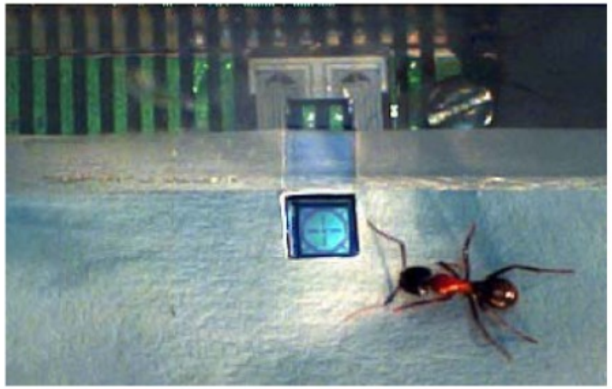


Why Nano?

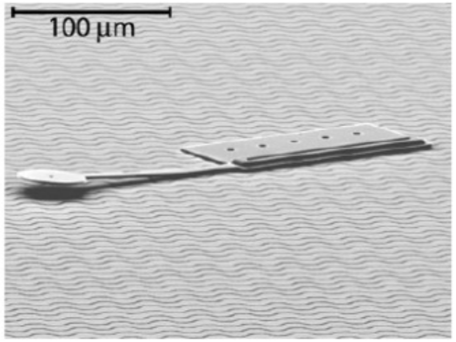
Mite spinning on micromotor
(Sandia National Labs)



"Bugbot" for traveling and taking photos in human digestive system
(Carnegie Mellon University)

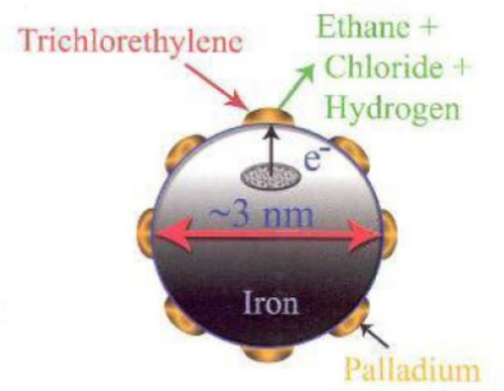


Ant's leg strength and motion measured on microsensor, for robot development (Stanford)

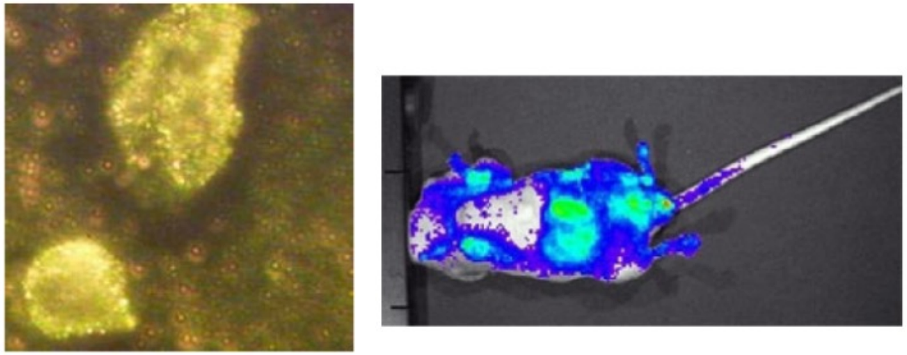


World's smallest mobile robot, with no wheels, gears or hinged joints
(Dartmouth College)

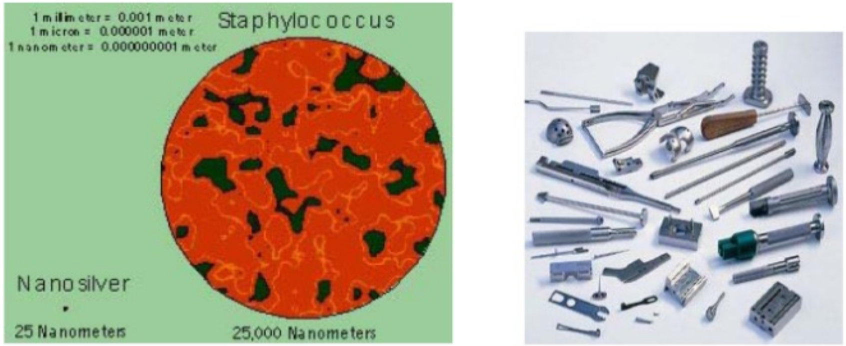
Why Nano?



Iron nanoparticles to clean poisons from water (Lehigh University)



Gold nanoparticles, some coated with antibodies, that fluoresce and heat up can track and destroy cancer cells (University of Illinois, Georgia Tech, Rice, U. Texas, and UCSF)



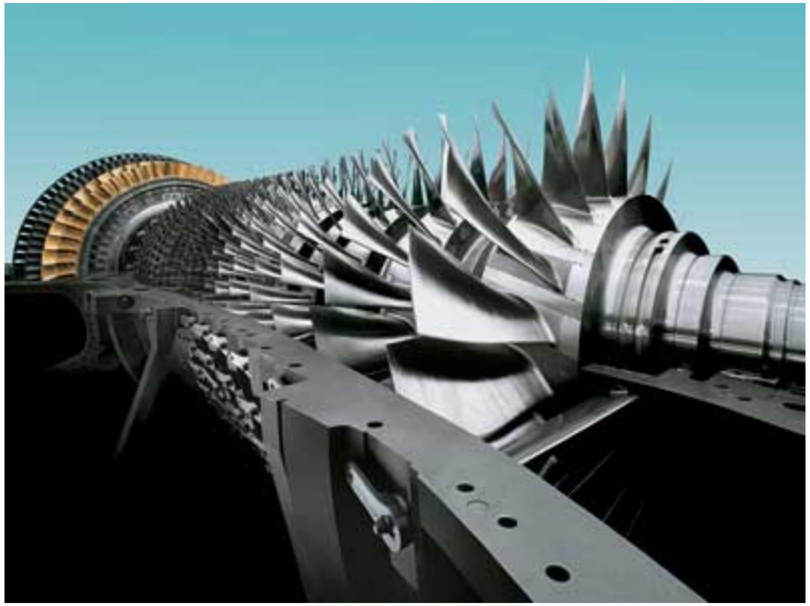
Using "Nano-silver" (solutions of silver nanoparticles) to coat medical tools, and in burn and surgical dressings, which protects against bacteria and fungus by inhibiting cellular metabolism and growth (Nanotech)

New Materials, New Products

Samsung Nano SilverSeal refrigerator
Nanosilver particles in the deodorizer unit and water dispenser sanitize the air and water that passes over them. Available only in South Korea for now.

Hummer H2 Sport Utility Truck
Made with about seven pounds of nanocomposite material, the cargo bed Hummer's H2 SUT is lighter and more scratch proof than older plastics. Besides the weight advantage, GM says the nanocomposite parts don't change shape when exposed to temperature changes.

New Materials, New Products



GE Power Turbine
Using ceramics enriched with nanoscale particles, GE hopes to build more powerful turbines that operate at higher temperatures. Available within the next five years.

NanoDynamics golf ball
This ball is engineered with nanoparticles to spin less, which should mean less slices and hooks. They'll cost $5 each.

Why Nano?

Easton CNT
(carbon nanotube)
baseball bat

ArcticShield
"stink-proof"
socks with
silver
nanoparticles

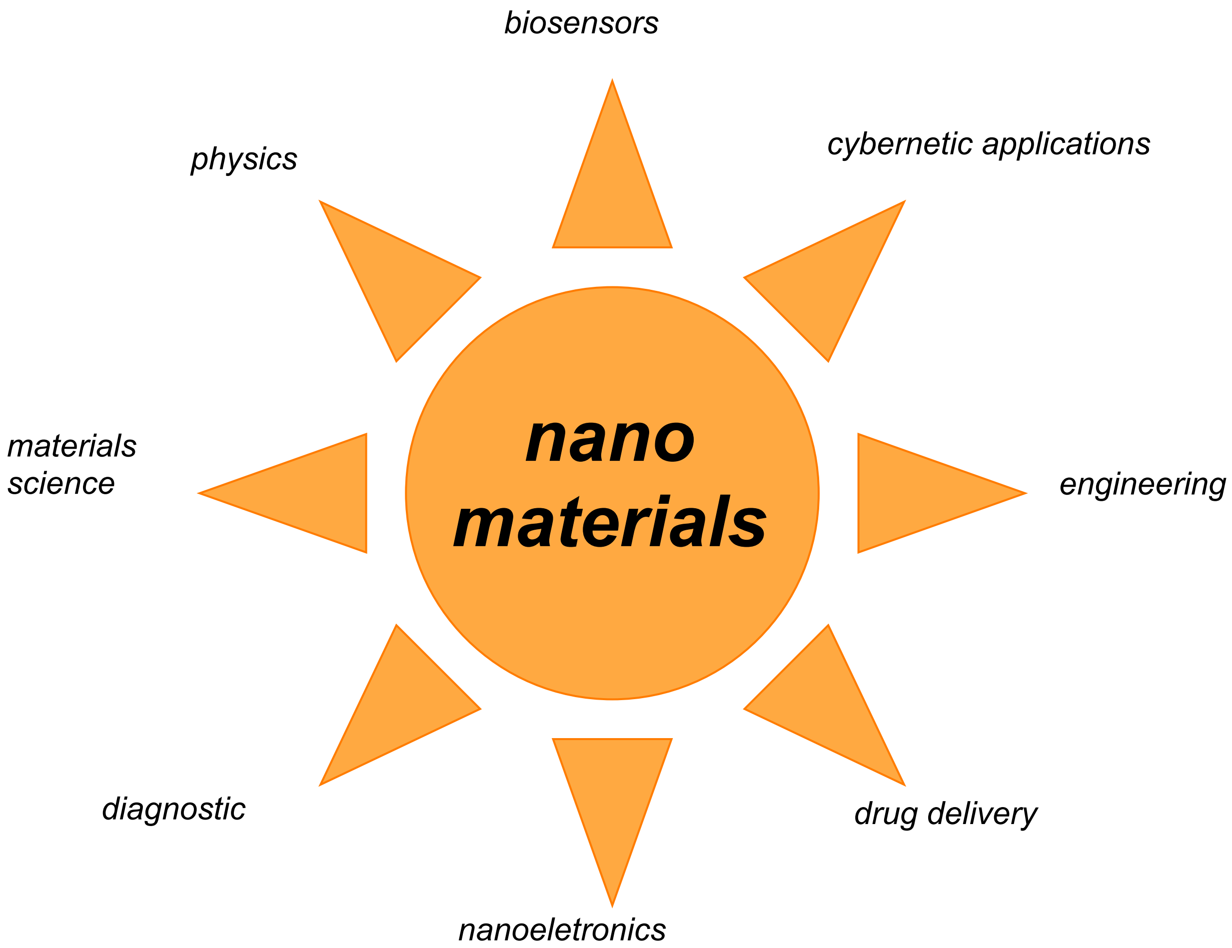
Nano Wear
sunblock with
TiO_2/ZnO_2
nanoparticles

IPOD Nano with 50nm
features in memory chip

LacVert Nano
hydrating cream

Zelens Fullerene
C-60 (buckyball)
Face Cream to
"attract and
neutralise the
damaging free
radicals"

design, creation and characterization of nanostructures and nanostructured materials


biosensors

physics

cybernetic applications

nano materials

materials science

engineering

diagnostic

drug delivery

nanoeletronics

Nanotechnology and Nanochemistry

Nanotechnology *is …*

…research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1 –100 nm …

National Science Foundation

Le nanotecnologie operano in un ambito d'investigazione ***multidisciplinare****, coinvolgendo molteplici settori di ricerca, tra cui:*

biologia molecolare,
chimica,
scienza dei materiali,
fisica (sia applicata che di base),
ingegneria meccanica,
ingegneria chimica ed elettronica.

Nanochimica*: l'insieme dei processi chimici che consentono di fabbricare nanomateriali a partire da semplici mattoni, "building blocks".*

Literature

books

Colloidal Gold. Principles. Methods, and Applications
M. A. Hayat, 3 volumi, Academic Press, 1989

Nanoparticles. From Theory to Application
Edited by Günter Schmid, Wiley-VCH, 2004

Metal Nanoparticles: Synthesis, Characterization, and Applications.
Edited by D. L. Feldheim and C. A. Foss; M. Dekker, Inc., 2002.

Supramolecular chemistry of organic- inorganic-hybrid material.
K. Rurack, R. Martinez-Manez Eds. Wiley, New York, 2010.

reviews

Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology
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Large Clusters and Colloids. Metals in the Embryonic State
G. Schmid, *Chem. Rev.* **1992**, *92*, 1709.

Chemistry Change with Size
C. N. R. Rao, G. U. Kulkarni, P. J. Thomas, P. P. Edwards, *Chem. Eur. J.* **2002**, *8*, 29.

On the development of colloidal nanoparticles towards multifunctional structures and their possible use for biological applications
T. Pellegrino, S. Kudera, T. Liedl, A. Muñoz Javier, L. Manna, W. J. Parak, *Small*, **2005**, *1*, 48.

Transition-metal nanoparticles in catalysis: from historical background to the state-of-the art.
Astruc, D. Nanoparticles and Catalysis (2008), 1-48.

Gold nanoparticles in nanomedicine: preparations, imaging, diagnostics, therapies and toxicity.
Boisselier E.; Astruc D. Chemical Society Reviews (2009), 38(6), 1759-82.

Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology
M. C. Daniel and D. Astruc, Chem. Rev., 2004, ***104****, 293-346.*

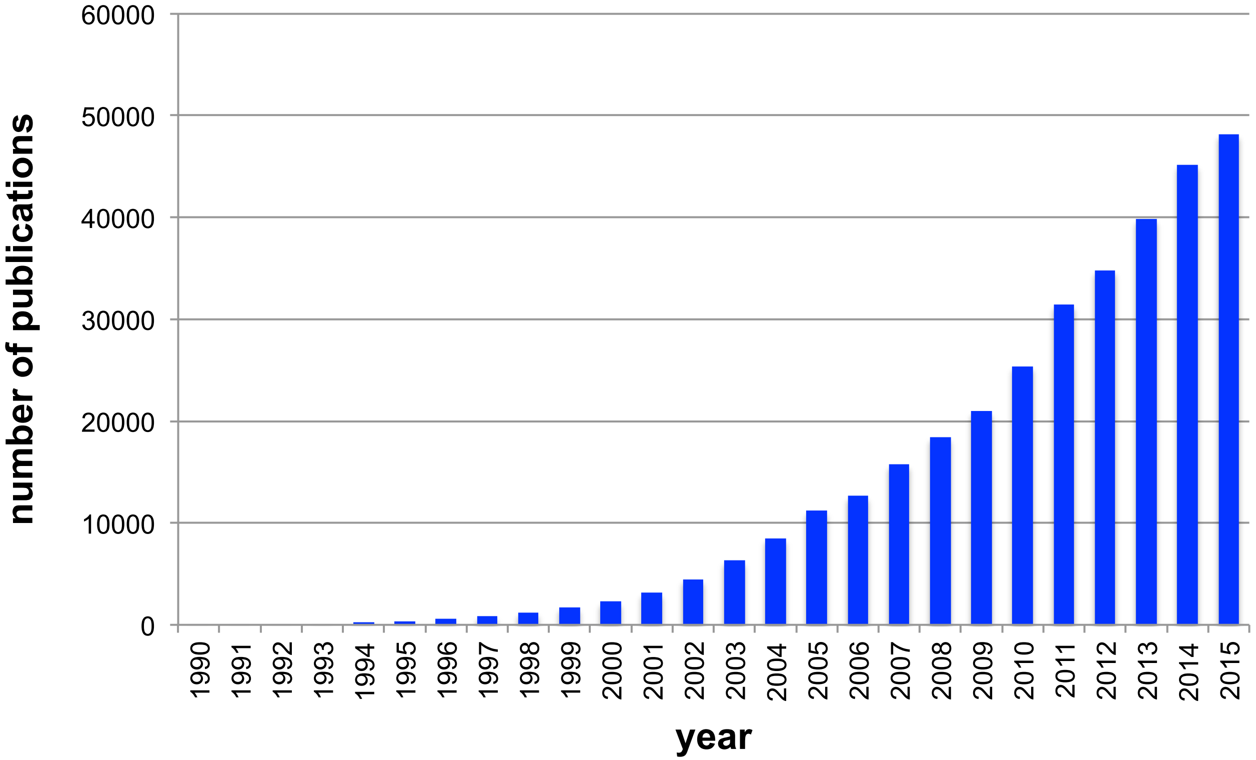
Multistage Nanovectors: From Concept to Novel Imaging Contrast Agents and Therapeutics
B. GODIN, E. TASCIOTTI, X. LIU, R. E. SERDA, M. FERRARI, Acc. Chem. Res. 2011, 44, 979-989.

and .....many, many more

…….and thousands and thousands of papers

publications

publications on nanoparticles



Why is Small Good?

-Faster

-Lighter

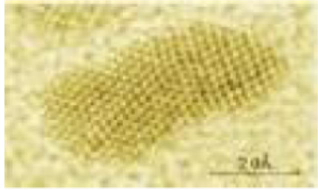
-Can get into small spaces

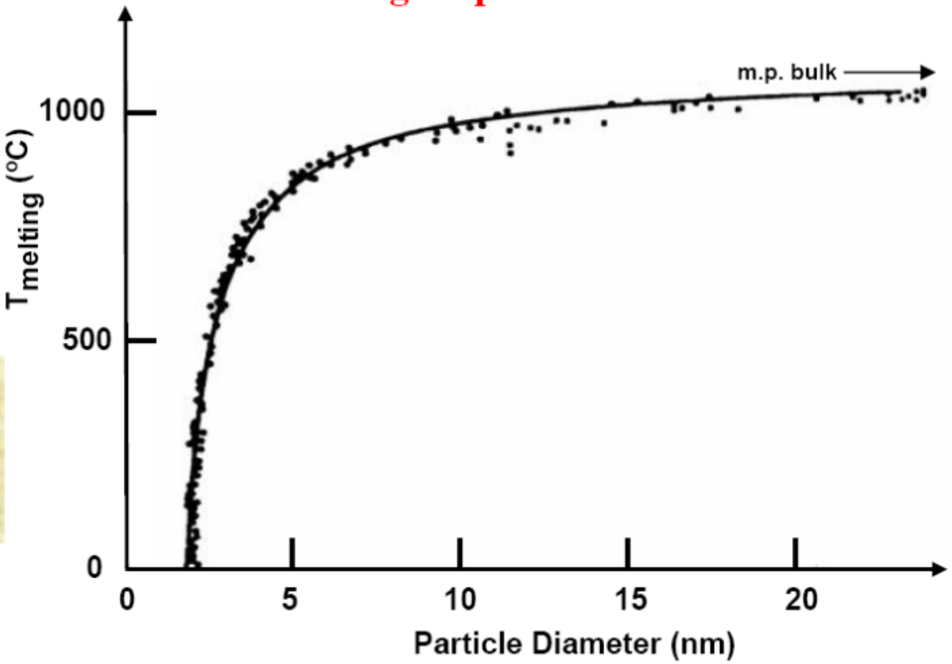
-Cheaper-More energy efficient

-Different properties at very small scale

properties at the nanoscale

- The melting point of gold decreases rapidly as the particle dimension reaches the nanometer scale.





Melting point of gold as a function of gold particle diameter

Reference: Buffat and Borel, Phys. Rev. A, vol. 13, p. 2287,1976.

A brief historical background

- gold nanoparticles are known since ancient time, 5º - 4º millenium B.C. (China, Egypt). We believe that ancient Egyptian known how to prepare "soluble" gold and they were used these solutions as "elisir".

- colloidal gold sols are used to obtain red glass

- around 1600 Paracelso (1493-1541) described the preparation of "aurum potable, oleum auri: quinta essentia auri" by reduction of acid tetrachloroauric using an alcoholic extract of plants.

  At that time medical doctors believed that "drinkable gold" exert curative properties for several diseases.

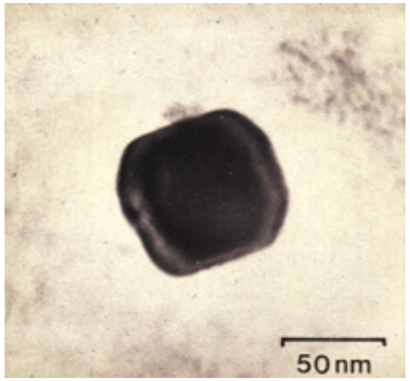
A brief historical background

The roman industry of IV century A.D., developed a sophisticated use of metal NPs, they were able to produce colored glass with particular optical properties.
For example the addition of Ag and Au compounds, enable to produce glass which appear to be green under reflected light and red under trasmitted light.
The famous "Licurgus cup" has been realized with this technique.

day light (reflected light)

trasmitted light

40 ppm of Au and 300 ppm of Ag



TEM image

Nanoparticles - hystorical background

- in 1857 Michael Faraday reported the first scientific studies on preparations of colloidal gold solutions, M. Faraday, *Phil.Trans.Roy. Soc.* **1857**, *147*, 145.
- around the half of 19th century the italian physician Enrico Selmi write a description of "colloids“, not very different from the actual definition.
- in 1861 the term "**colloid**" (from the greek *kolla)* was conied by the Scottish chemist Thomas Graham

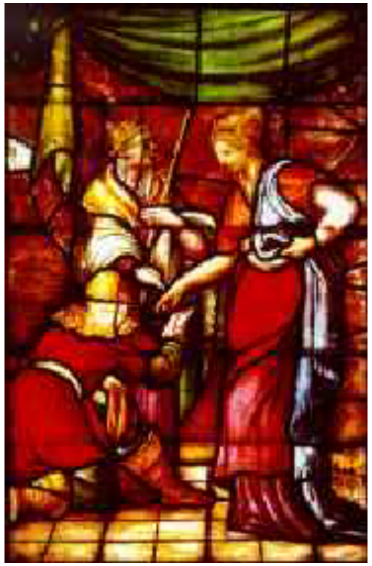
$$\left[AuCl_4\right]^- \xrightarrow[\text{reduction on } CS_2]{\text{white phosphorous}} \text{solution of colloids}$$

two phase system

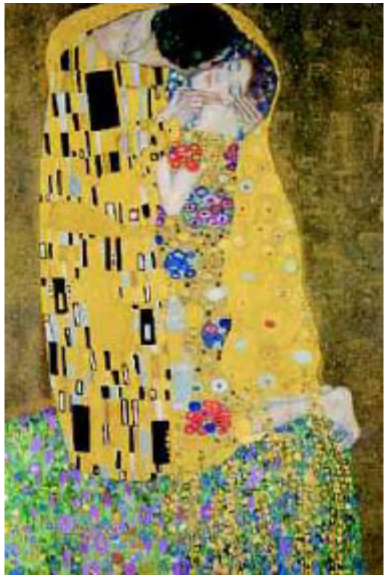
diameter of 3 ÷ 30 nm

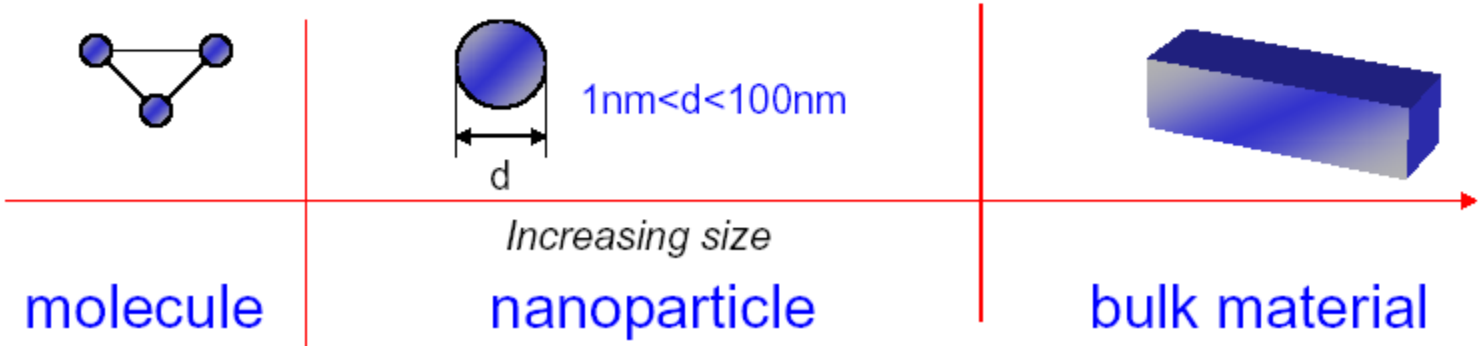
Nanoscale Materials

Florence - Santa Croce



Milan - Duomo





1nm<d<100nm

d

Increasing size

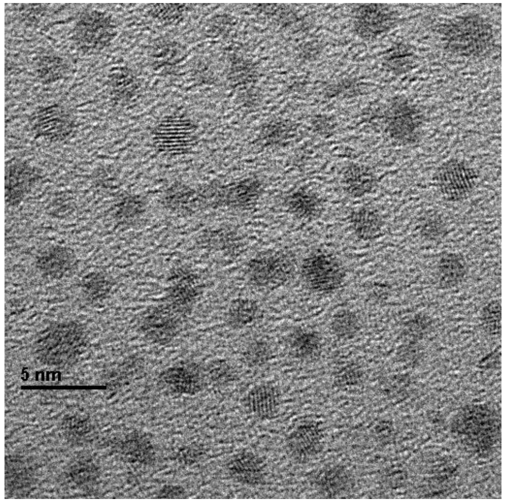
molecule

nanoparticle

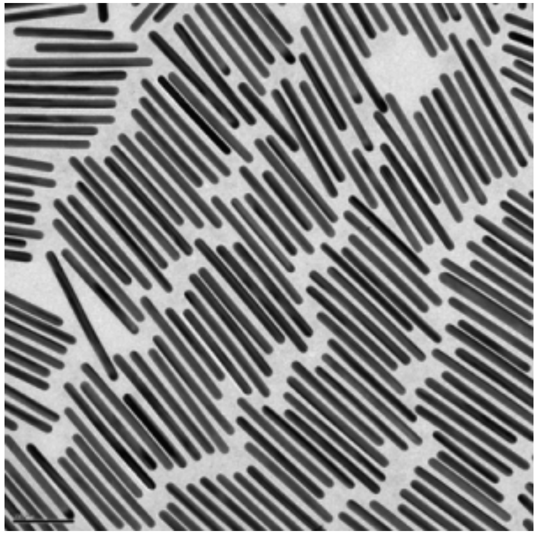
bulk material

Nanoscale materials have different properties when compared to their bulk counterparts!

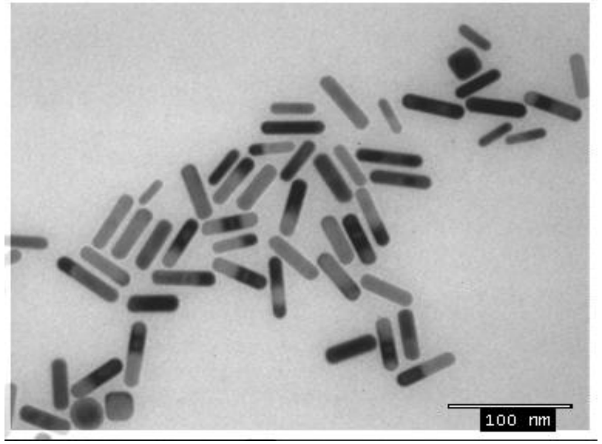
Nanoscale Materials



Nanoparticles - quantum dots



nanowires



nanorods

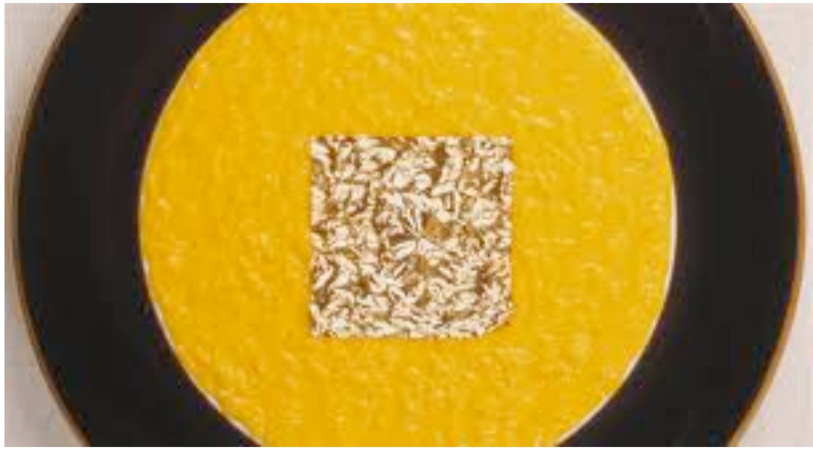
0 dimensional nanomaterials:
unique properties due to
quantum confinement
and very high surface/volume ratio

1 dimensional nanomaterials:
extremely efficient
classical properties

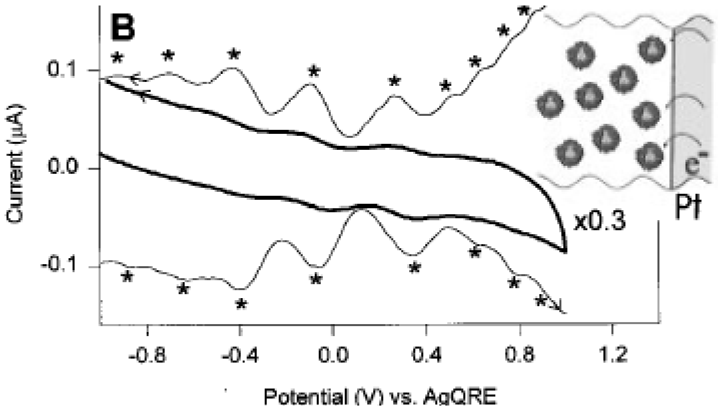
These ultra-long devices exhibit tremendous photothermal properties, converting up to 90% of incident light energy to heat.

Properties of Metal Nanoparticles

Optical Properties



Electronic Properties



Nanoscale Materials Have Different Properties when compared to their bulk counterparts!

Nanoscale Materials

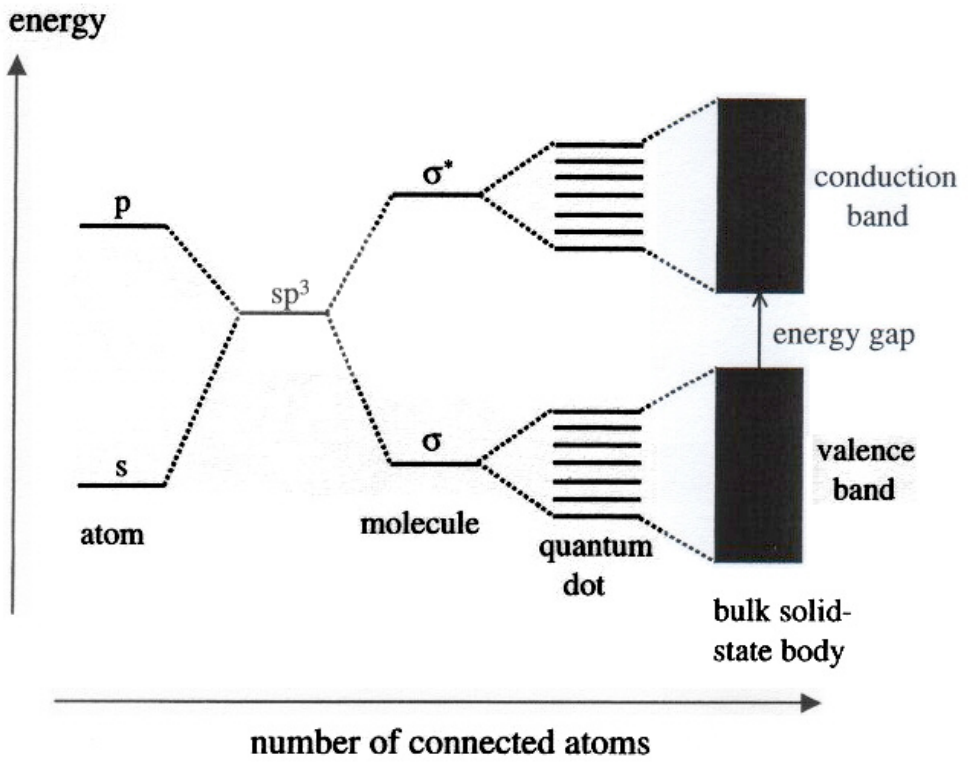


Fig. 2-1 Electronic energy levels depending on the number of bound atoms. By binding more and more atoms together, the discrete energy levels of the atomic orbitals merge into energy bands (here shown for a semiconducting material) [16]. Therefore semiconducting nanocrystals (quantum dots) can be regarded as a hybrid between small molecules and bulk material.

Synthesis of metal nanoparticles

***PVD** (physical vapor deposition)*
formation of clusters in the gas phase - Au metal as strating material
for example, the nanoparticles are formed from bulk metal by irradiating it with a laser beam.
At low laser flux, the material is heated by the absorbed laser energy and evaporates
or sublimates and deposited over a solid support, under UHV condition.

es. cathodic arc deposition, sputter deposition, electron beam physical vapor deposition, laser ablation

***CVD** (chemical vapor deposition)*
organometallic compounds as starting material
In a typical CVD process, the wafer (substrate) is exposed to one or more volatile precursors,
which react and/or decompose on the substrate surface to produce the desired deposit.
Frequently, volatile by-products are also produced, which are removed by gas flow through
the reaction chamber.

problem: control of the NP size

Synthesis of metal nanoparticles

- control of size, shape and composition with synthetic methodologies that allows to produce significative quantities of NPs.

- **molecular approach to colloidal metals**: use of molecular precursors

- many of the known methods are applicabile to different metallic elements of the periodic table, for exemple the reduction with hydrides.

- colloidal NPs are unstable and aggragate if not stibilized

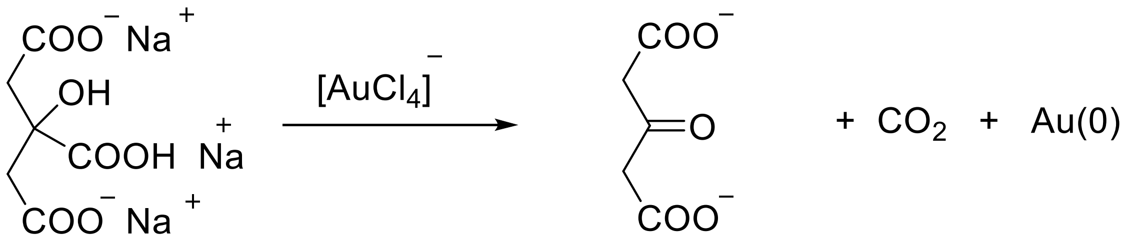
Synthesis of metal nanoparticles

Two methods against aggregation:

- **electrostatic stabilization**
- **steric stabilization**

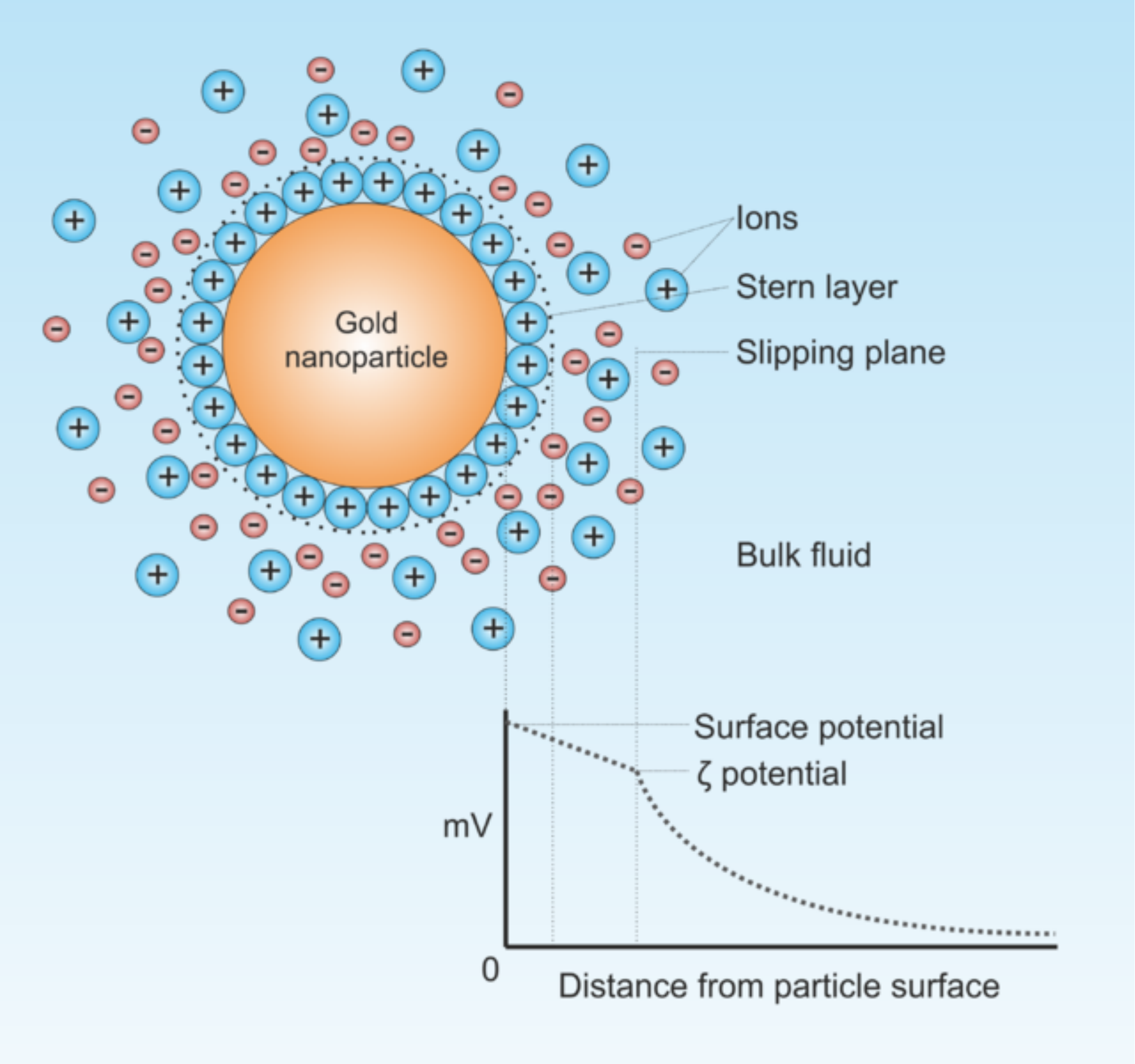
- 12-64 nm J. Turkevitch, P. C. Stevenson, J. Hillier, *Disc. Farady Soc.* **1951**, *11*, 55.

Reduction with **sodium citrate** developped by Frens in 1973: this is the most used method for the preparation of gold colloids.



it is easy
•it requires only water
•it requires skills
•has reproducibility issues

NPs size may increases using more diluted solutions.



Potential difference as a function of distance from gold nanoparticle surface. ***Larryisgood***

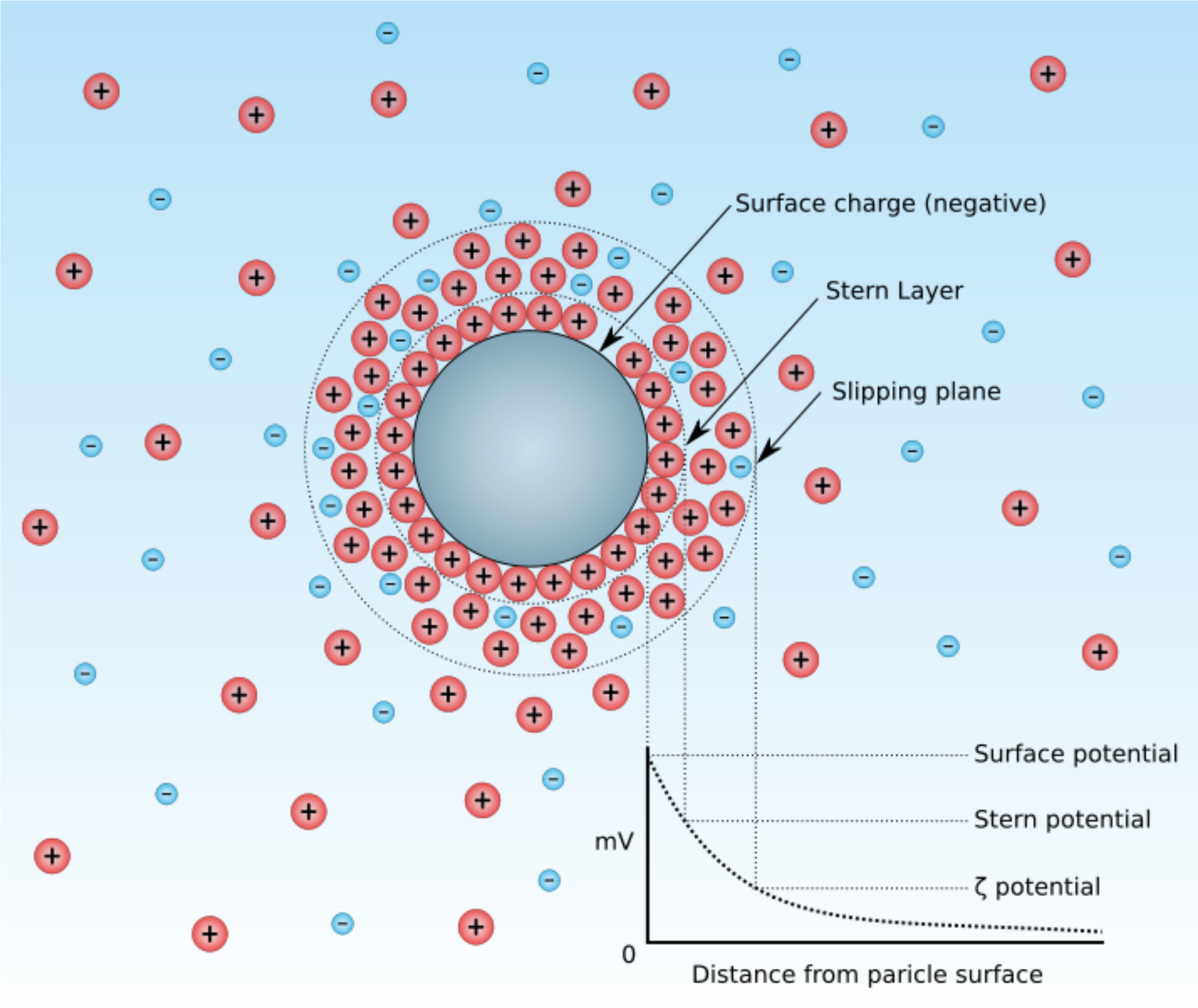


Diagram showing the ionic concentration and potential difference as a function of distance from the charged surface of a particle suspended in a dispersion medium.

Synthesis of metal nanoparticles

Electrostatic stabilization: the electrical double layer

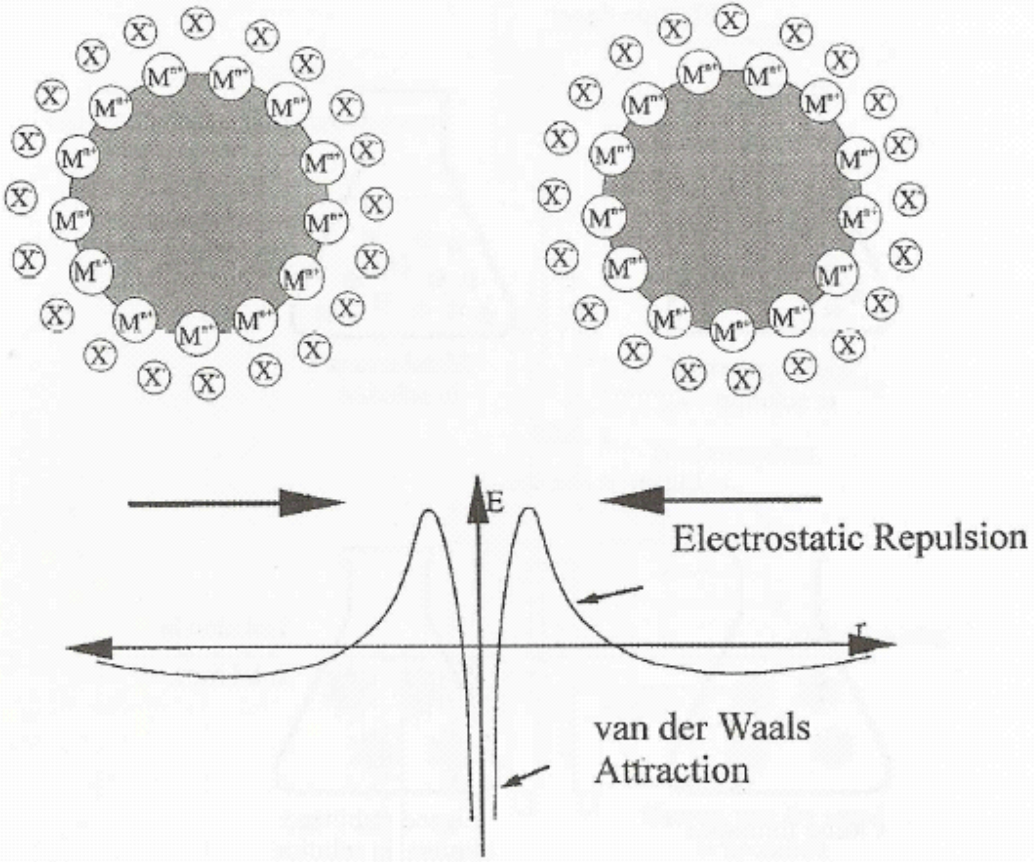


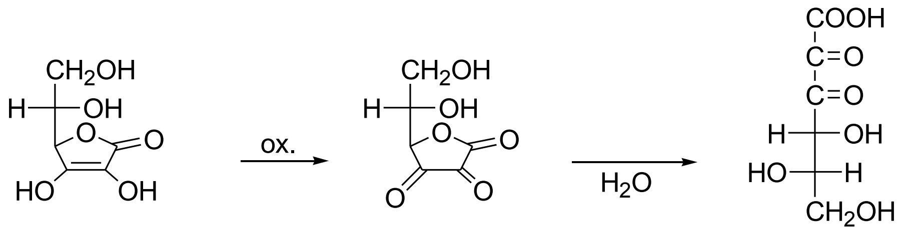
FIGURE 2.24 Electrostatic stabilization of metal colloids. Van der Waals attraction and electrostatic repulsion compete with each other.[27]

the energetic maximum can be easily overtake increasing for example the ionic strength or by increasing the thermal movement of the NPs.

Synthesis of metal nanoparticles

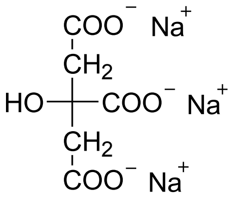
reduction of $HAuCl_4$ with different reducing agents

- 3-4 nm sodium borohydride ($NaBH_4$)
- 12 nm



ascorbic acid

- 12-64 nm



sodium citrate

Synthesis of metal nanoparticles

- the strength of the reducing agent determine the NP size

- the reaction conditions are also very important in determining the average diameter

  - the size may be reduced by: increasing reductant
    decreasing volume
    increasing stirring
    increasing temperature

Synthesis of metal nanoparticles

Steric stabilization

polymers, surfactants, and legands may be used to form a protective monolayer

polymers: they should present specific groups that bound to the NPs surface

Gold Number: quntity of polimer that stabilize 1 g of a solution of
50 mg/L of colloidal gold against aggregation in the presence of NaCl 1%

This definition was introduced by **Richard A. Zsigmondy in 1898**
Chemistry Nobel Price 1925 “for his demonstration

PVP [poly(vinylpyrrolidone)] and **PVA**, poly(vinyl alcohol) o
CTAB (cetyltrimethilammonium bromide)

These polymers have been used also to stabilize Pt and Ag NPs

Synthesis of metal nanoparticles

reduction of transition metals salts

- by using solvents that may easily be oxidized as alcohols that are oxidized to aldehydes or ketones

- Hirai and Toshima, “alcohol reduction process” and polymers for the stabilization

$$RhCl_3 + 3/2\ R_1R_2CHOH \longrightarrow Rh(0) + 3/2\ R_1R_2C{=}O + 3\ HCl$$

Other reducing agents:

Ascorbic acid, hydrogen, formaldehyde, hydrazine

- In **1993** Paul Mulvaney reports the first example of gold colloids protected by alkyl or aryl tiols. *Langmuir*, **1993**, *9,* 3408-3413.

Characterization of NPs

TEM *(transmission electron microscopy): give information about structure*
Dimension, dispersion, shape, and composition of the metal core

HRTEM si ottengono informazioni sulle distanzi interplanari, TEM in alta risoluzione.

HAADF-STEM high-angle annular dark-field imaging in the scanning electron microscope
è una tomografia elettronica adatta ad analizzare nanomateriali cristallini

H

X-ray diffraction

XRD
SAXS small-angle X-ray scattering (down to 1 nm)
anomalous SAXS (synchrotron radiatio)
WAXS wide-angle X-ray scattering

EXAFS extended X-ray absorption fine structure

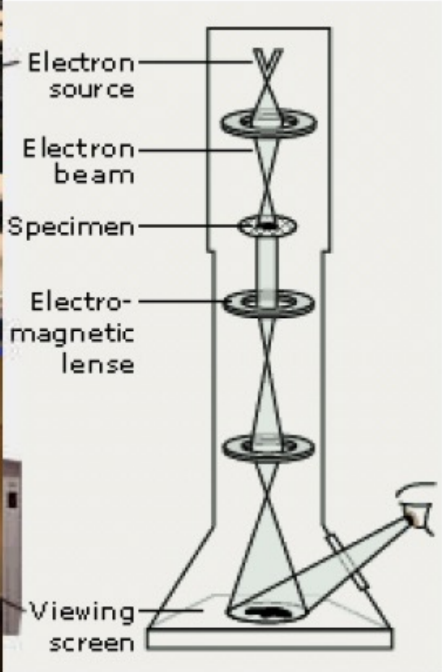
XPS X-ray photoelectron spectroscopy

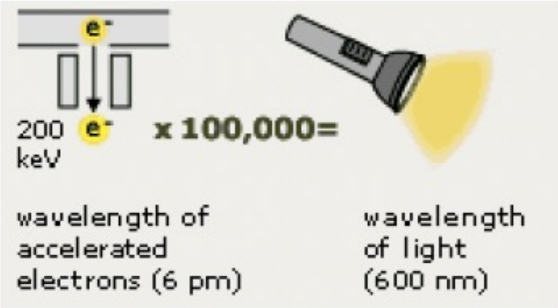
Mössbauer spectroscopy
XANES X-ray absorption near-edge structure

STS *scanning-tunneling spectroscopy*

Transmission Electron Microscope (TEM)

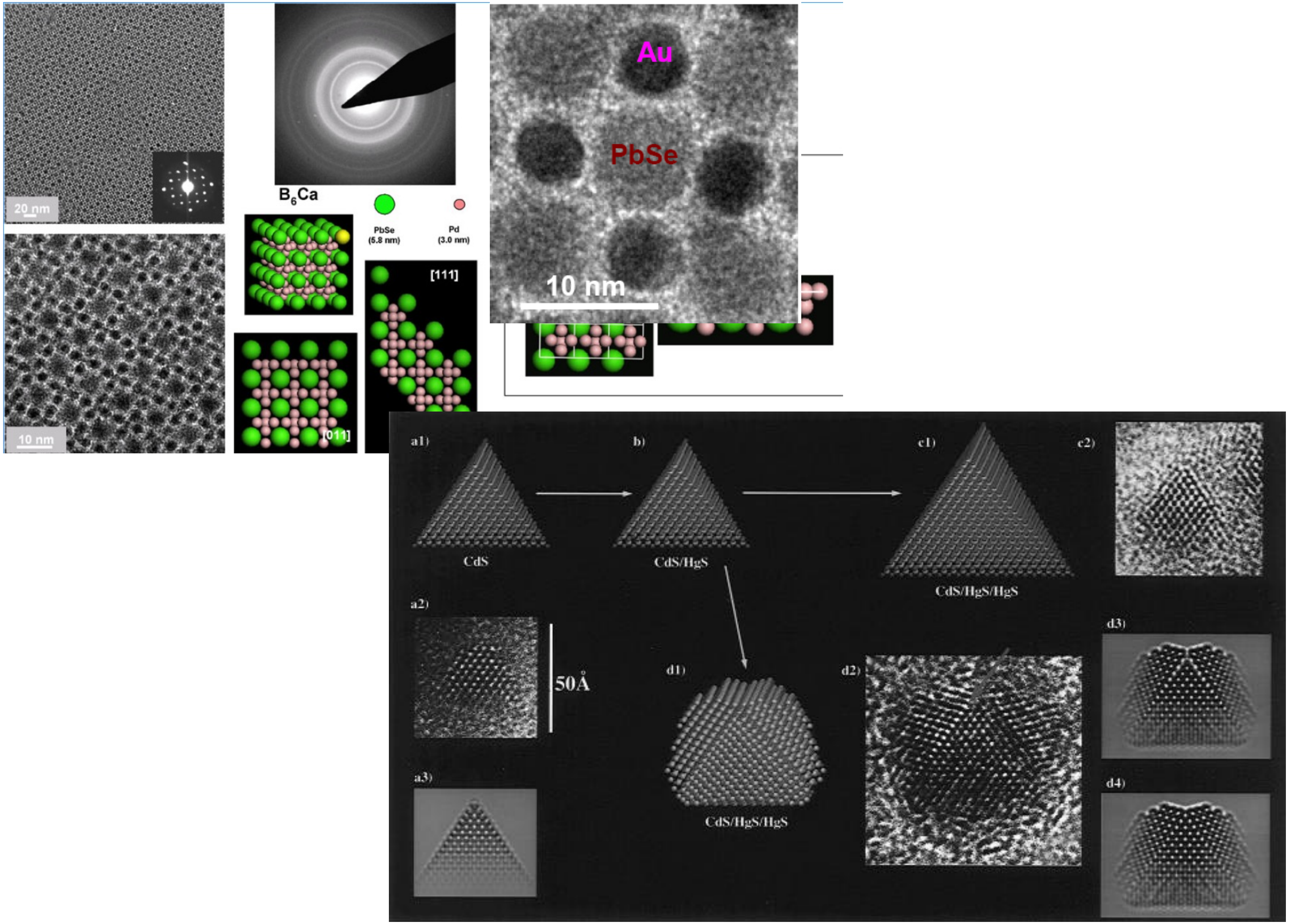
TEM
Copenhagen - 200 kV





	Optical	TEM
Radiation	*Light*	*Electrons*
Lenses	*Glas*	*Magnetic fields*
Wavelength	*ca. 0,5 μm*	*ca. 2 picometer*
Resolution	*ca. 0,5 μm*	*0,1 - 0,2 nm*
Sample thickness	*ca. 25 - 50 μm*	*ca. 10 - 200 nm*

- Å resolution
- *Transmission*,
  ie only thin slices


20 nm
10 nm
B_6Ca
PbSe (5.8 nm)
Pd (3.0 nm)
[111]
[011]
Au
PbSe
10 nm
a1)
b)
c1)
c2)
CdS
CdS/HgS
CdS/HgS/HgS
a2)
50Å
d1)
d2)
d3)
d4)
a3)
CdS/HgS/HgS

NANOPARTICELLE - SINTESI

Au, Pd, Pt,

full-shell clusters: clusters are like onions, each atom like to complete his coordination

for metals the coordination number is 12

↓

the first full-shell cluster is composed of 1+12 = 13 atoms

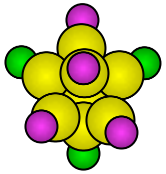
the shell *n*th includes $10n^2 + 2$ atoms

***n* shell**	1	2	3	4	5	6	7	8	9	10
n. atoms last shell	12	42	92	162	252	362	492	642	812	1002
n. total atoms	13	55	147	309	561	923	1415	2057	2869	3871
% surface atoms	92.3	76.4	62.6	52.4	44.9	39.2	34.8	31.2	28.3	25.8
average d (nm)		1.4	1.9	2.0	2.8	3.0			4.4	4.6

UNDECAGOLD

Step 1. $HAuCl_4 + 2PPh_3 + H_2O \xrightarrow[]{\text{EtOH or THF}} Ph_3PAuCl + Ph_3PO + 3HCl$

Step 2. $Ph_3PAuCl + NaBH_4 \xrightarrow[]{\text{EtOH or THF}} \boxed{Au_{11}(PPh_3)_7Cl_3}$



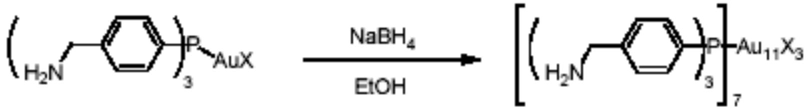
Step 3. $Au_{11}(PPh_3)_7Cl_3 + {\sim}30CH_3(CH_2)_{11}SH \xrightarrow{\text{THF}} Au_{11\text{-}13}(PPh_3)_x(SC12)_yCl_z$

Step 4. Column chromatography to remove PPh_3O, Ph_3PAuCl, $[CH_3(CH_2)_{11}S]_2$

"undecagold" derivatives have been widely used as markers of biological compounds and for histochemical analysis

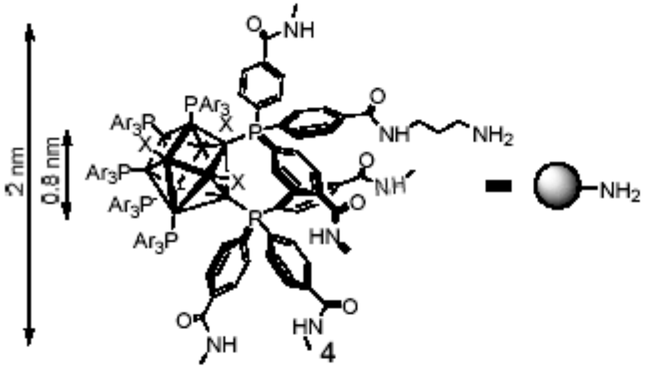
P. A. Bartlett, B. Bauer, S. J. Singer, *J. Am. Chem. Soc.* **1978**, *100*, 5085.
F. Cariati, L. Naldini, *Inorg. Chim. Acta*, **1971**, *5*, 172.

UNDECAGOLD



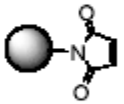
2a X = I
2b X = CN

3a X = I
3b X = CN

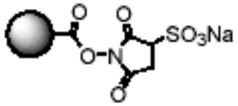


Undecagold

to bound thiols



Monomaleimido Undecagold



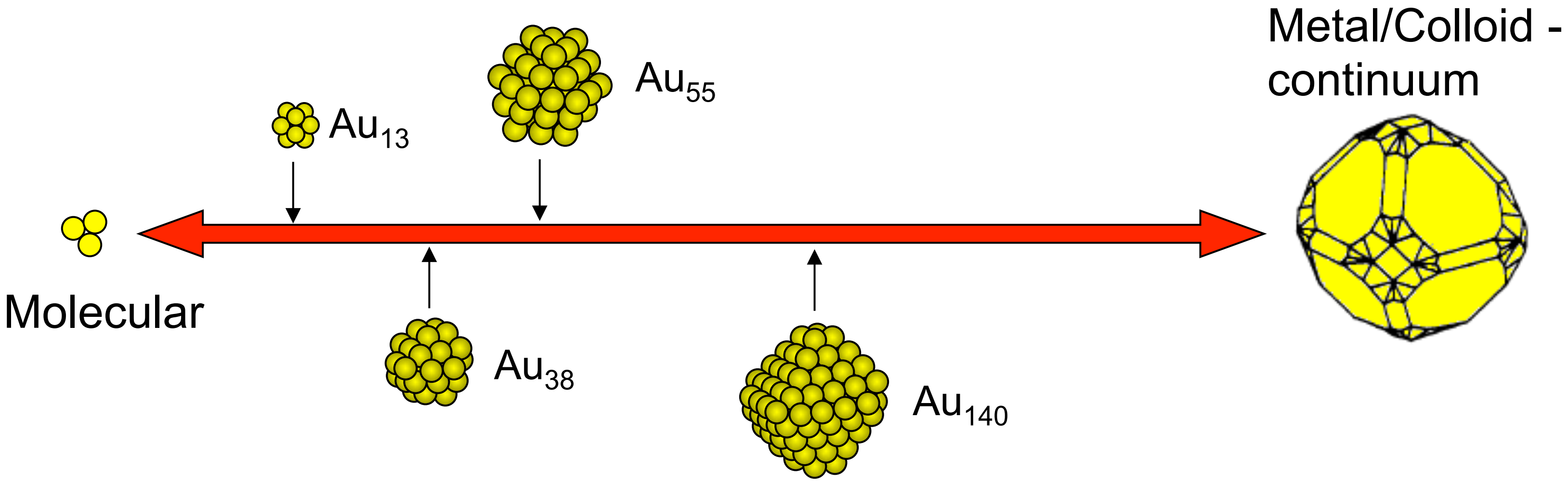
it reacts with amines

Sulfo-succinimido Undecagold

H. Yang, P. A. Frey, *Biochemistry*, **1984**, *23*, 3849, 3857, 3863.

- conjugates of peptide, ATP, nucleic acids, lipids, phospholipidis, carbohydrates, antibodies, etc. have been prepared.

Au_{55}



$Au_{55}(PPh_3)_{12}Cl_6$ is the most studied full-shell cluster since it represent a transition between molecular and colloidal behaviour

$$\mathbf{(C_6H_5)_3PAuCl} \xrightarrow[\text{Benzene 50 °C}]{B_2H_6} \mathbf{Au_{55}[C_6H_5)_3P]_{12}Cl_6}$$

29%

the syntheic method enable one to obtain a monodispersed cluster and because of this it could be used in the formation of fcc 3D crystals .

G. Schmid, P. Pfeil, R. Boese, F. Bandermann, S. Meyer, G. H. M. Calis, J. W. A. van der Velden, *Chem. Ber.* **1981**, *114*, 3634.

Au_{55}

Chromatographic Isolation of “Missing” Au55 Clusters Protected by Alkanethiolates

Hironori Tsunoyama,† Yuichi Negishi,† and Tatsuya Tsukuda*,†,‡

J. Am. Chem. Soc. **2006**, *128*, 6036.

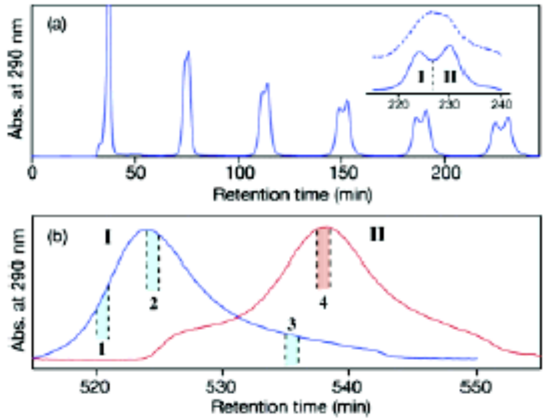


Figure 1. (a) Chromatogram of recycling GPC of the Au:SC_{18} clusters. Dotted curve in the inset is the data for the sample without etching treatment. (b) Recycling chromatograms of two fractions **I** and **II**.

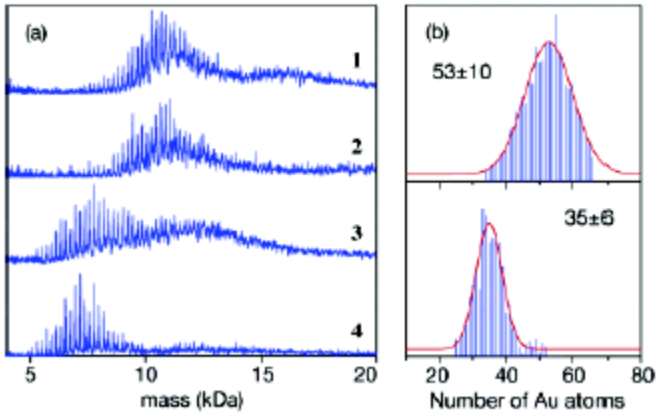


Figure 2. (a) LDI mass spectra of fractions **1**−**4** in the positive ion mode. (b) Histograms of the core numbers for fractions **2** and **4**.

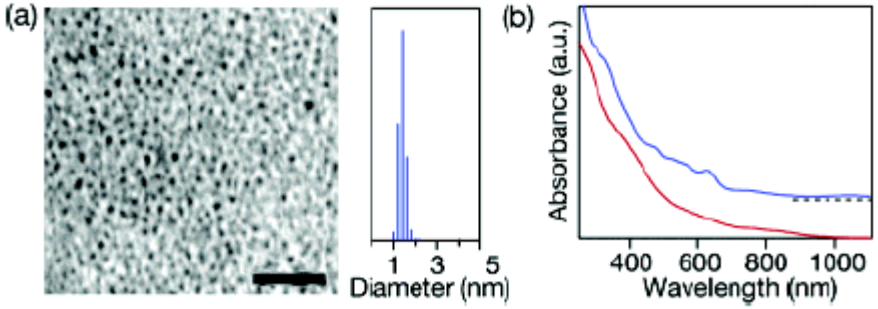
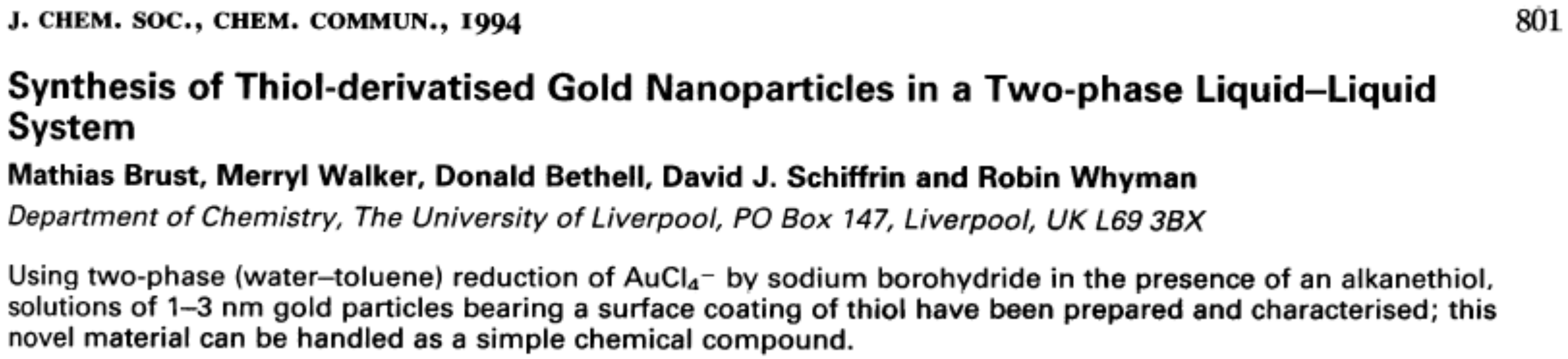


Figure 3. (a) TEM image and core-size distribution of Au_{55}:SC_{18}. The scale bar represents 20 nm. (b) Optical absorption spectra of Au_{55}:SC_{18} (red) and the 8 kDa clusters (blue).

Monolayer protected clusters MPCs



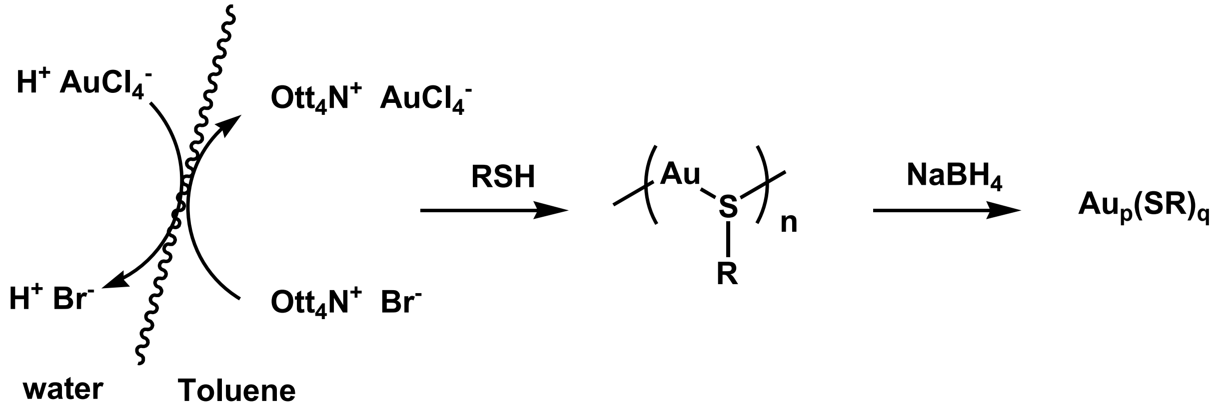
J. CHEM. SOC., CHEM. COMMUN., 1994 801

Synthesis of Thiol-derivatised Gold Nanoparticles in a Two-phase Liquid–Liquid System

Mathias Brust, Merryl Walker, Donald Bethell, David J. Schiffrin and Robin Whyman

Department of Chemistry, The University of Liverpool, PO Box 147, Liverpool, UK L69 3BX

Using two-phase (water–toluene) reduction of $AuCl_4^-$ by sodium borohydride in the presence of an alkanethiol, solutions of 1–3 nm gold particles bearing a surface coating of thiol have been prepared and characterised; this novel material can be handled as a simple chemical compound.

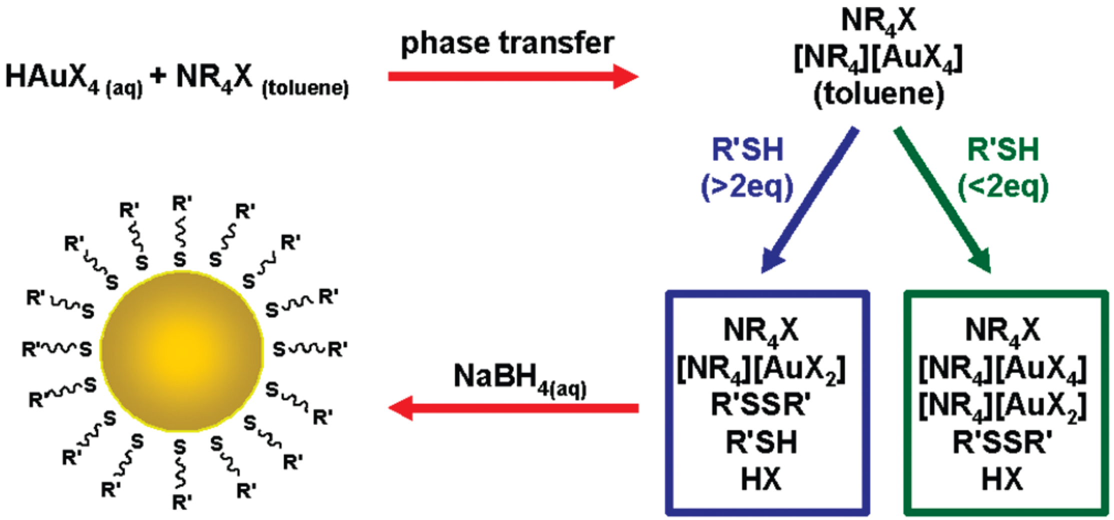


➡ MPCs OF DIFFERENT SIZE MAY BE OBTAINED USING DIFFEREN REACTION CONDITIONS:

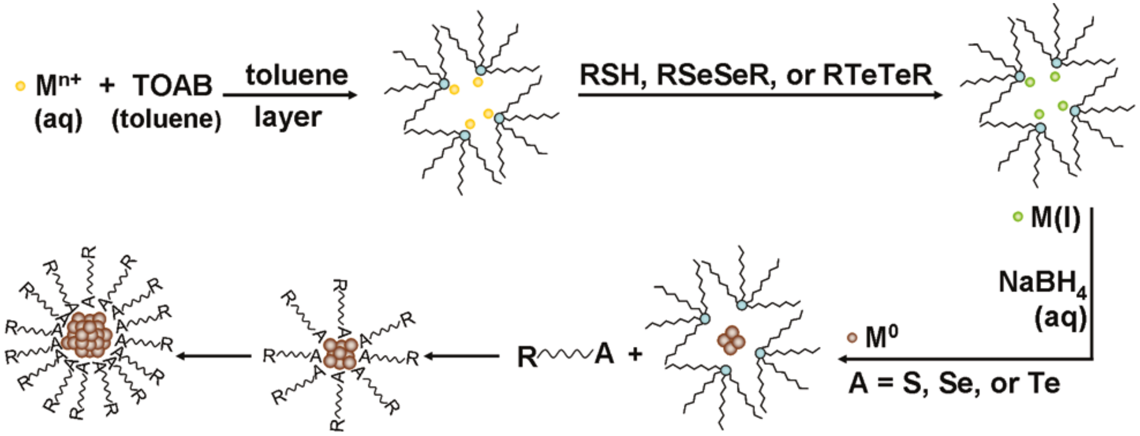
■ RATIO RSH/Au ■ REDUCTION RATE ■ TEMPERATURE

Au NPs synthesis

Revised View of the Two-Phase Brust-Schiffrin Au Nanoparticle Synthesis



P. J. G. Goulet, R. Bruce Lennox J. Am. Chem. Soc. ***2010****, 132, 9582–9584.*

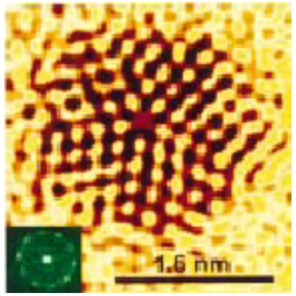


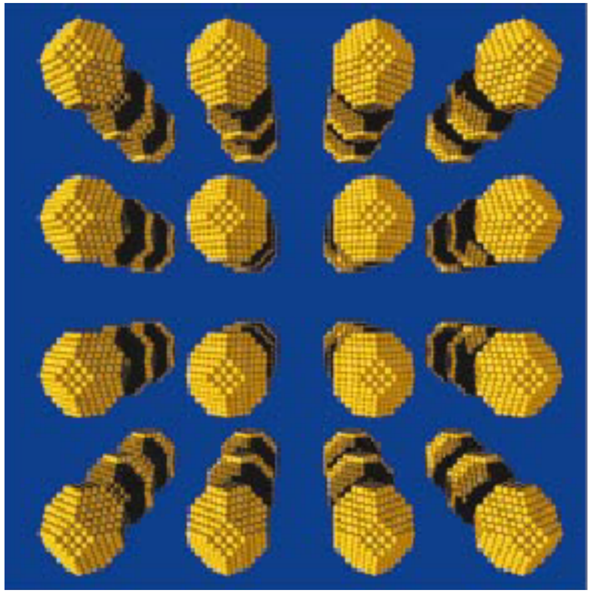
Y. Li, O. Zaluzhna, B. Xu, Y. Gao, J. M. Modest, Y. J. Tong J. Am. Chem. Soc. ***2011****, 133, 2092–2095.*

Nanoparticles – Au$_{140}$

the core

Au$_{140}$





Whetten, R. L. et al. *Acc. Chem. Res.* **1999**, *32*, 397

Nanoparticles – the core

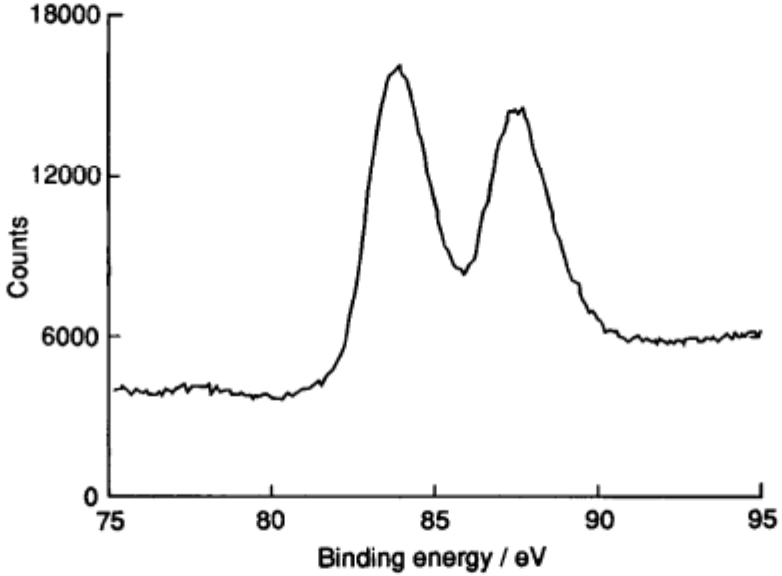
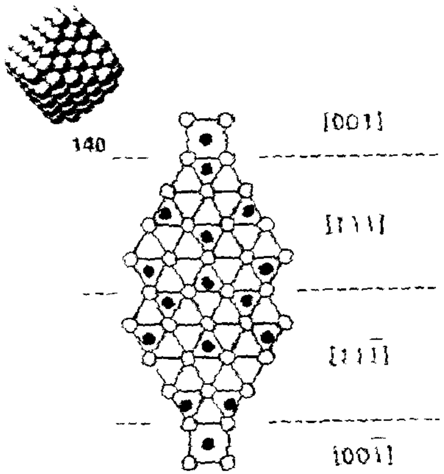
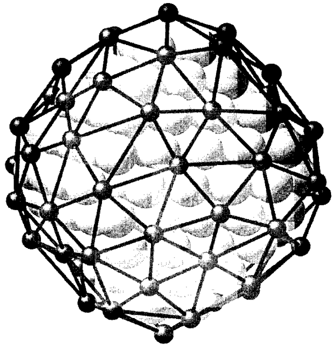
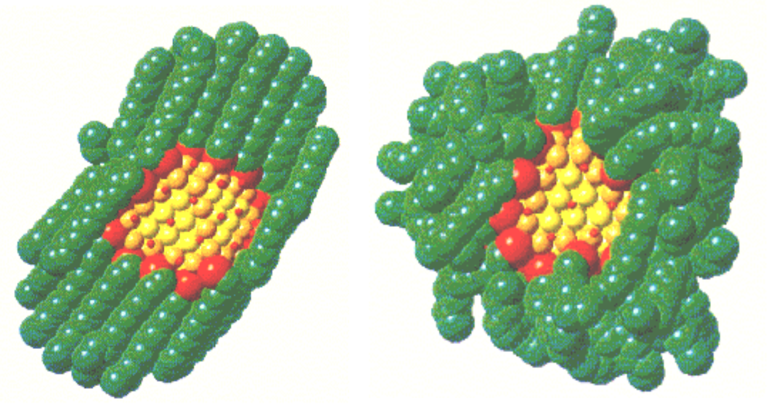


Fig. 3 XPS spectrum of the nanoparticles showing the Au $4f_{7/2}$ and $4f_{5/2}$ doublet with binding energies of 83.8 and 87.5 eV respectively. These are typical values for Au^0.

Nanoparticles - the monolayer







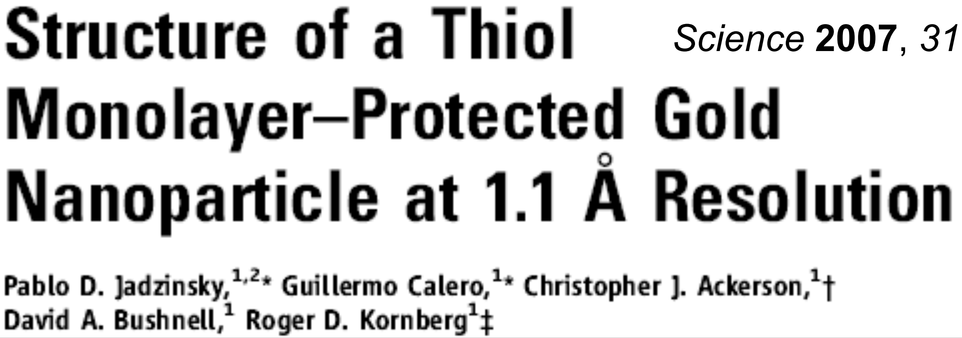
200 K

350 K

$Au_{140}(C_{12}H_{25}S)_{62}$

W. D. Luedtke, U. Landman *J. Phys. Chem.* **1996**, *100*, 13323; *J. Phys. Chem. B* **1998**, *102*, 6566

Au-NPs



Structure of a Thiol Monolayer–Protected Gold Nanoparticle at 1.1 Å Resolution

Pablo D. Jadzinsky,[1,2]* Guillermo Calero,[1]* Christopher J. Ackerson,[1]†
David A. Bushnell,[1] Roger D. Kornberg[1]‡

Science **2007**, *318*, 430.

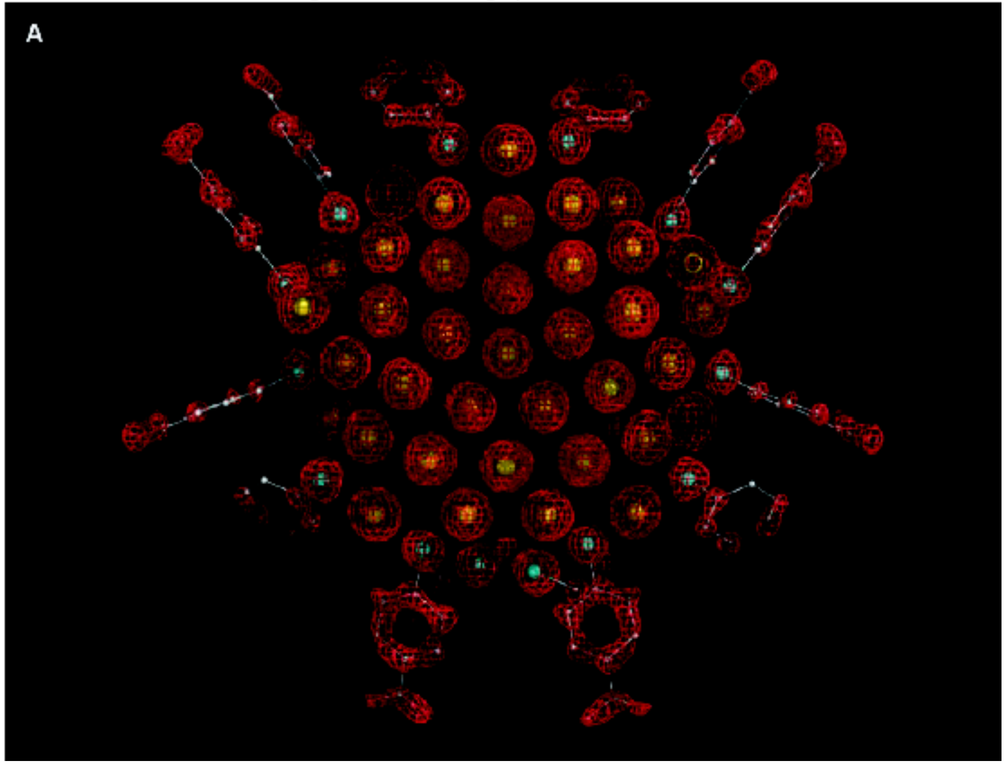
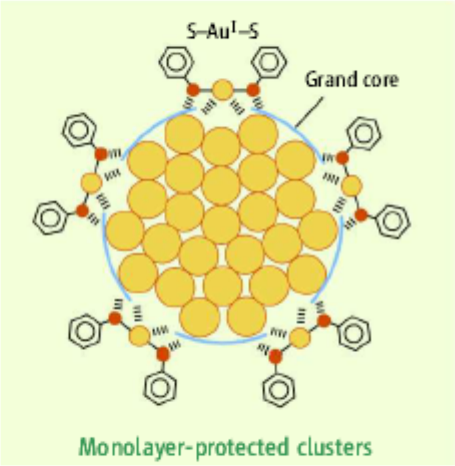
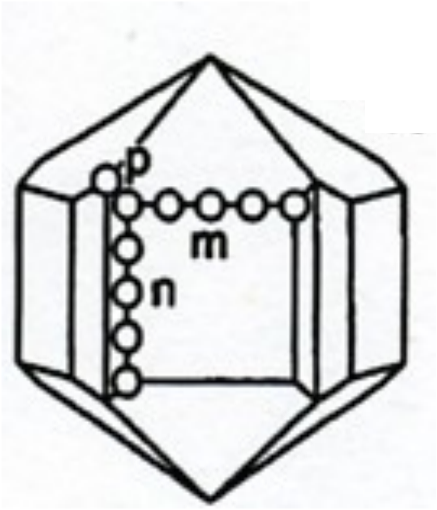


Fig. 1. X-ray crystal structure determination of the Au102(p-MBA)44 nanoparticle. (A) Electron density map(redmesh)andatomic structure (gold atoms depicted as yellow spheres, and p-MBA shown as framework and with small spheres [sulfur in cyan, carbon in gray, and oxygen in red]).



Structure of a thiol monolayer-protected Gold Nanoparticle at 1.1 Å resolution



MD (m,n,p)

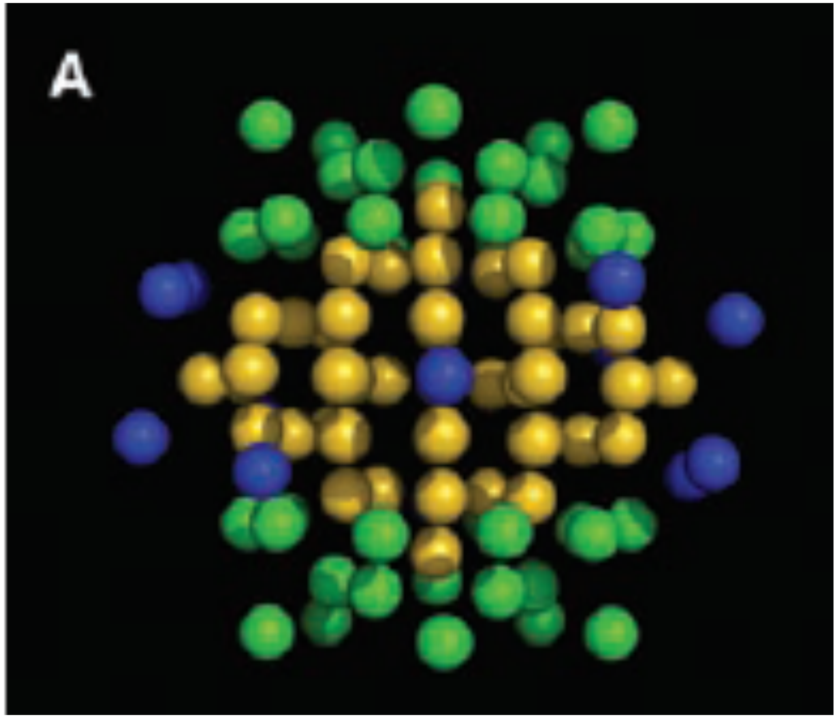
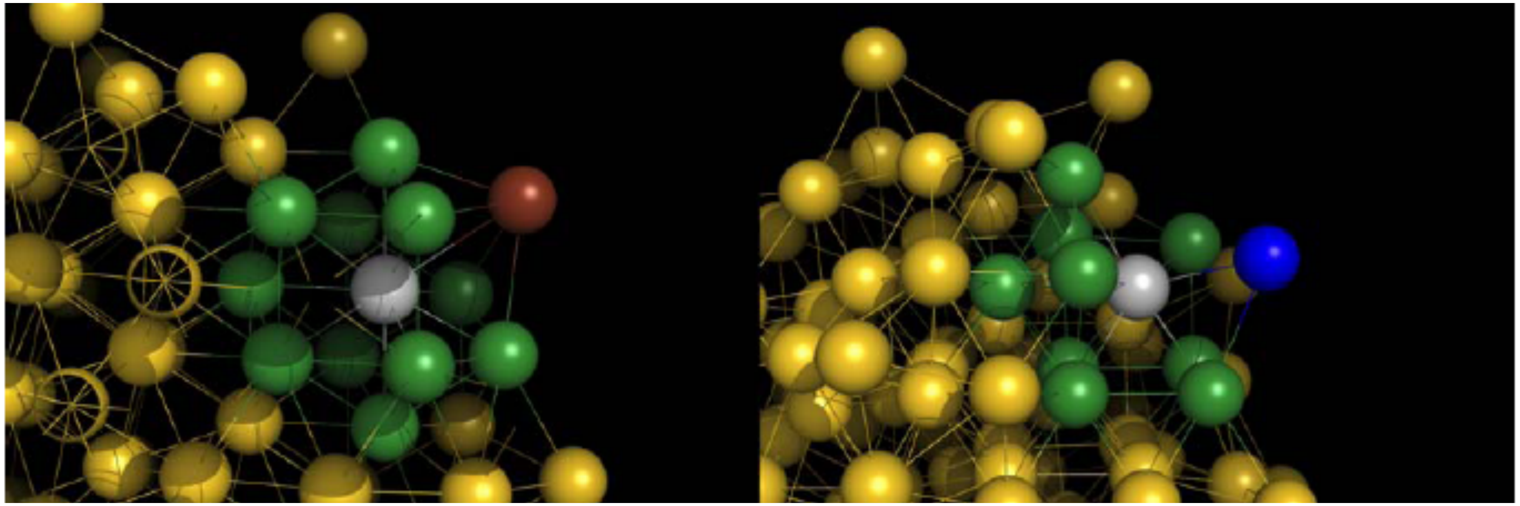
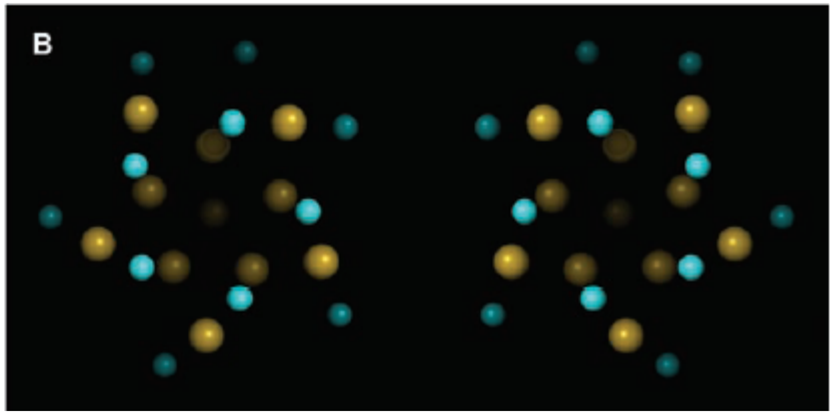


Fig.A: Packing of gold
atoms in the nanoparticle. (A) MD (2,1,2)
in yellow, two 20-atom“caps” at the
poles in green, and the 13-atom
equatorial band in blue.

Structure of a thiol monolayer-protected Gold Nanoparticle at 1.1 Å resolution

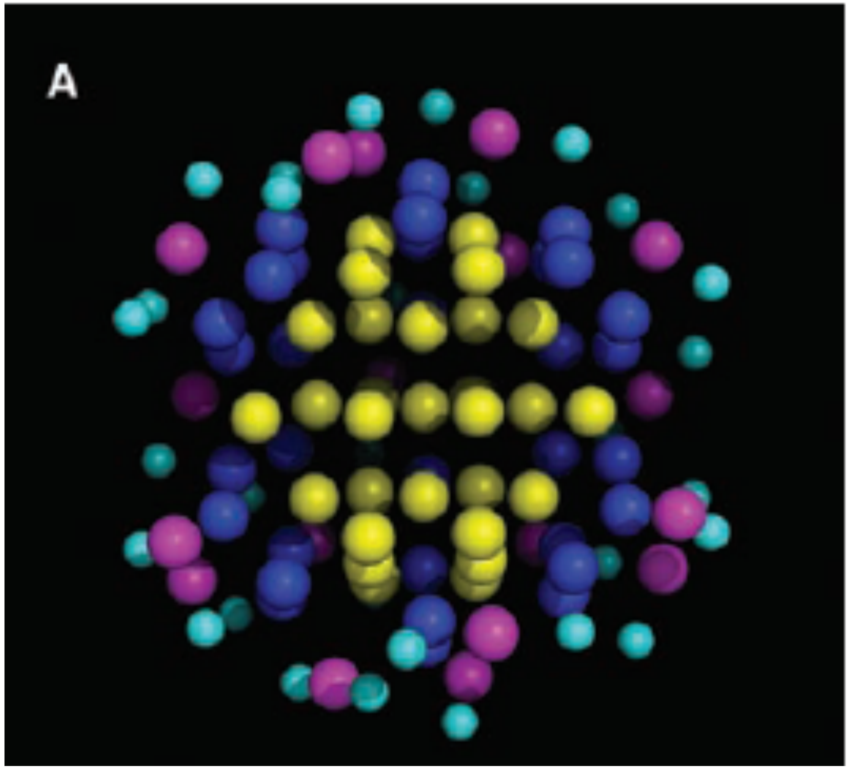


The local environments of the 13 atoms of the equatorial band.



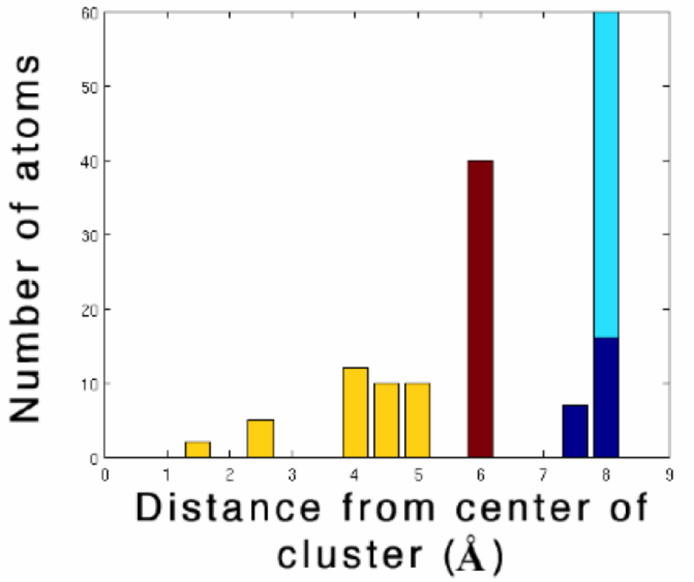
View down the cluster axis of the two enantiomeric particles

Structure of a thiol monolayer-protected Gold Nanoparticle at 1.1 Å resolution

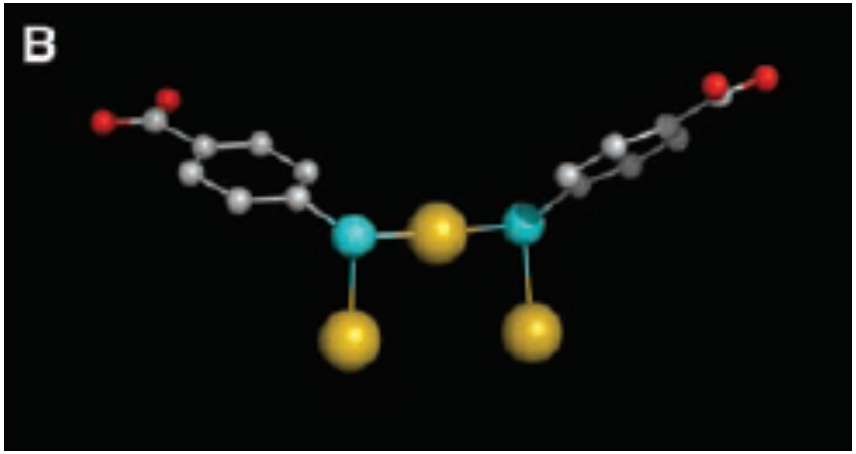


Successive shells of gold atoms interacting with zero (yellow), one (blue), or two (magenta) sulfur atoms. Sulfur atoms are cyan.

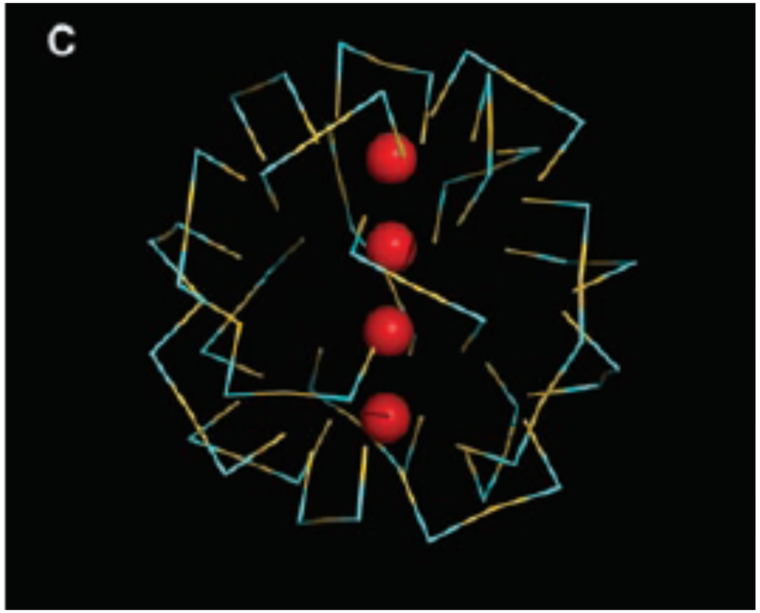
Histogram of distances from the center of the cluster of the different shells. Yellow, the 49-atom MD; brown, gold atoms bound to one sulfur atom; blue, gold atoms bound to two sulfur atoms; cyan, sulfur atoms.



Structure of a thiol monolayer-protected Gold Nanoparticle at 1.1 Å resolution

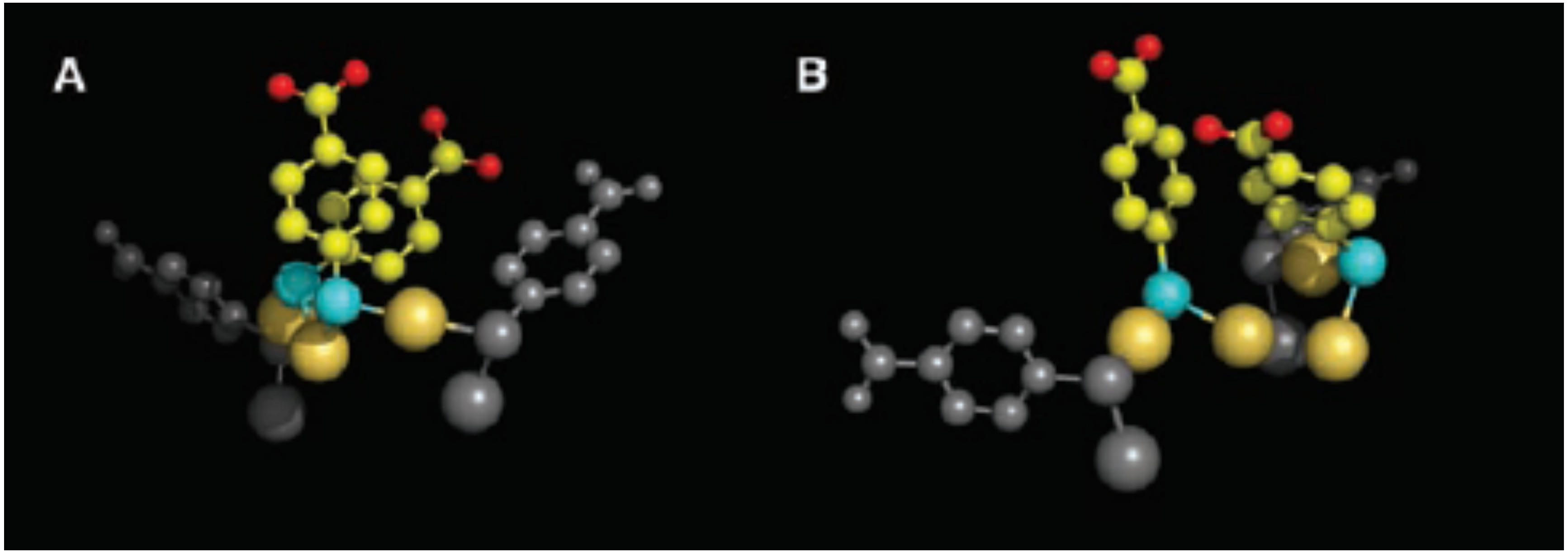


Example of two p-MBAs interacting with three gold atoms in a bridge conformation, here termed a staple motif. Gold atoms are yellow, sulfur atoms are cyan, oxygen atoms are red, and carbon atoms are gray.



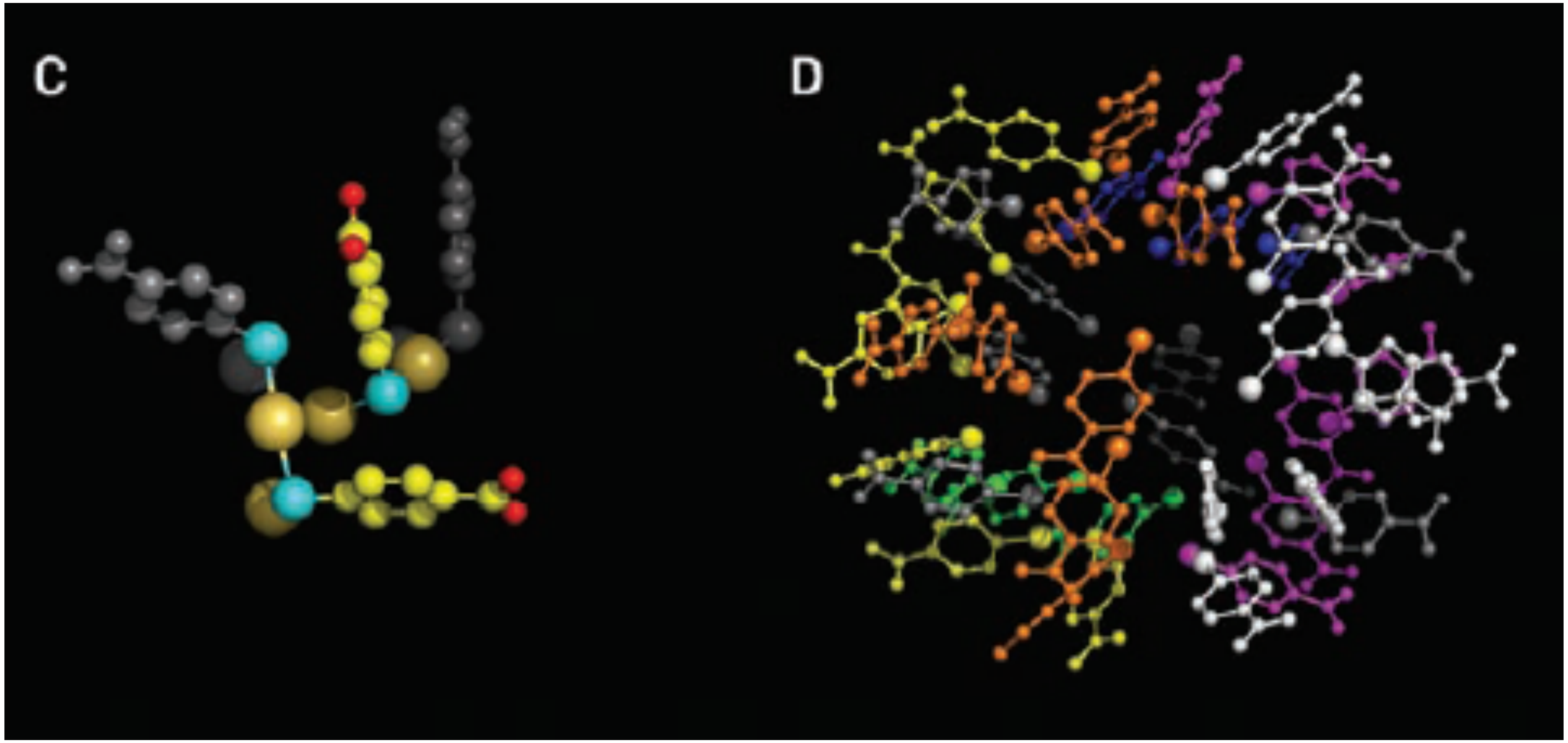
Distribution of staple motifs in the surface of the nanoparticle. Staple motifs are depicted symbolically, with gold in yellow and sulfur in cyan. Only the gold atoms on the axis of the MD are shown (in red).

Structure of a thiol monolayer-protected Gold Nanoparticle at 1.1 Å resolution



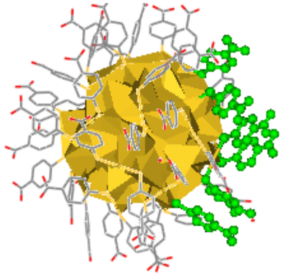
π-π stacking interaction: A) face-to-face B) edge-to-face

Structure of a thiol monolayer-protected Gold Nanoparticle at 1.1 Å resolution

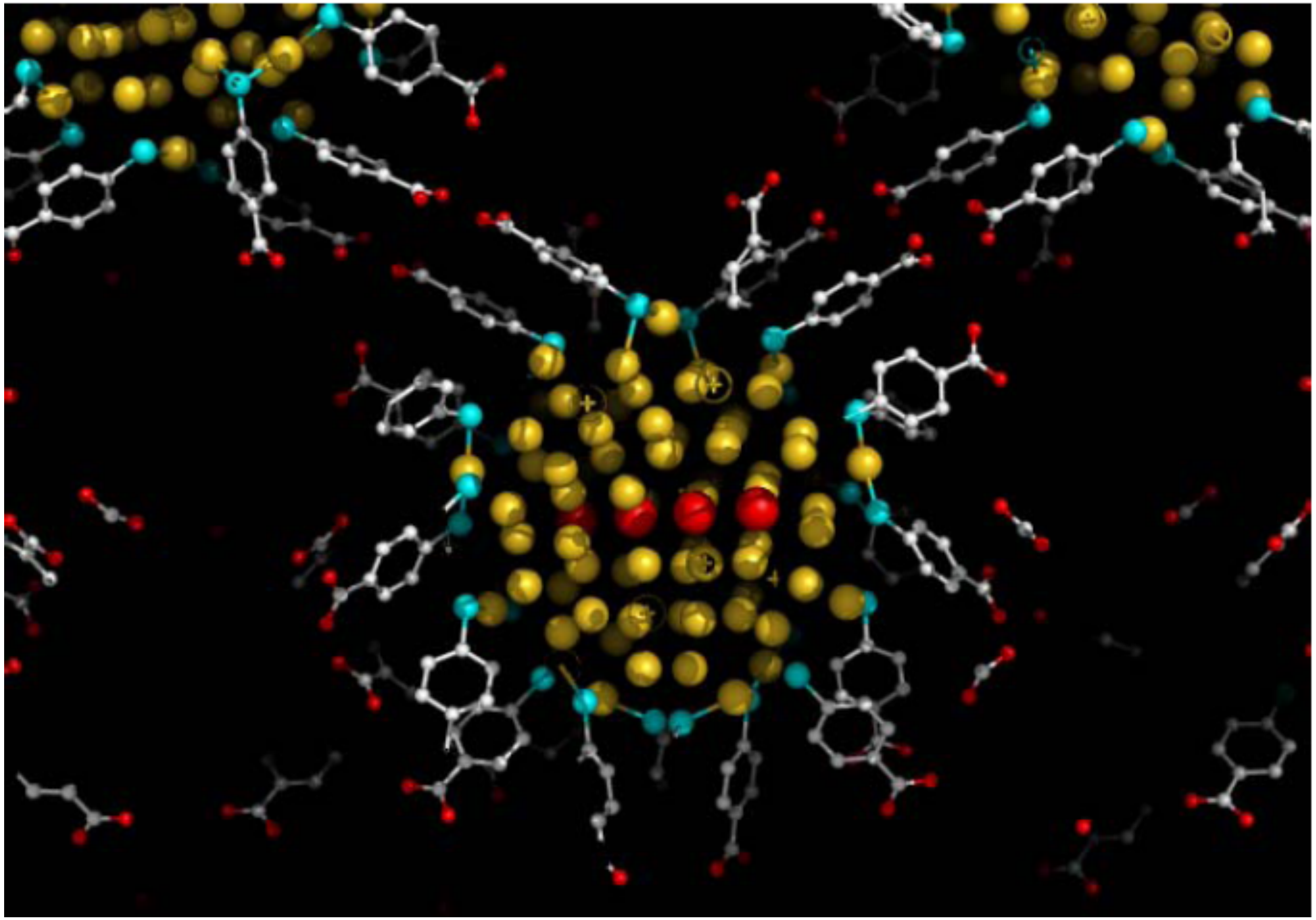


(C) S-Ph stabilization

(D) Chains of interacting p-MBAs, extending across the surface of the nanoparticle, indicated by a different color for each chain.

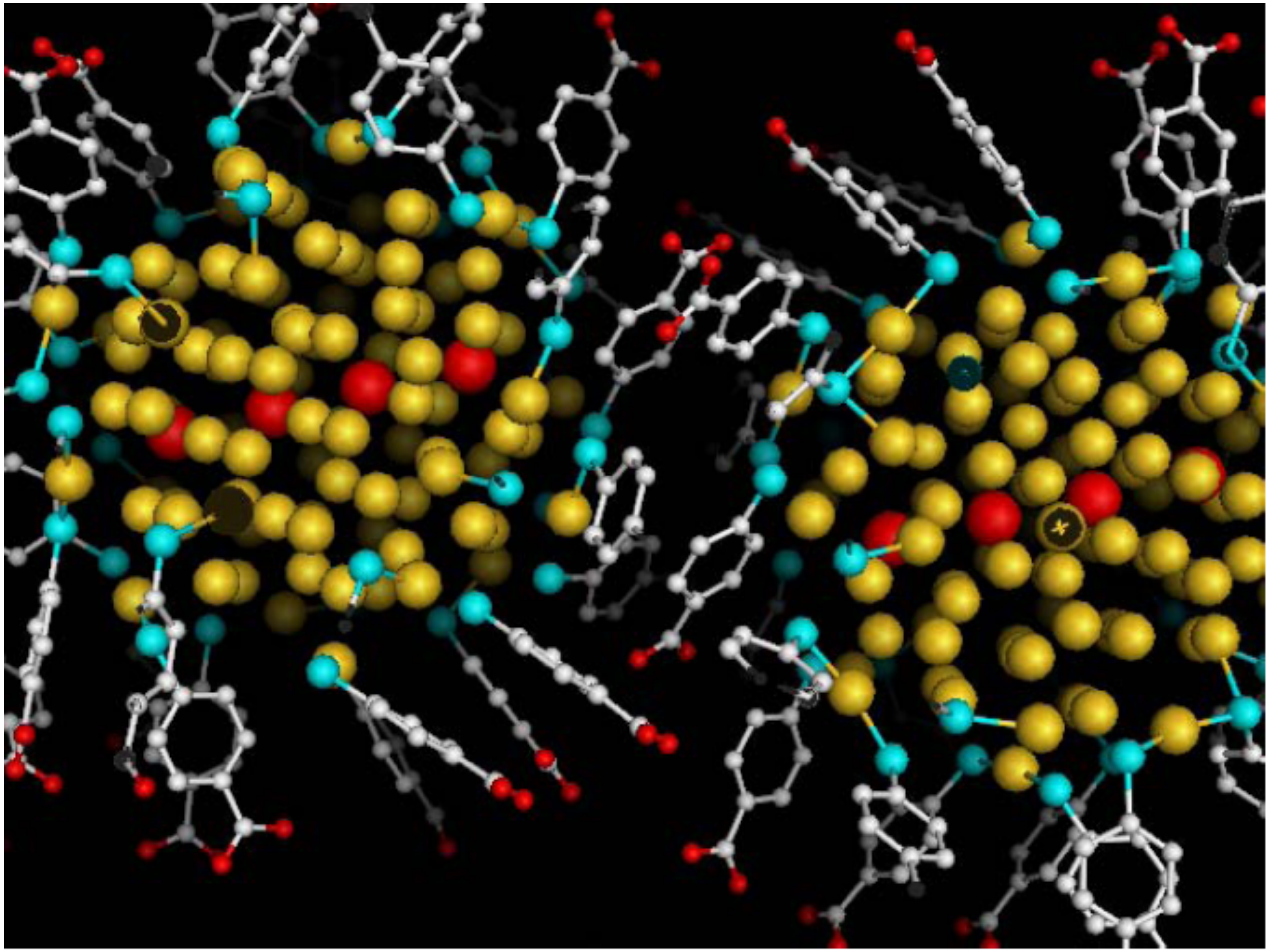


Structure of a thiol monolayer-protected Gold Nanoparticle at 1.1 Å resolution



View of the crystal structure showing interparticle interaction mediated throughhydrogen bonding between carboxylic acids.

Structure of a thiol monolayer-protected Gold Nanoparticle at 1.1 Å resolution



View of the crystal structure showing interparticle interactions mediated between stacked phenyl rings.

Crystal Structure of the Gold Nanoparticle [N(C8H17)4][Au25(SCH2CH2Ph)18]

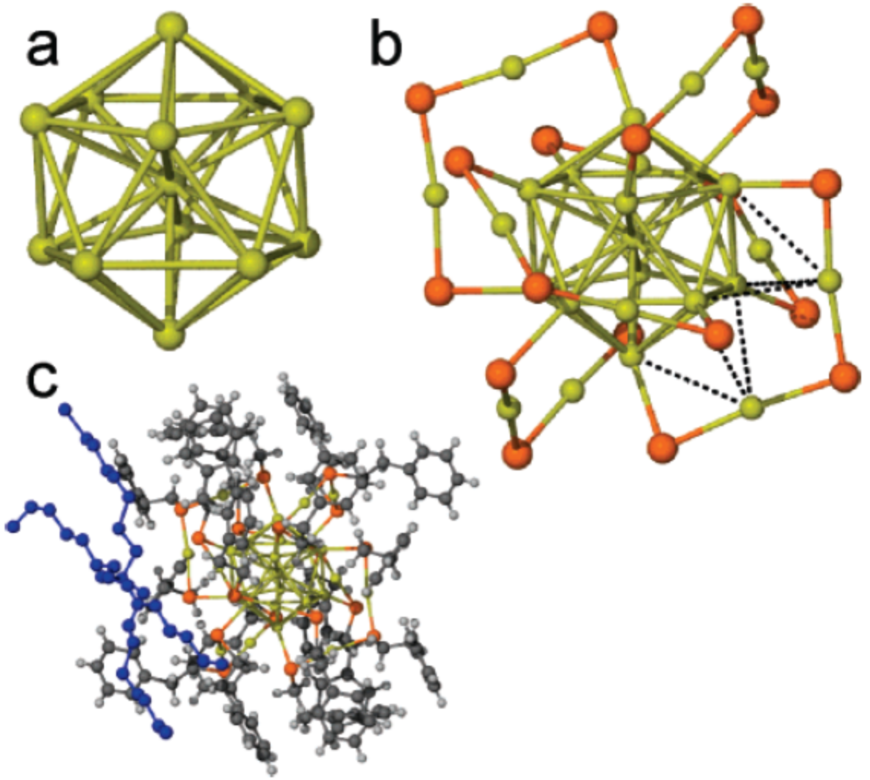


Figure 1. Breakdown of X-ray crystal structure of $[\mathrm{TOA}^+][\mathrm{Au}_{25}(\mathrm{SCH_2CH_2Ph})_{18}{}^-]$ as seen from [001]. (a) Arrangement of the Au_{13} core with 12 atoms on the vertices of an icosahedron and one in the center. (b) Depiction of gold and sulfur atoms, showing six orthogonal $-\mathrm{Au_2(SCH_2CH_2Ph)_3}-$ “staples” surrounding the Au_{13} core (two examples of possible aurophilic bonding shown as dashed lines). (c) $[\mathrm{TOA}^+][\mathrm{Au}_{25}(\mathrm{SCH_2CH_2Ph})_{18}{}^-]$ structure with the ligands and TOA^+ cation (depicted in blue) (Legend: Gold = yellow; Sulfur = orange; Carbon = gray; Hydrogen = off-white; the TOA^+ counterion is over two positions with one removed for clarity).

M. W. Heaven, A. Dass, P. S. White, K. M. Holt, R. W. Murray **J. AM. CHEM. SOC. 2008**, 130, 3754-3755

Conversion of Anionic [Au25(SCH2CH2Ph)18]- Cluster to Charge Neutral Cluster via Air Oxidation

M. Zhu, W. T. Eckenhoff, T. Pintauer, R. Jin *J. Phys. Chem. C, Vol. 112, No. 37, 2008*

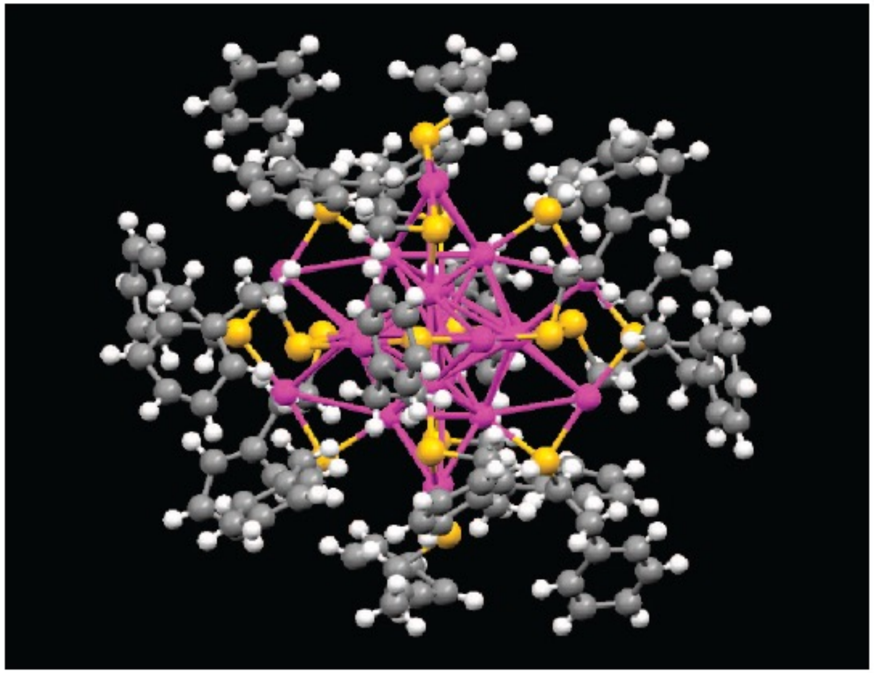


Figure 2. Crystal structure of a charge neutral $Au_{25}(SCH_2CH_2Ph)_{18}$ cluster (magenta, Au; orange, S; gray, C; white, H atom). Space group: *Pccn*; for clarity, only one cluster in the unit cell (containing four clusters) is shown.

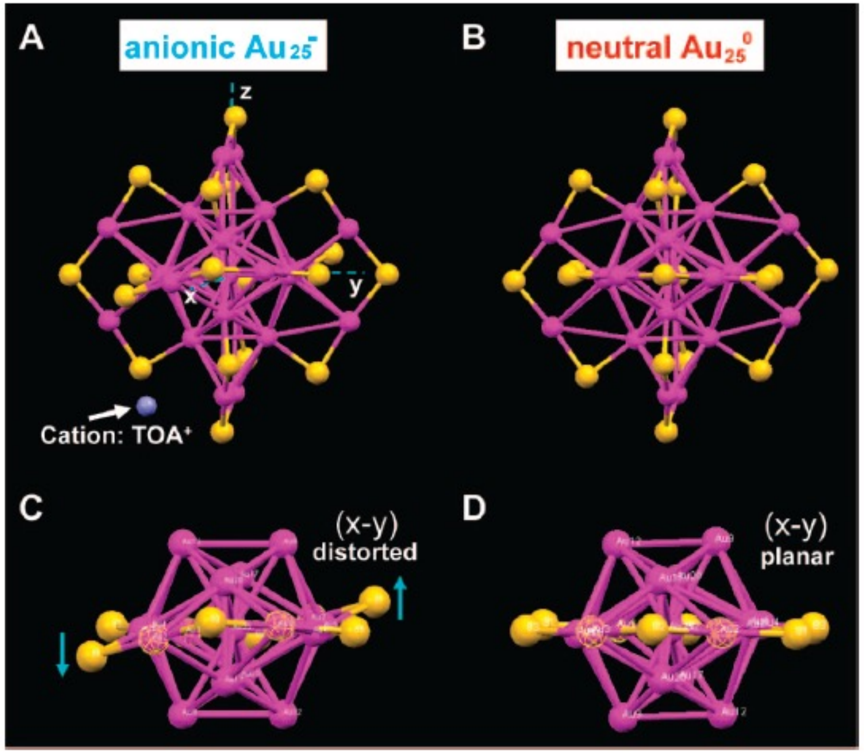


Figure 3. Comparison of the crystal structures of Au_{25} anionic (A,C) and neutral (B,D) clusters. Both clusters are capped by 18 phenylethanethiol ligands (for clarity C and H atoms are omitted); for anionic Au_{25}, the counterion is tetraoctylammonium TOA^+ (only N (in blue) is shown for clarity).

Correlating the Crystal Structure of A Thiol-Protected Au25 Cluster and Optical Properties

M. Zhu, C. M. Aikens, F. J. Hollander, G. C. Schatz, R. Jin **J. AM. CHEM. SOC. 2008**, *130*, 5883–5885

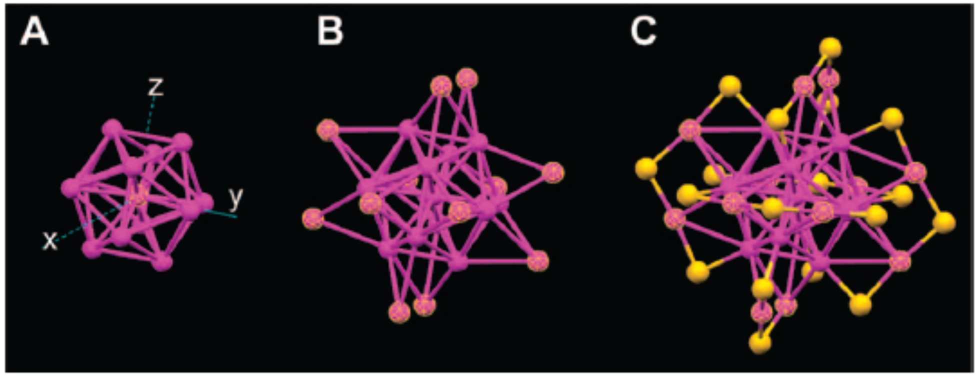


Figure 1. Crystal structure of a $Au_{25}(SR)_{18}$ cluster (R is phenylethyl group): (A) the icosahedral Au_{13} core; (B) the Au_{13} core plus the exterior 12 Au atoms; (C) the whole Au_{25} cluster protected by 18 thiolate ligands (for clarity, only S was shown, magenta, Au; yellow, S).

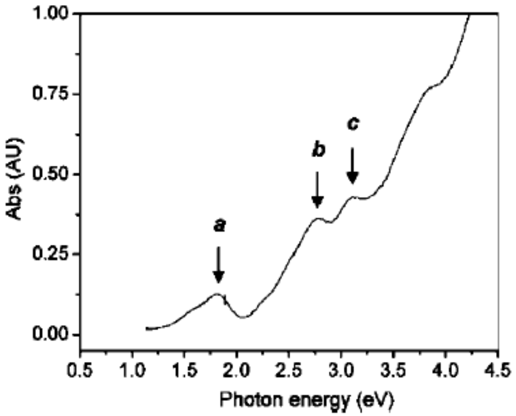


Figure 2. The UV−vis spectrum of Au_{25} clusters (single crystals redissolved in toluene). No Jacobian correction was done.

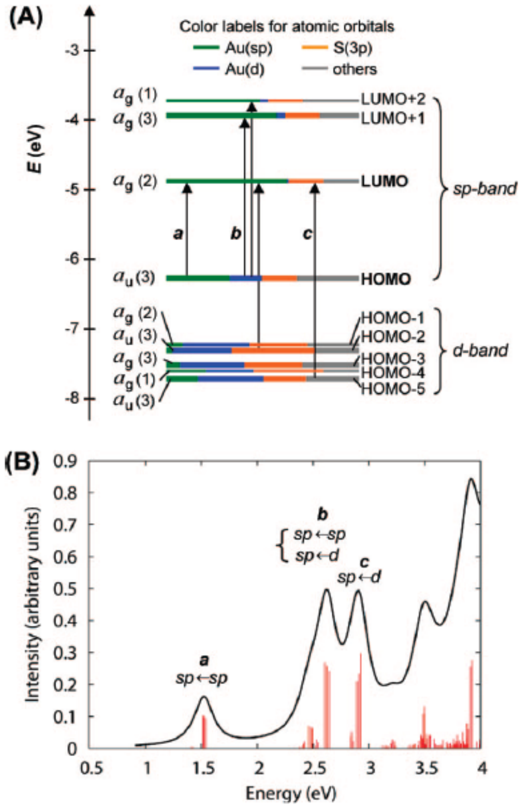
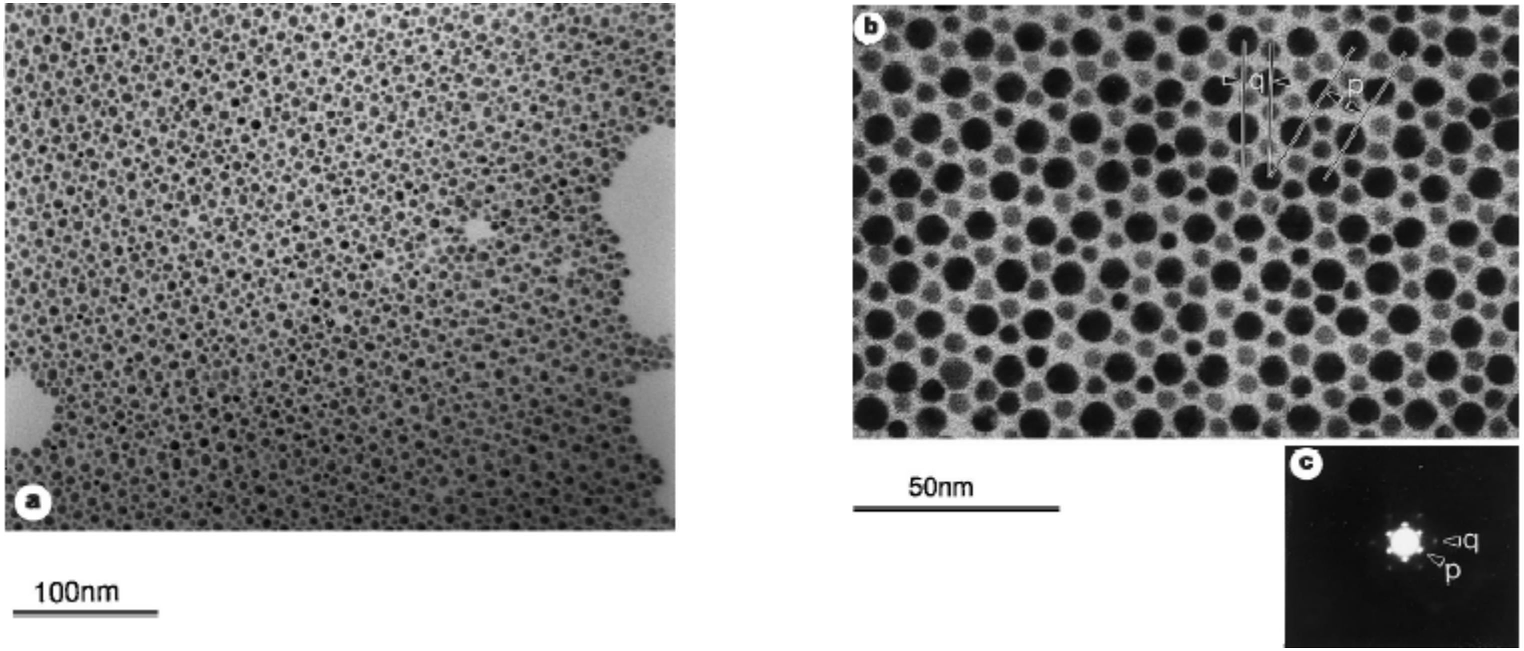


Figure 3. (A) Kohn−Sham orbital energy level diagram for a model compound $Au_{25}(SH)_{18}^{-}$. The energies are in units of eV. Each KS orbital is drawn to indicate the relative contributions (line length with color labels) of the atomic orbitals of Au (6sp) in green, Au (5d) in blue, S (3p) in yellow, and others in gray (those unspecified atomic orbitals, each with a < 1% contribution). The left column of the KS orbitals shows the orbital symmetry (g, u) and degeneracy (in parenthesis); the right column shows the HOMO and LUMO sets. (B) The theoretical absorption spectrum of $Au_{25}(SH)_{18}^{-}$. Peak assignments: peak a corresponds to 1.8 eV observed, peak b corresponds to 2.75 eV (observed), and peak c corresponds to 3.1 eV (observed).

Nanoparticles - spontaneous ordering

when monodispersed....

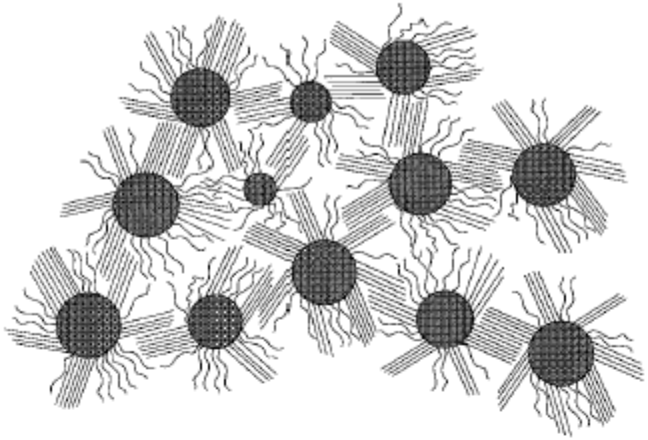


An ordered raft comprising Au nanoparticles of two distinct sizes with R_B/R_A < 0:58. Shown are electron micrographs at low (a) and higher (b) magnification. c, The low-angle superlattice electron diffraction pattern obtained from this bimodal raft structure.

C. J. Kiely, J. Fink,M. Brust, D. Bethell, D. J. Schiffrin, *Nature*, **1998**, *396*, 444.

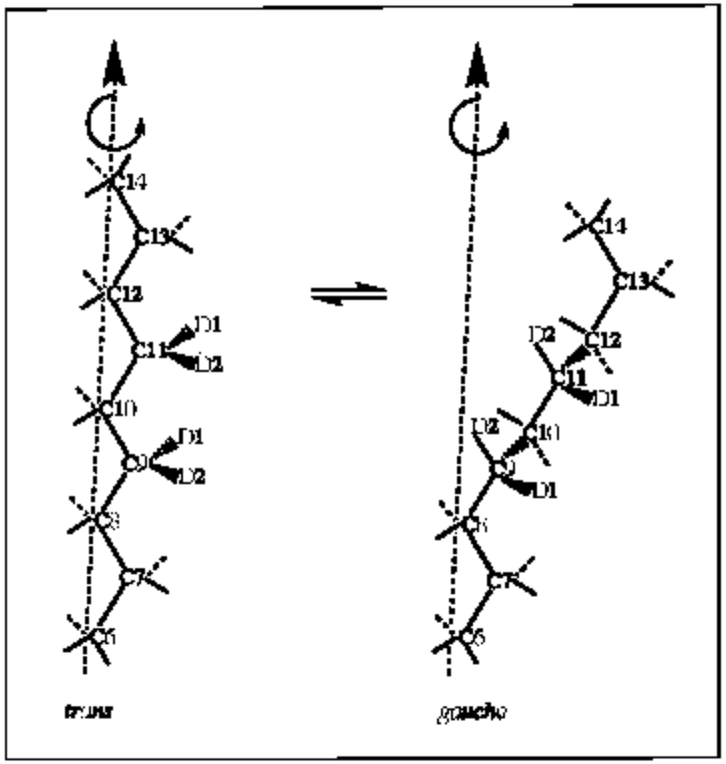
3D alkanethiolate monolayers

Scheme 1. A Schematic 2D Representation of the RS/Au Nanoparticle Packing Structure in the Solid State[a]



[a] In this description, *domains* or *bundles* of ordered alkylthiolate chains on a given Au particle will interdigitate into the chain domains of neighboring particles in order to compensate for the substantial decrease in the chain density which occurs toward the methyl chain end. Chains with large populations of *gauche* bonds may arise from (i) those which occupy interstitial regions in the particle lattice and cannot efficiently overlap with adjacent chains or from (ii) chains residing at domain boundaries.

Scheme 2. The Types of Chain Dynamic Processes Suggested by the ^{2}H NMR Line Shapes of the Deuterated C_{18}S/Au Nanoparticles[a]



[a] These processes involve *trans-gauche* bond isomerization and pseudorotational motion of individual chain segments about the long axis of the alkanethiolate molecule.

A. Badia, L. Cuccia, L. Demers, F. Morin, B. R. Lennox, *J. Am. Chem. Soc.*, **1997**, *119*, 2682.

3D alkanethiolate monolayers

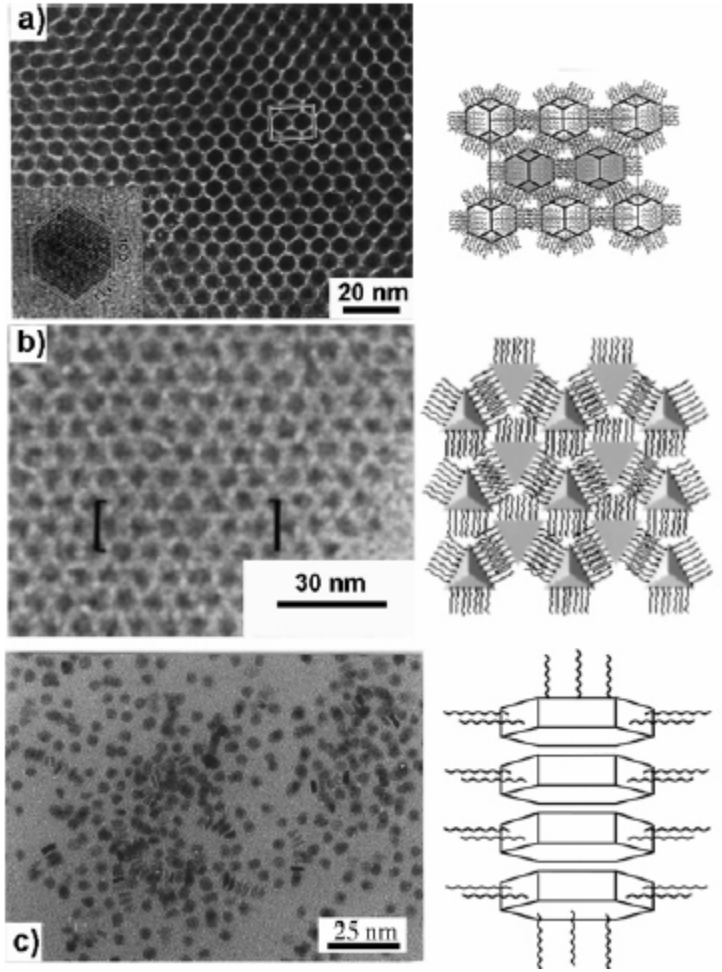
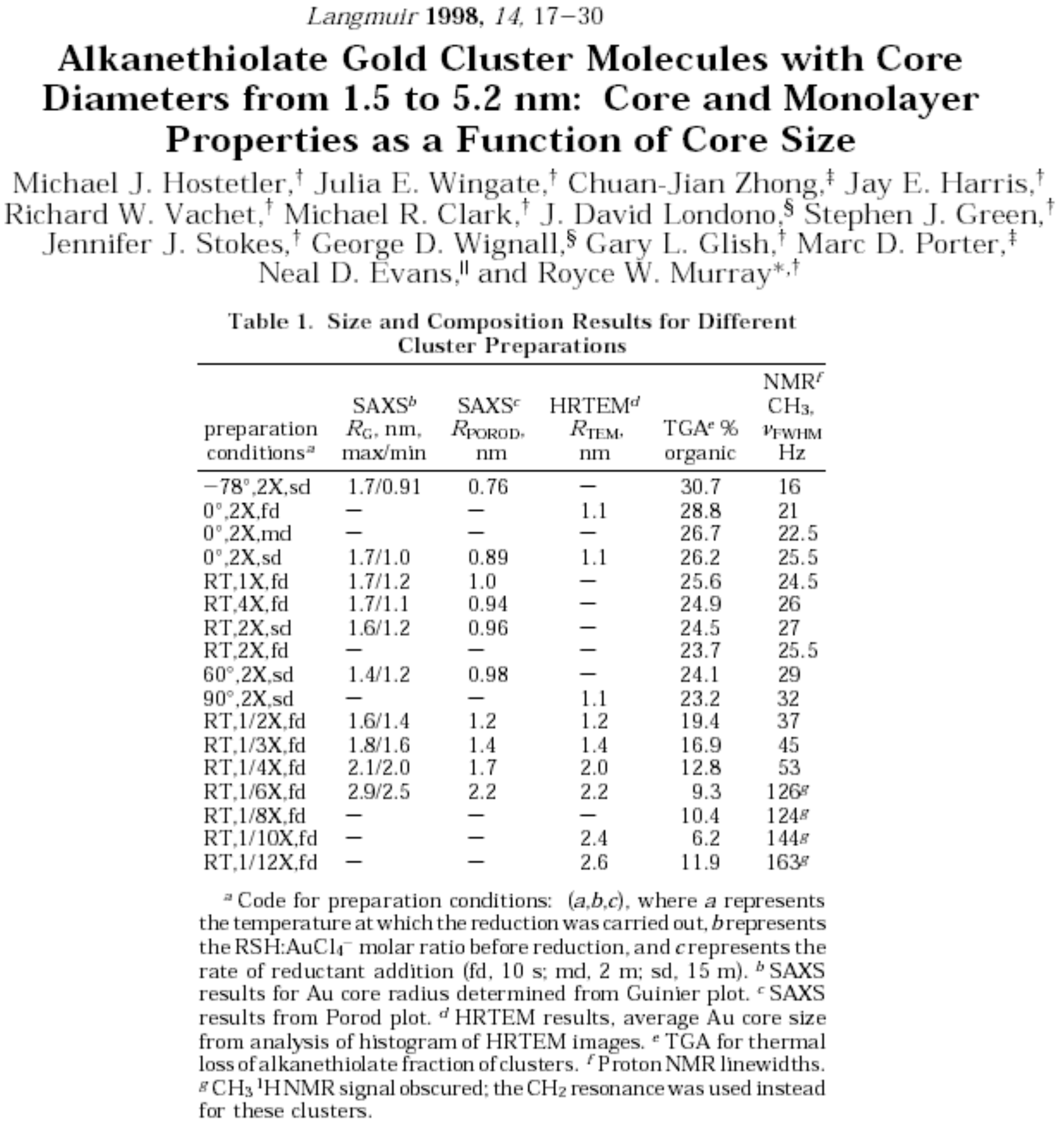


Figure 11. (a) (Left) TEM image of a face-centered, cubicpacked, array of silver nanoparticles, passivated with a dodecanethiolate monolayer, with a truncated octahedral morphology (see inset). (Right) Representation of the proposed packing of the particles via interdigitation of the bundled alkyl chains on each face. (b) (Left) TEM image of a monolayer of self-assembled silver tetrahedra passivated with dodecanethiolates. The bracketed area most closely matches the proposed model.



Langmuir **1998,** *14,* 17−30

Alkanethiolate Gold Cluster Molecules with Core Diameters from 1.5 to 5.2 nm: Core and Monolayer Properties as a Function of Core Size

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Table 1. Size and Composition Results for Different Cluster Preparations

preparation conditions[a]	SAXS[b] R_G, nm, max/min	SAXS[c] R_{POROD}, nm	HRTEM[d] R_{TEM}, nm	TGA[e] % organic	NMR[f] CH_3, ν_{FWHM} Hz
−78°,2X,sd	1.7/0.91	0.76	−	30.7	16
0°,2X,fd	−	−	1.1	28.8	21
0°,2X,md	−	−	−	26.7	22.5
0°,2X,sd	1.7/1.0	0.89	1.1	26.2	25.5
RT,1X,fd	1.7/1.2	1.0	−	25.6	24.5
RT,4X,fd	1.7/1.1	0.94	−	24.9	26
RT,2X,sd	1.6/1.2	0.96	−	24.5	27
RT,2X,fd	−	−	−	23.7	25.5
60°,2X,sd	1.4/1.2	0.98	−	24.1	29
90°,2X,sd	−	−	1.1	23.2	32
RT,1/2X,fd	1.6/1.4	1.2	1.2	19.4	37
RT,1/3X,fd	1.8/1.6	1.4	1.4	16.9	45
RT,1/4X,fd	2.1/2.0	1.7	2.0	12.8	53
RT,1/6X,fd	2.9/2.5	2.2	2.2	9.3	126[g]
RT,1/8X,fd	−	−	−	10.4	124[g]
RT,1/10X,fd	−	−	2.4	6.2	144[g]
RT,1/12X,fd	−	−	2.6	11.9	163[g]

[a] Code for preparation conditions: (*a*,*b*,*c*), where *a* represents the temperature at which the reduction was carried out, *b* represents the RSH:$AuCl_4^-$ molar ratio before reduction, and *c* represents the rate of reductant addition (fd, 10 s; md, 2 m; sd, 15 m). [b] SAXS results for Au core radius determined from Guinier plot. [c] SAXS results from Porod plot. [d] HRTEM results, average Au core size from analysis of histogram of HRTEM images. [e] TGA for thermal loss of alkanethiolate fraction of clusters. [f] Proton NMR linewidths. [g] CH_3 ^1H NMR signal obscured; the CH_2 resonance was used instead for these clusters.

Nanoparticles - caracterization

TEM

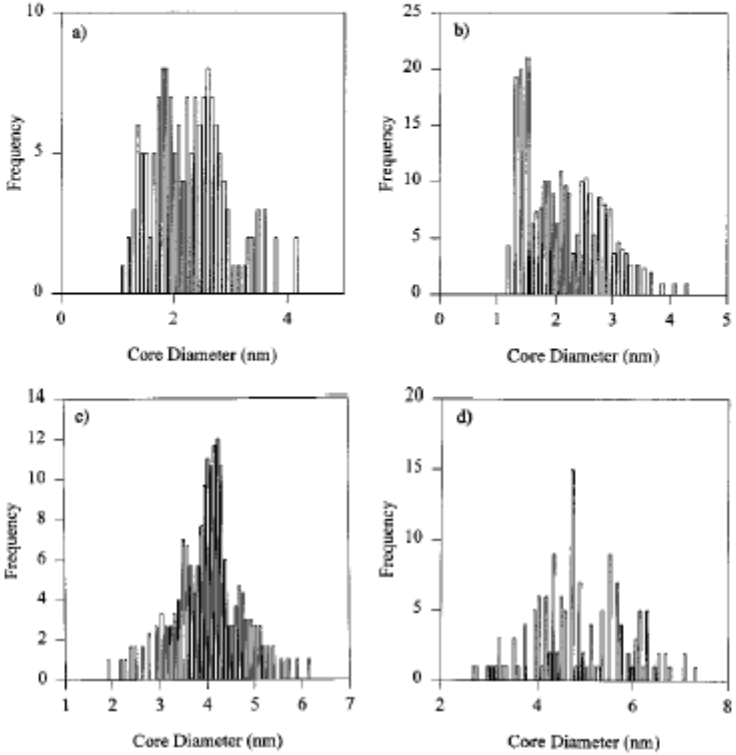


Figure 2. Size histograms (a and d are for films shown in Figure 1): (a) (0°,2X,fd); (b) (0°,2X,sd); (c) (RT,1/4X,fd); (d) (RT, 1/6X,fd).

NANOPARTICELLE - characterization

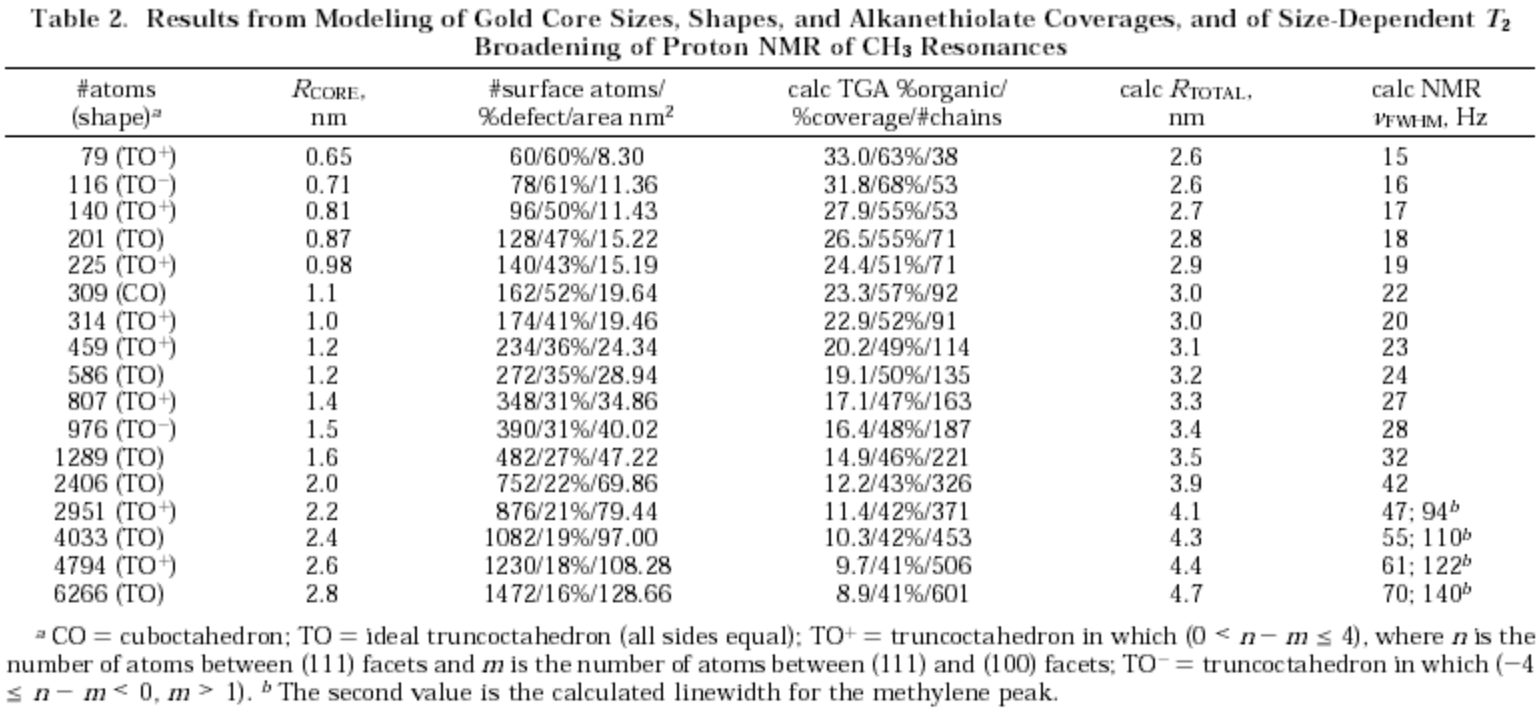


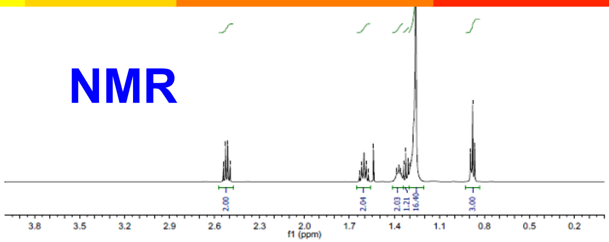
Table 2. Results from Modeling of Gold Core Sizes, Shapes, and Alkanethiolate Coverages, and of Size-Dependent T_2 Broadening of Proton NMR of CH_3 Resonances

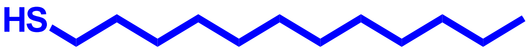
#atoms (shape)[a]	R_{CORE}, nm	#surface atoms/ %defect/area nm^2	calc TGA %organic/ %coverage/#chains	calc R_{TOTAL}, nm	calc NMR ν_{FWHM}, Hz
79 (TO^+)	0.65	60/60%/8.30	33.0/63%/38	2.6	15
116 (TO^-)	0.71	78/61%/11.36	31.8/68%/53	2.6	16
140 (TO^+)	0.81	96/50%/11.43	27.9/55%/53	2.7	17
201 (TO)	0.87	128/47%/15.22	26.5/55%/71	2.8	18
225 (TO^+)	0.98	140/43%/15.19	24.4/51%/71	2.9	19
309 (CO)	1.1	162/52%/19.64	23.3/57%/92	3.0	22
314 (TO^+)	1.0	174/41%/19.46	22.9/52%/91	3.0	20
459 (TO^+)	1.2	234/36%/24.34	20.2/49%/114	3.1	23
586 (TO)	1.2	272/35%/28.94	19.1/50%/135	3.2	24
807 (TO^+)	1.4	348/31%/34.86	17.1/47%/163	3.3	27
976 (TO^-)	1.5	390/31%/40.02	16.4/48%/187	3.4	28
1289 (TO)	1.6	482/27%/47.22	14.9/46%/221	3.5	32
2406 (TO)	2.0	752/22%/69.86	12.2/43%/326	3.9	42
2951 (TO^+)	2.2	876/21%/79.44	11.4/42%/371	4.1	47; 94[b]
4033 (TO)	2.4	1082/19%/97.00	10.3/42%/453	4.3	55; 110[b]
4794 (TO^+)	2.6	1230/18%/108.28	9.7/41%/506	4.4	61; 122[b]
6266 (TO)	2.8	1472/16%/128.66	8.9/41%/601	4.7	70; 140[b]

[a] CO = cuboctahedron; TO = ideal truncoctahedron (all sides equal); TO^+ = truncoctahedron in which ($0 < n - m \leq 4$), where n is the number of atoms between (111) facets and m is the number of atoms between (111) and (100) facets; TO^- = truncoctahedron in which ($-4 \leq n - m < 0$, $m > 1$). [b] The second value is the calculated linewidth for the methylene peak.

characterization

NMR





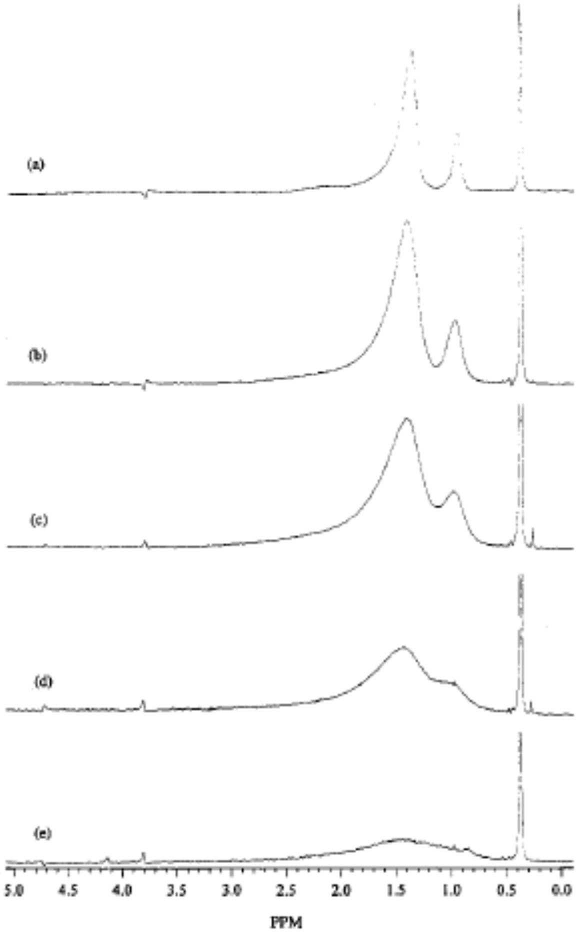


Figure 5. The ^{1}H NMR spectra (C_6D_6) of dodecanethiolate-protected Au clusters. Each spectrum was Fourier transformed using a line broadening of 1 Hz: (a) (−78°,2X,sd); (b) (90°,2X,sd); (c) (RT,1/3X,fd); (d) (RT,1/4X,fd); (e) (RT,1/12X,fd).

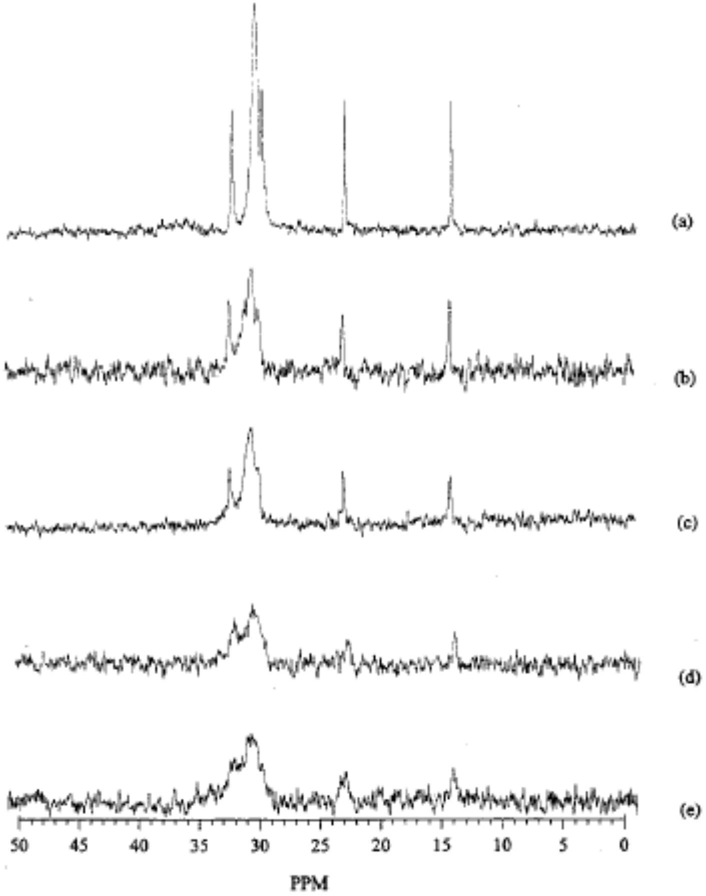


Figure 4. The ^{13}C NMR spectra (C_6D_6) of dodecanethiolate-protected Au clusters. Each spectrum was Fourier transformed using a line broadening of 3 Hz: (a) (−78°,2X,sd); (b) (90°,2X,sd); (c) (RT,1/3X,fd); (d) (RT,1/4X,fd); (e) (RT,1/6X,fd).

NANOPARTICELLE - characterization

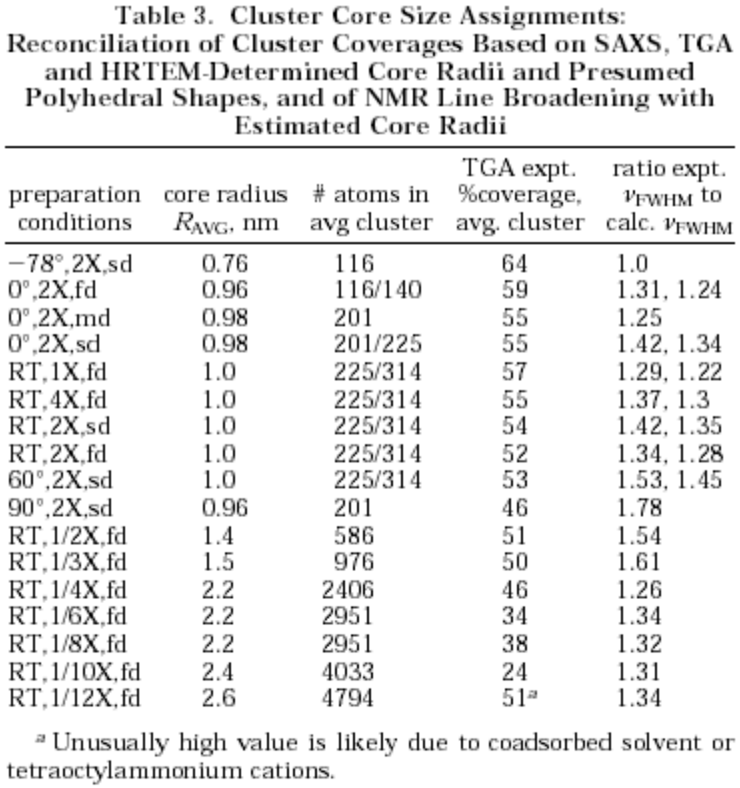


Table 3. Cluster Core Size Assignments: Reconciliation of Cluster Coverages Based on SAXS, TGA and HRTEM-Determined Core Radii and Presumed Polyhedral Shapes, and of NMR Line Broadening with Estimated Core Radii

preparation conditions	core radius R_{AVG}, nm	# atoms in avg cluster	TGA expt. %coverage, avg. cluster	ratio expt. ν_{FWHM} to calc. ν_{FWHM}
−78°,2X,sd	0.76	116	64	1.0
0°,2X,fd	0.96	116/140	59	1.31, 1.24
0°,2X,md	0.98	201	55	1.25
0°,2X,sd	0.98	201/225	55	1.42, 1.34
RT,1X,fd	1.0	225/314	57	1.29, 1.22
RT,4X,fd	1.0	225/314	55	1.37, 1.3
RT,2X,sd	1.0	225/314	54	1.42, 1.35
RT,2X,fd	1.0	225/314	52	1.34, 1.28
60°,2X,sd	1.0	225/314	53	1.53, 1.45
90°,2X,sd	0.96	201	46	1.78
RT,1/2X,fd	1.4	586	51	1.54
RT,1/3X,fd	1.5	976	50	1.61
RT,1/4X,fd	2.2	2406	46	1.26
RT,1/6X,fd	2.2	2951	34	1.34
RT,1/8X,fd	2.2	2951	38	1.32
RT,1/10X,fd	2.4	4033	24	1.31
RT,1/12X,fd	2.6	4794	51[a]	1.34

[a] Unusually high value is likely due to coadsorbed solvent or tetraoctylammonium cations.

characterization

UV-Vis spectra

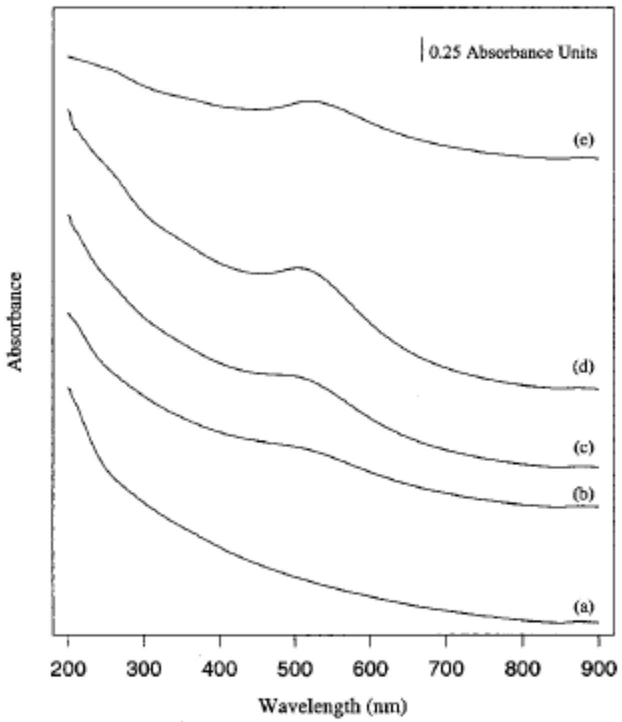
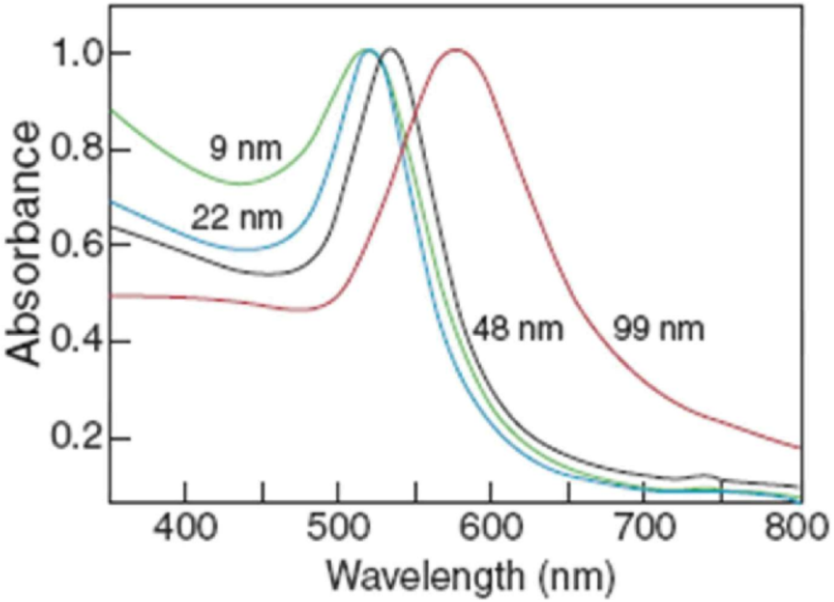
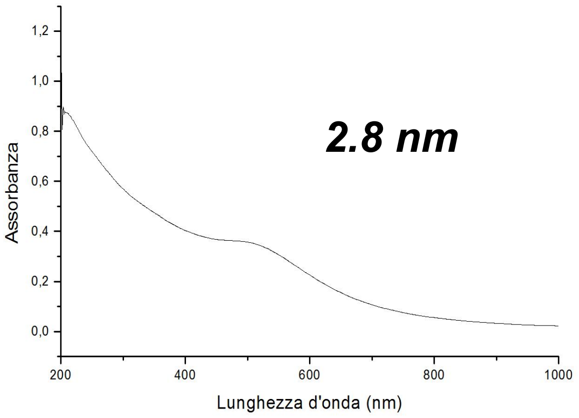
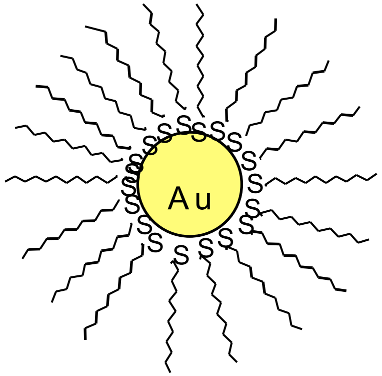


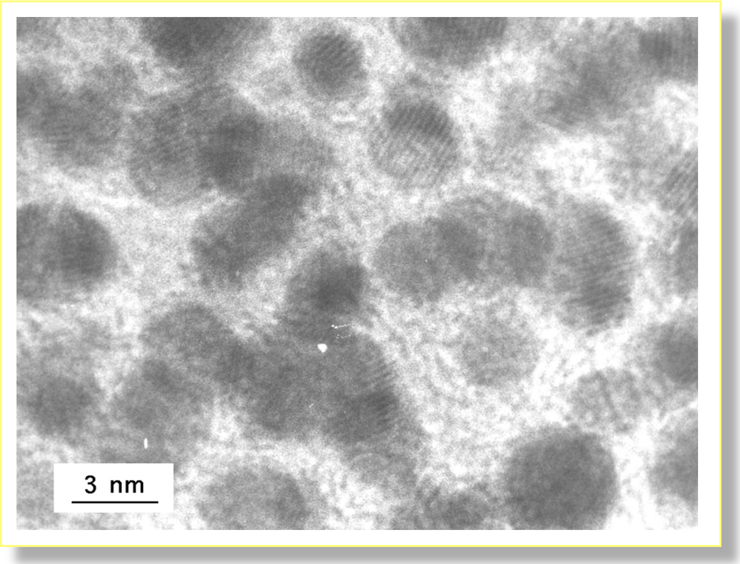
Figure 7. The UV/vis spectra (hexane) of dodecanethiolate-protected Au clusters: (a) (−78°,2X,sd), C = 3×10^{-6} M, MW = 3.4×10^4 amu; (b) (90°,2X,sd), C = 2×10^{-6} M, MW = 5.5×10^4 amu; (c) (RT,1/3X,fd), C = 4×10^{-7} M, MW = 2.3×10^5 amu; (d) (RT,1/4X,fd), C = 2×10^{-7} M, MW = 5.5×10^5 amu; (e) (RT,1/12X,fd), C = 9×10^{-8} M, MW = 1.1×10^6 amu.



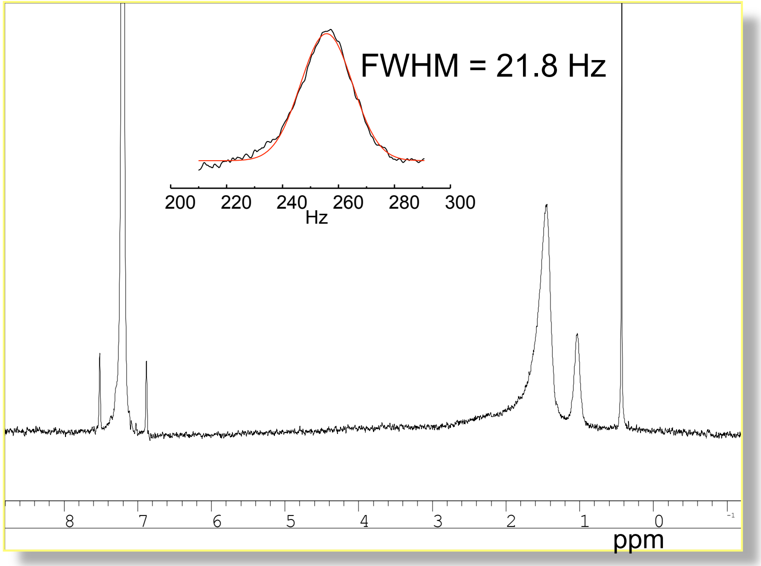


MPCC12

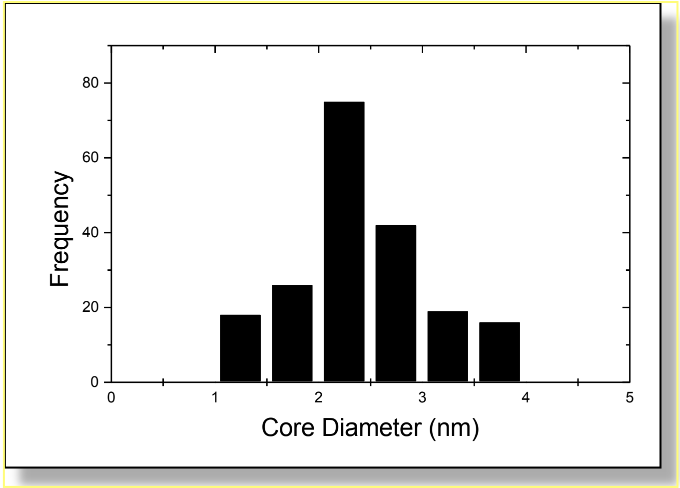




HRTEM



^{1}H NMR (250 MHz, C_6D_6)



Core size histogram: core diameter 2.2 ± 0.4 nm

MPC-C12

$Au_{116}(SR)_{50}$ (MW=)

MPC-C12 - TGA Analysis