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**

NANOPARTICLES

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.

reviews

Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology
J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103.

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.

……….and thousands of papers

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.

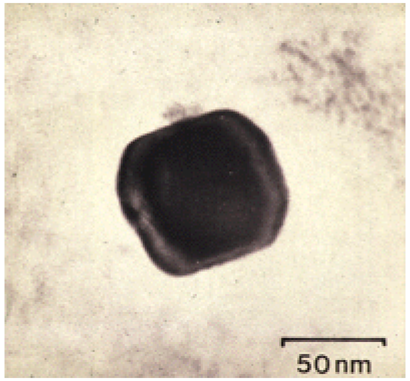
A brief historical background

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

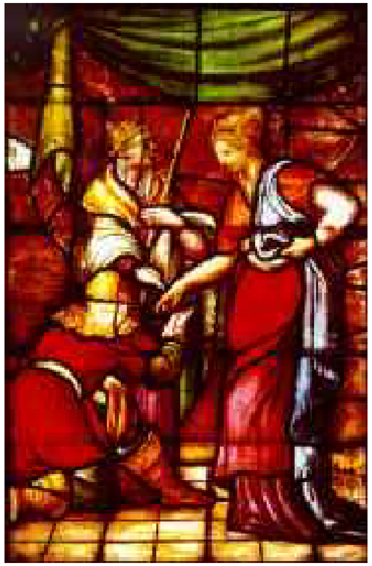
$$\left[\mathrm{AuCl_4}\right]^{-} \xrightarrow[\text{reduction on } \mathrm{CS_2}]{\text{white phosphorous}} \text{solution of colloids}$$

two phase system

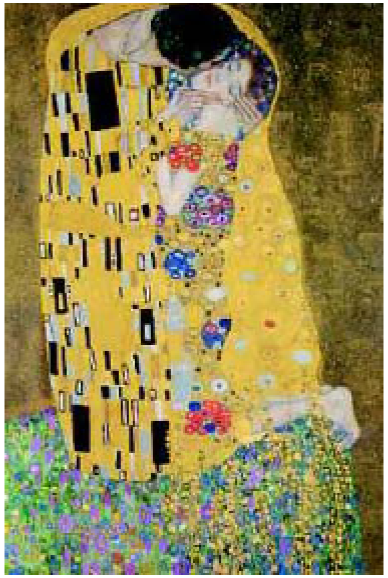
diameter of 3 ÷ 30 nm

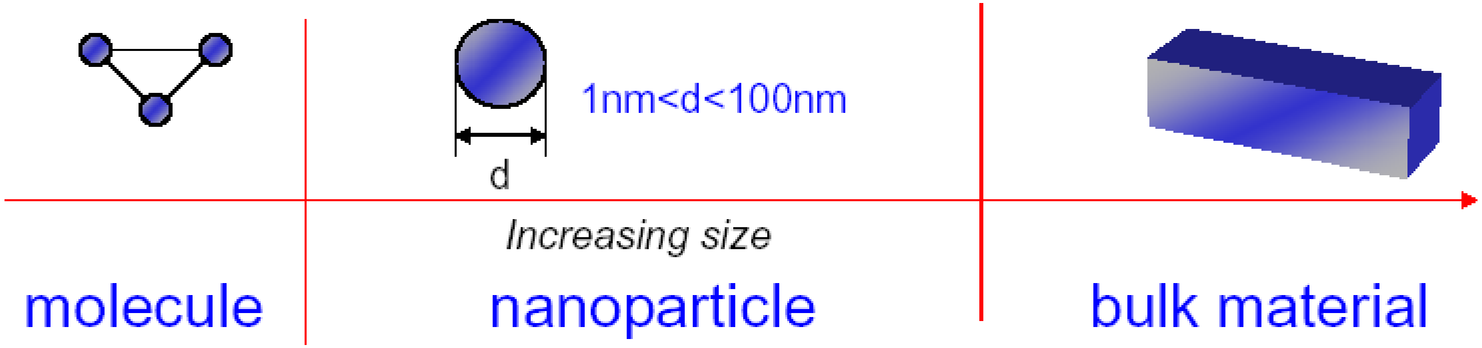
Nanoscale Materials

Florence - Santa Croce



Milan - Duomo

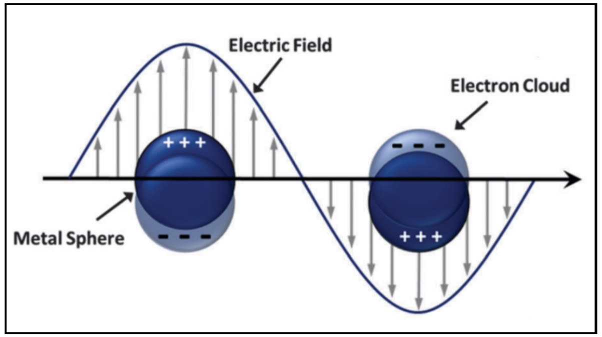




Nanoscale materials have different properties when compared to their bulk counterparts!

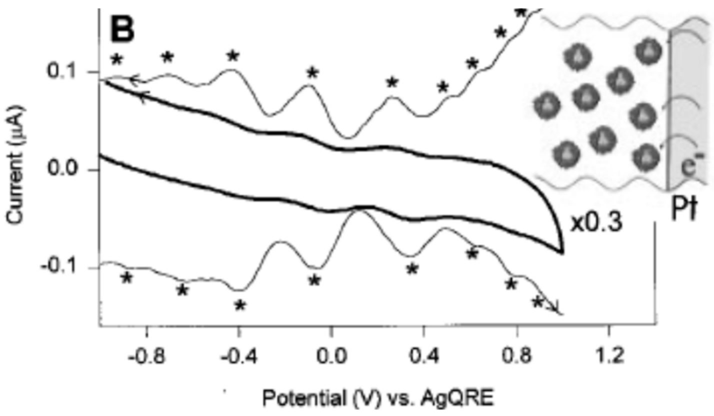
Properties of Metal Nanoparticles

Optical Properties

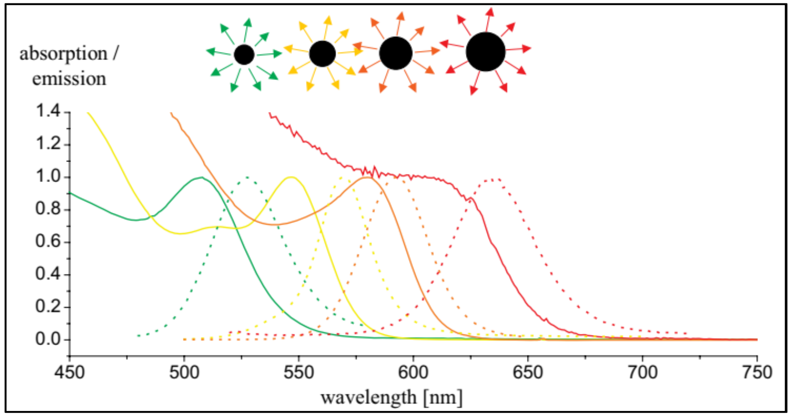


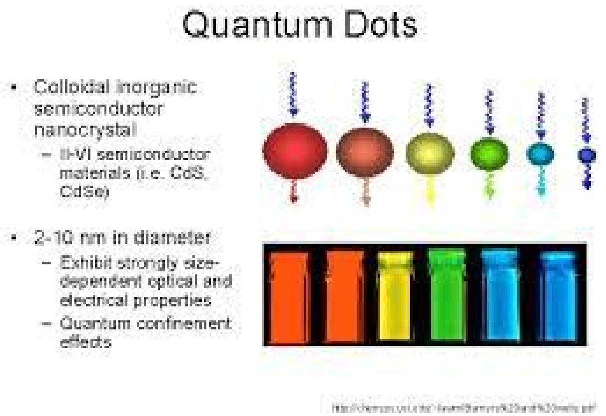
Nanoscale Materials have different properties when compared to their bulk counterparts!

Electronic Properties



Otical properies of semiconductor NPs





Quantum Dots

- Colloidal inorganic semiconductor nanocrystal
  - II-VI semiconductor materials (i.e. CdS, CdSe)
- 2-10 nm in diameter
  - Exhibit strongly size-dependent optical and electrical properties
  - Quantum confinement effects

Nanoscale Materials

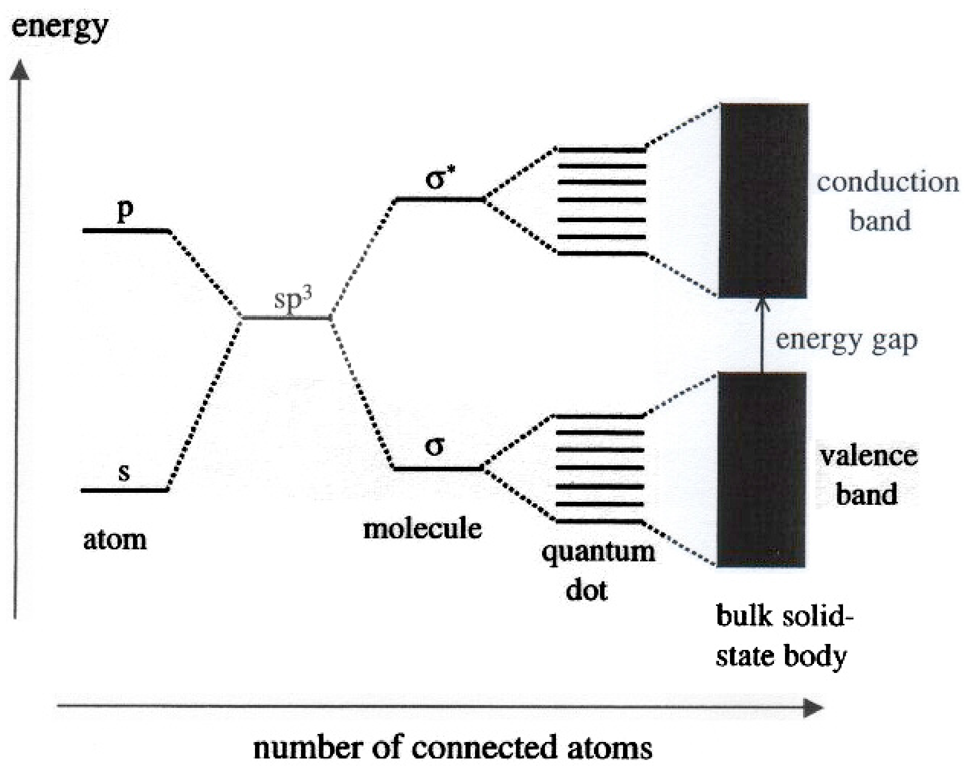
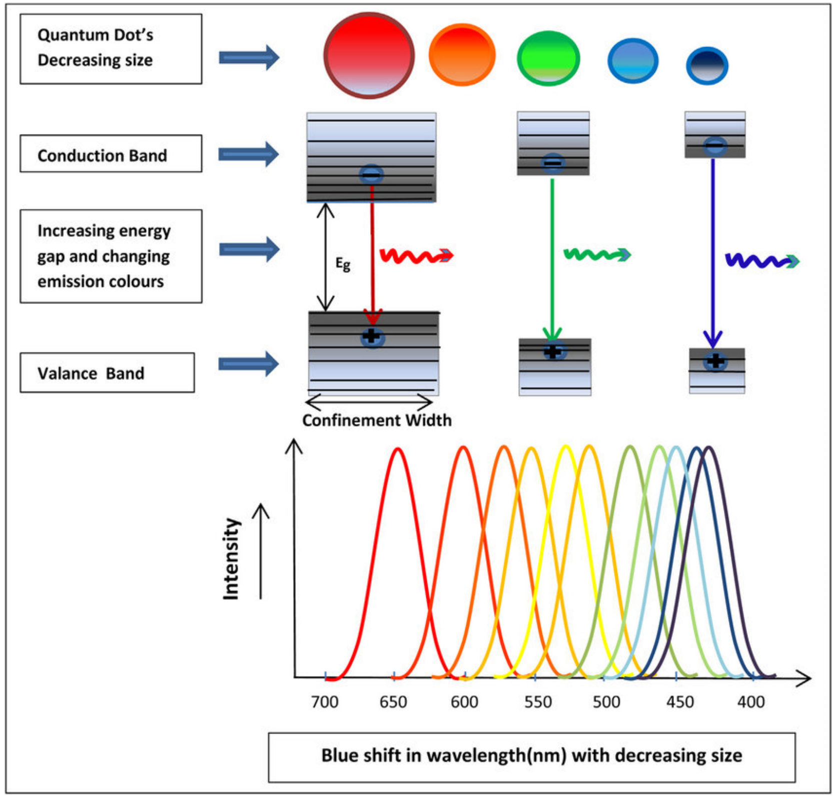
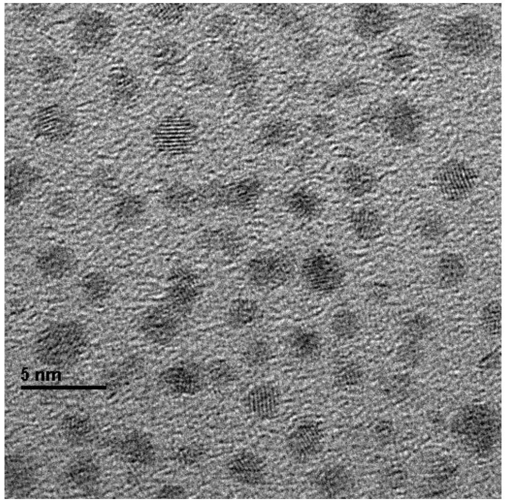


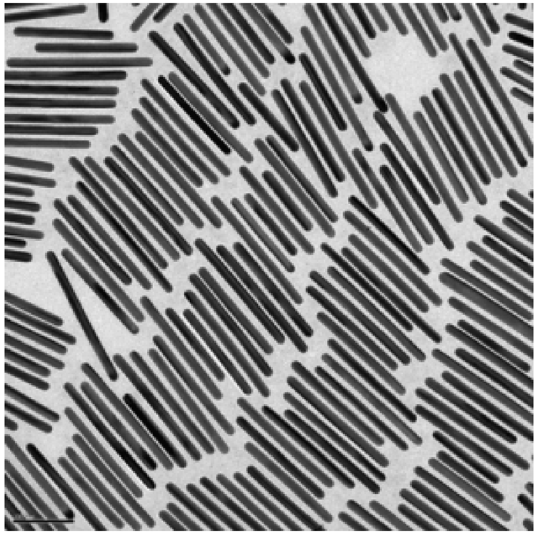
Fig. 2-1 Electronic energy levels depending on the number of bound atoms. By binding more and more atoms together, the discrete energy levels of the atomic orbitals merge into energy bands (here shown for a semiconducting material) [16]. Therefore semiconducting nanocrystals (quantum dots) can be regarded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



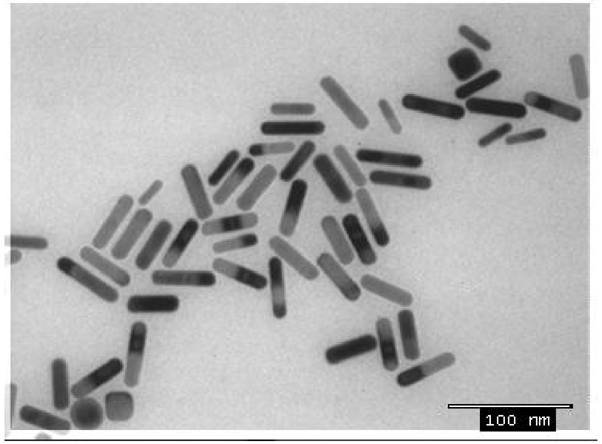
Nanoscale Materials



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

size range	class	major property	example
< 2 nm	cluster	molecular- to metal-like	Au_{11}, Au_{28}, Au_{39}, Au_{55}, Au_{102}
2 – 10 nm	catalytic particle	enhanced catalytic activity	tiny nanoparticles
0–300 nm	plasmonic crystal	surface plasmon resonance	polyhedrons, rods, wires, plates

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

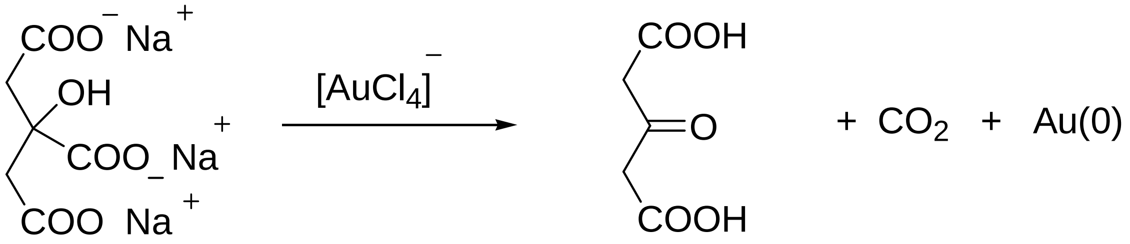
Synthesis of metal nanoparticles

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.

Synthesis of metal nanoparticles

Electrostatic stabilization: the electrical double layer

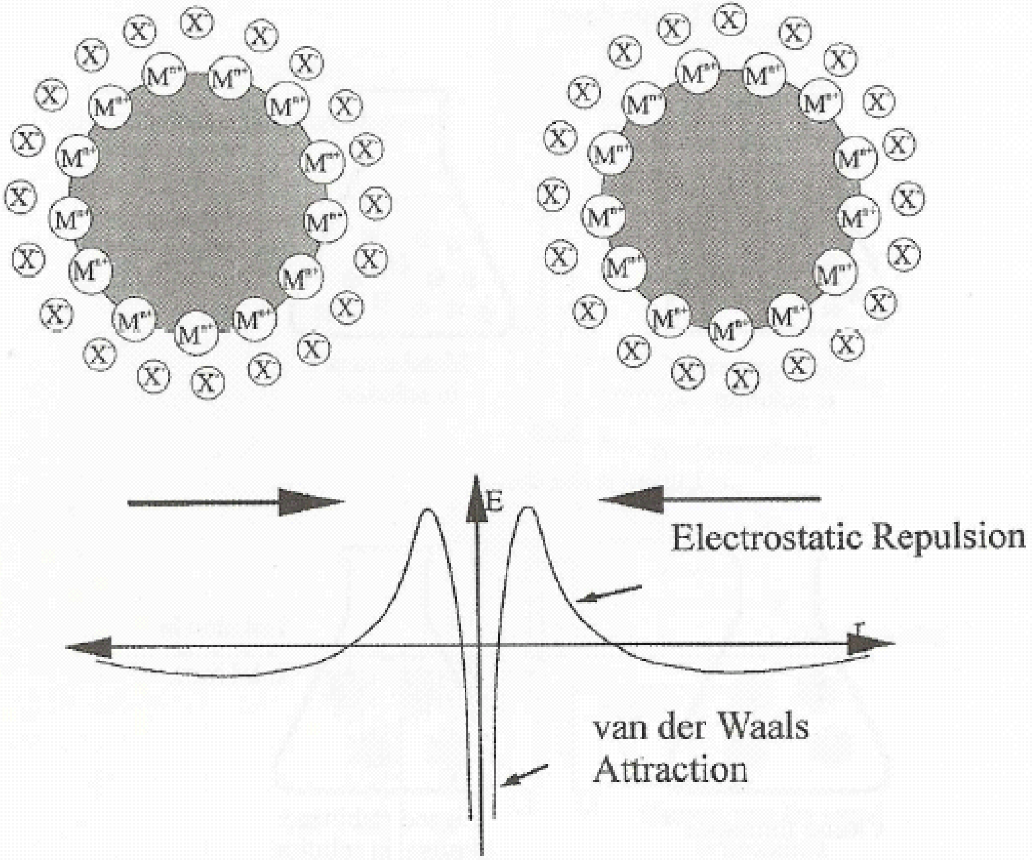


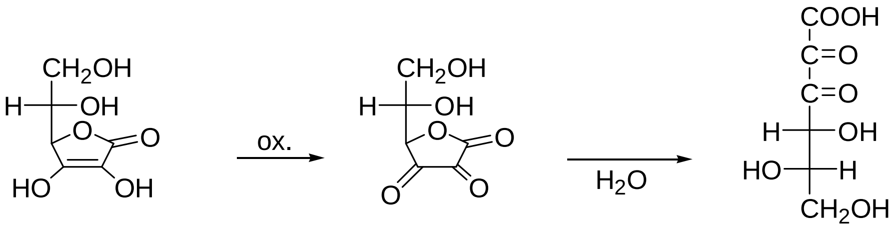
FIGURE 2.24 Electrostatic stabilization of metal colloids. Van der Waals attraction and electrostatic repulsion compete with each other.[27]

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

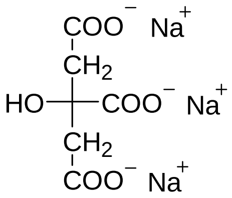
reduction of $HAuCl_4$ with different reducing agents

- 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 polymer that stabilize 1 g of a solution of 50 mg/L of colloidal gold against aggregation in the presence of NaCl 1%

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

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

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

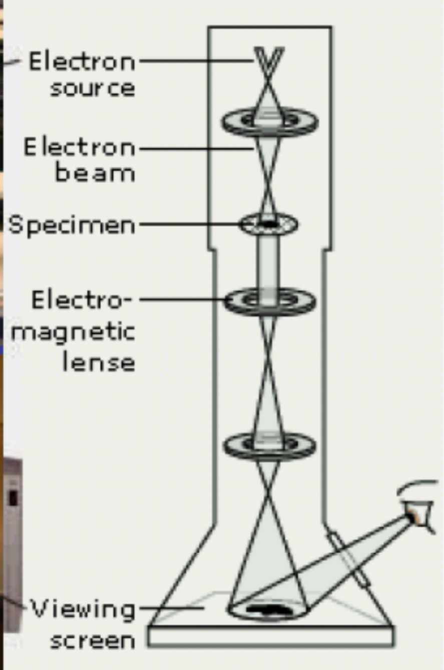
XPS X-ray photoelectron spectroscopy

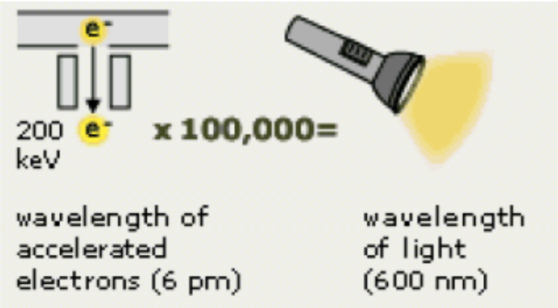
Mössbauer spectroscopy
XANES X-ray absorption near-edge structure

***STS** scanning-tunneling spectroscopy*

Transmission Electron Microscope (TEM)

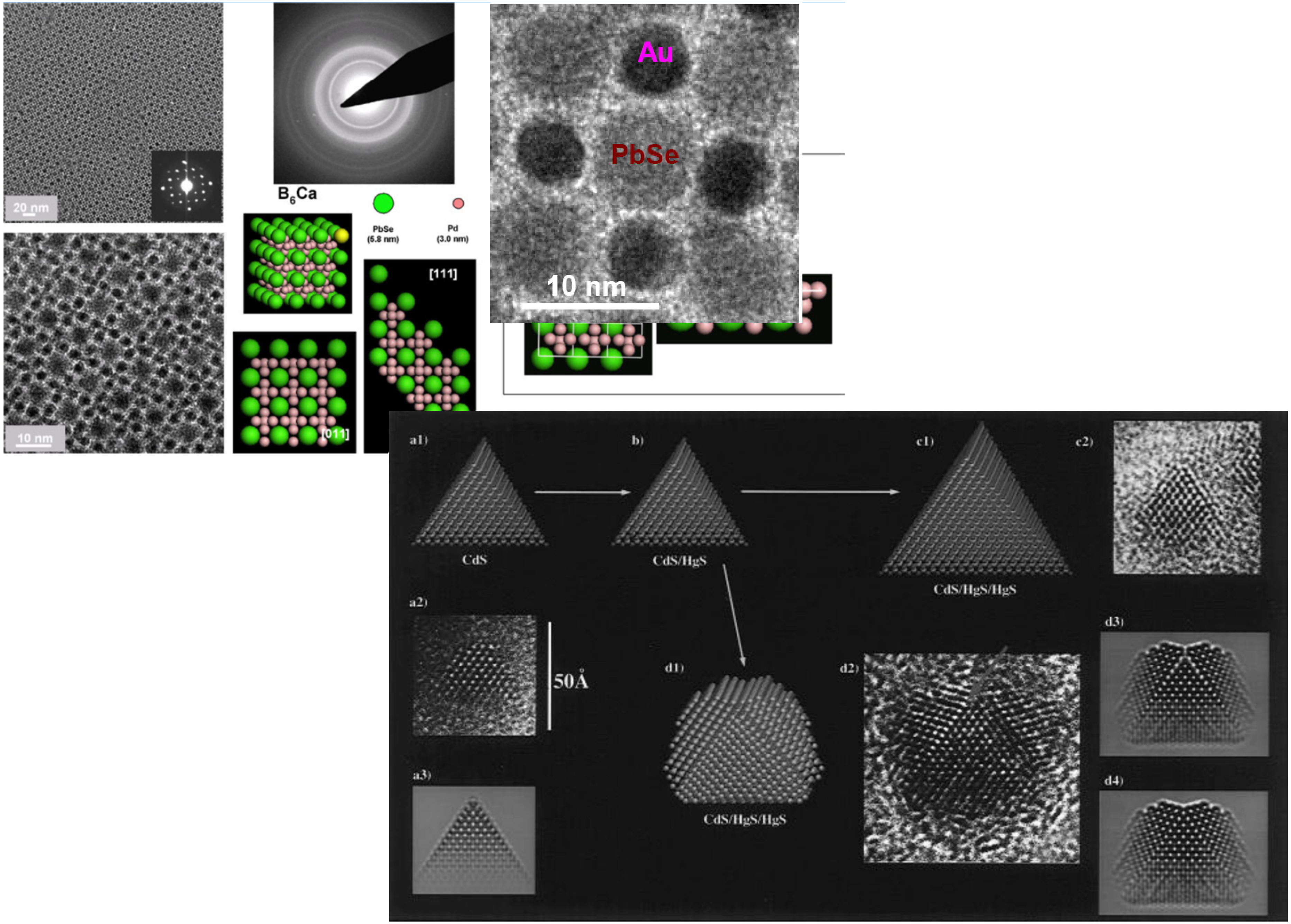
TEM
Copenhagen - 200 kV





	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

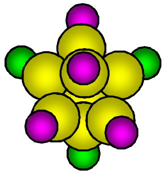
the shell *n*th includes $10n^2 + 2$ atoms

***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. $HAuCl_4 + 2PPh_3 + H_2O \xrightarrow{\substack{\text{EtOH}\\ \text{or THF}}} Ph_3PAuCl + Ph_3PO + 3HCl$

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



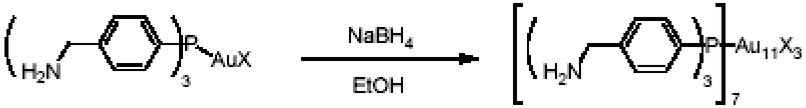
Step 3. $Au_{11}(PPh_3)_7Cl_3 + {\sim}30CH_3(CH_2)_{11}SH \xrightarrow{\text{THF}} Au_{11\text{-}13}(PPh_3)_x(SC12)_yCl_z$

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

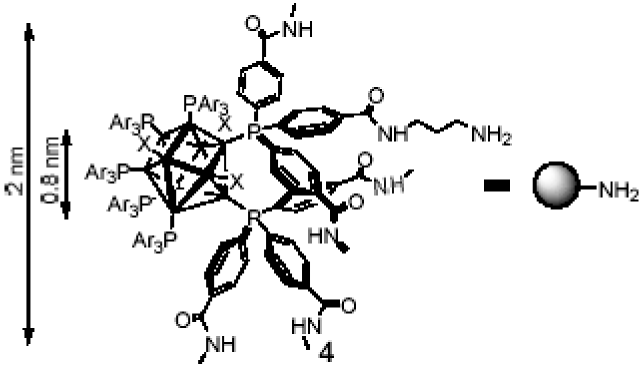
P. A. Bartlett, B. Bauer, S. J. Singer, *J. Am. Chem. Soc.* **1978**, *100*, 5085.
F. Cariati, L. Naldini, *Inorg. Chim. Acta*, **1971**, *5*, 172.

UNDECAGOLD



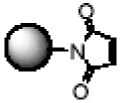
2a X = I
2b X = CN

3a X = I
3b X = CN



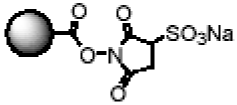
Undecagold

to bound thiols



Monomaleimmido Undecagold

it reacts with amines

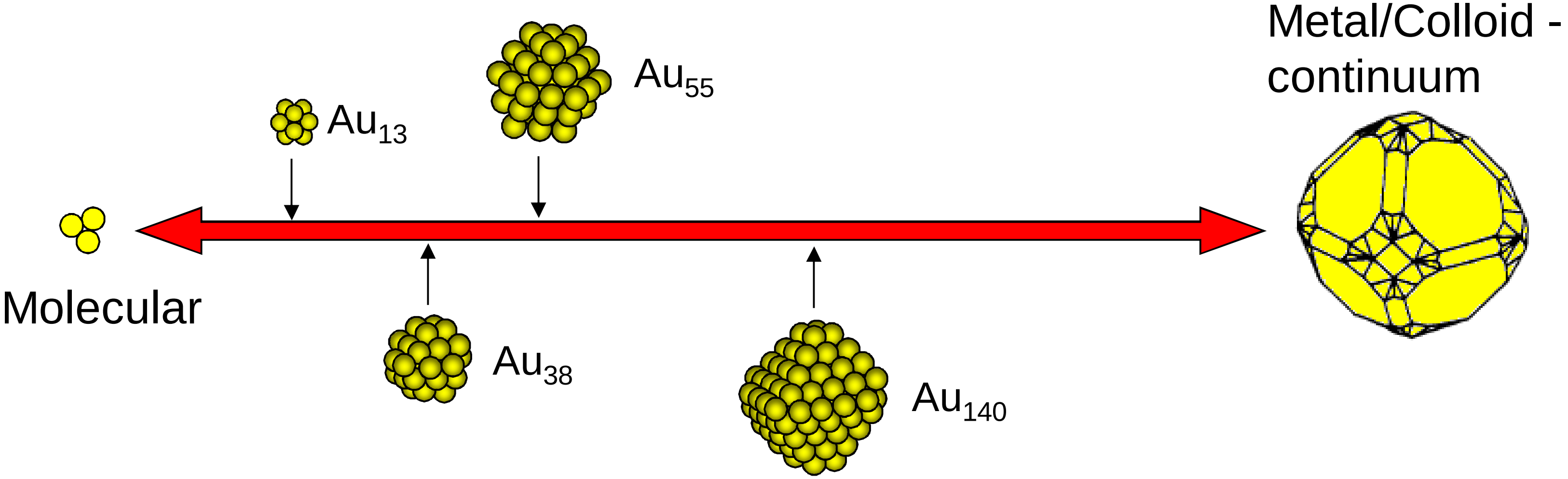


Sulfo-succinimmido Undecagold

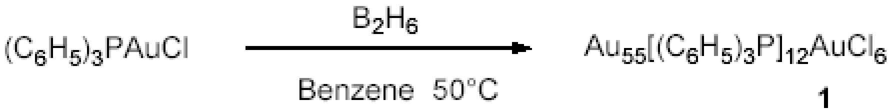
H. Yang, P. A. Frey, *Biochemistry*, **1984**, *23*, 3849, 3857, 3863.

- 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



$$(C_6H_5)_3PAuCl \xrightarrow[\text{Benzene } 50^\circ C]{B_2H_6} Au_{55}[(C_6H_5)_3P]_{12}AuCl_6$$

1 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.

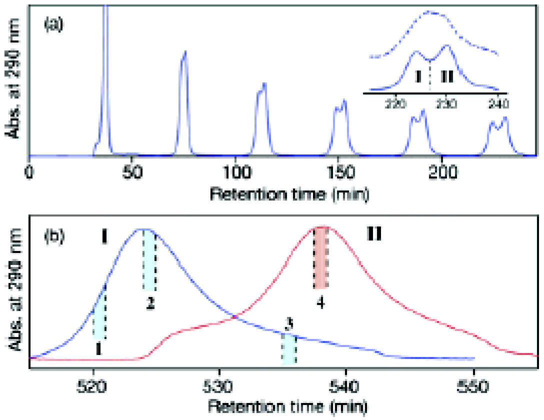


Figure 1. (a) Chromatogram of recycling GPC of the Au:SC_{18} clusters. Dotted curve in the inset is the data for the sample without etching treatment. (b) Recycling chromatograms of two fractions **I** and **II**.

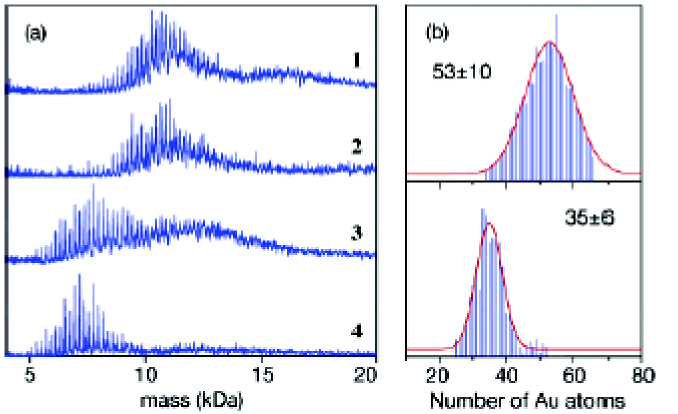


Figure 2. (a) LDI mass spectra of fractions **1**−**4** in the positive ion mode. (b) Histograms of the core numbers for fractions **2** and **4**.

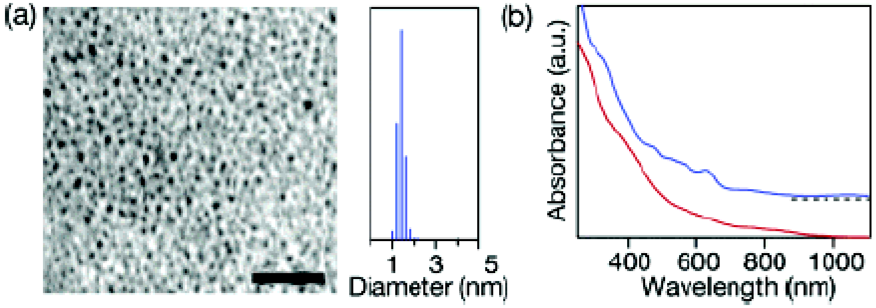
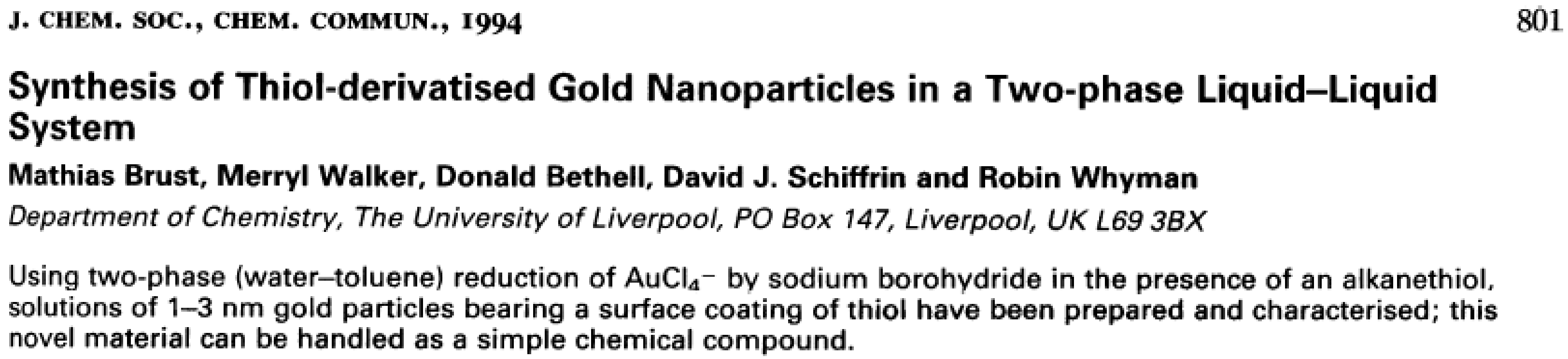


Figure 3. (a) TEM image and core-size distribution of Au_{55}:SC_{18}. The scale bar represents 20 nm. (b) Optical absorption spectra of Au_{55}:SC_{18} (red) and the 8 kDa clusters (blue).

Monolayer protected clusters MPCs



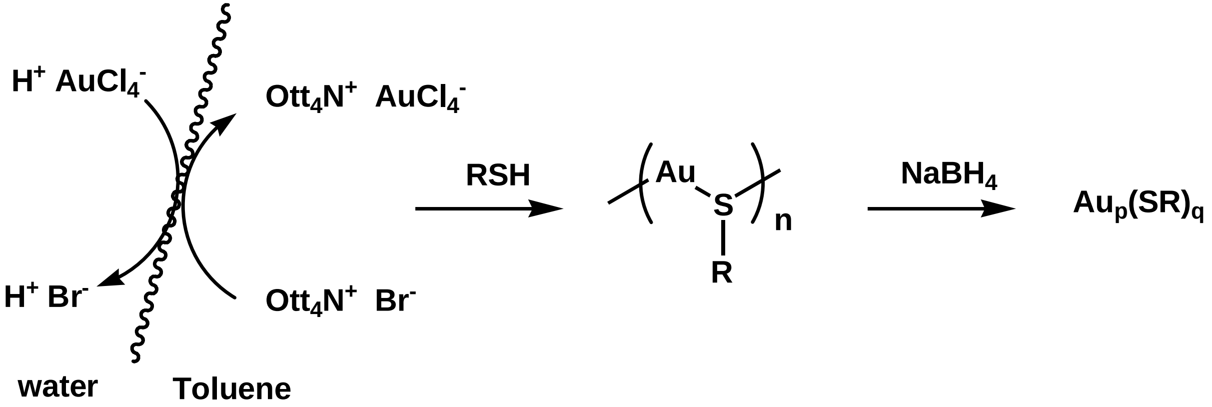
J. CHEM. SOC., CHEM. COMMUN., 1994 801

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.

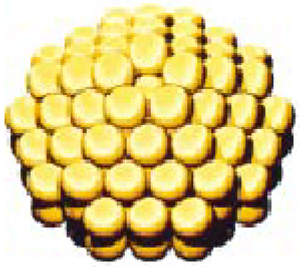


➡ MPCs OF DIFFERENT SIZE MAY BE OBTAINED USING DIFFEREN REACTION CONDITIONS:

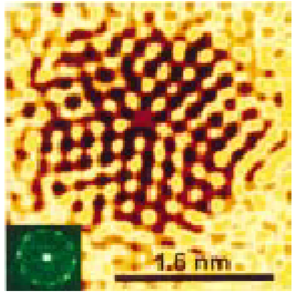
■ RATIO RSH/Au ■ REDUCTION RATE ■ TEMPERATURE

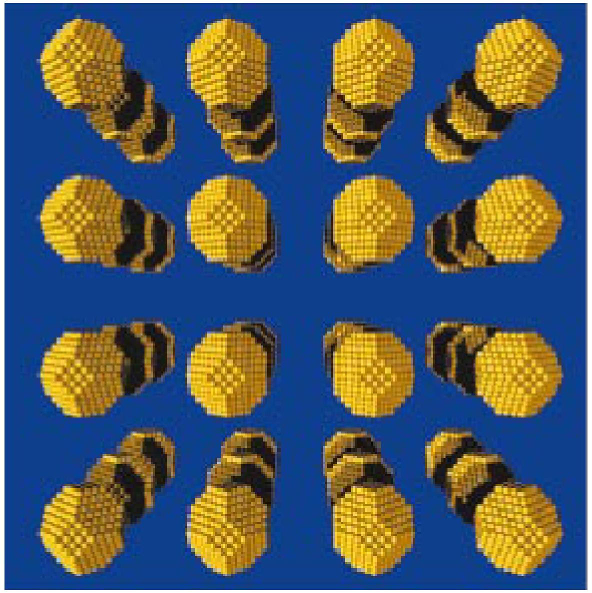
Nanoparticles – Au_{140}

the core



Au_{140}





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

Nanoparticles – the core

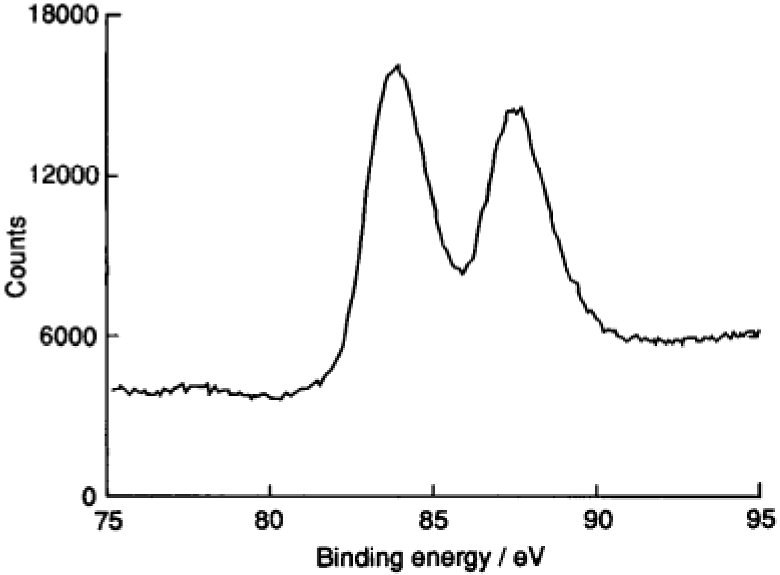
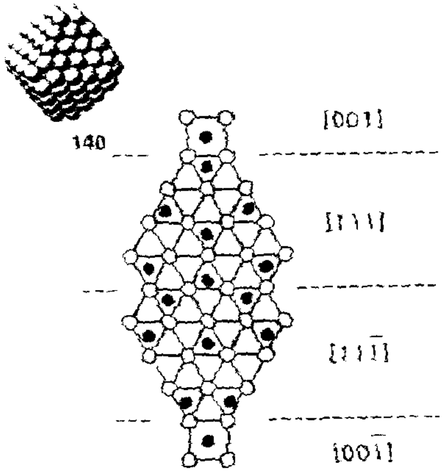
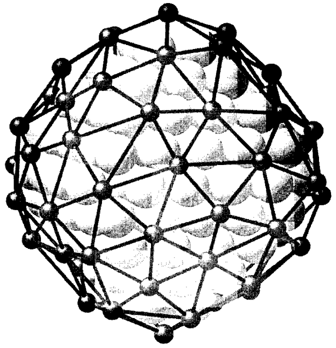
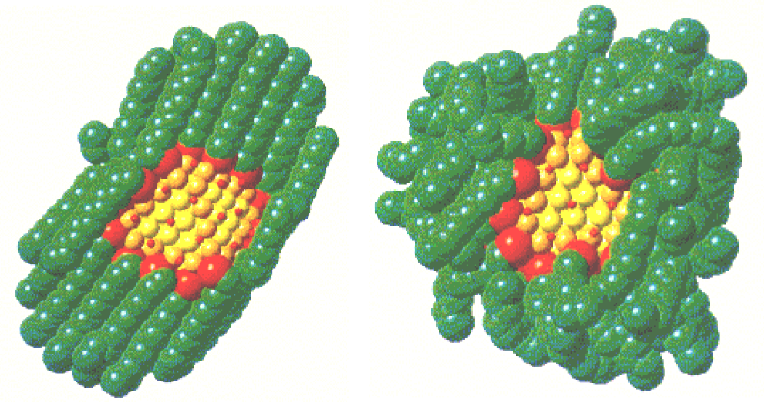


Fig. 3 XPS spectrum of the nanoparticles showing the Au $4f_{7/2}$ and $4f_{5/2}$ doublet with binding energies of 83.8 and 87.5 eV respectively. These are typical values for Au^0.

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

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

Pablo D. Jadzinsky,[1,2]* Guillermo Calero,[1]* Christopher J. Ackerson,[1]†
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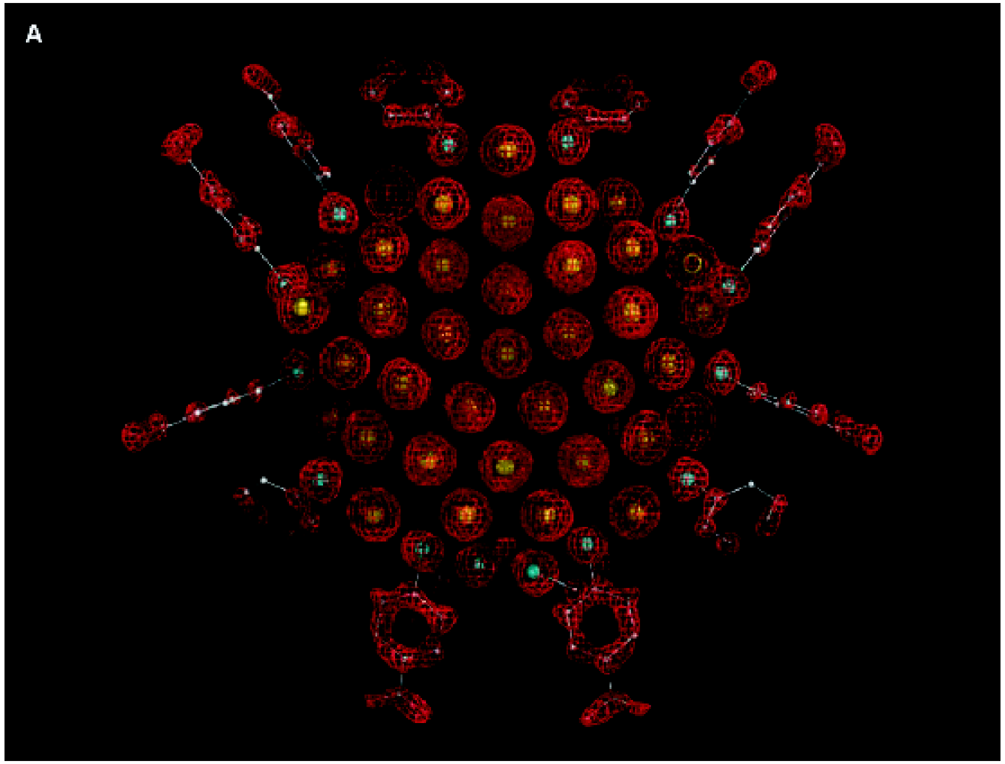

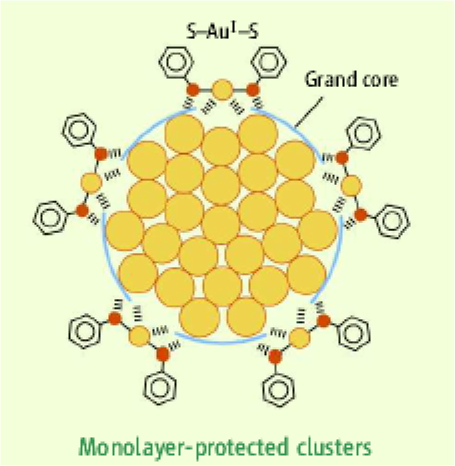

Fig. 1. X-ray crystal structure determination of the Au102(p-MBA)44 nanoparticle. (A) Electron density map(redmesh)andatomic structure (gold atoms depicted as yellow spheres, and p-MBA shown as framework and with small spheres [sulfur in cyan, carbon in gray, and oxygen in red]).

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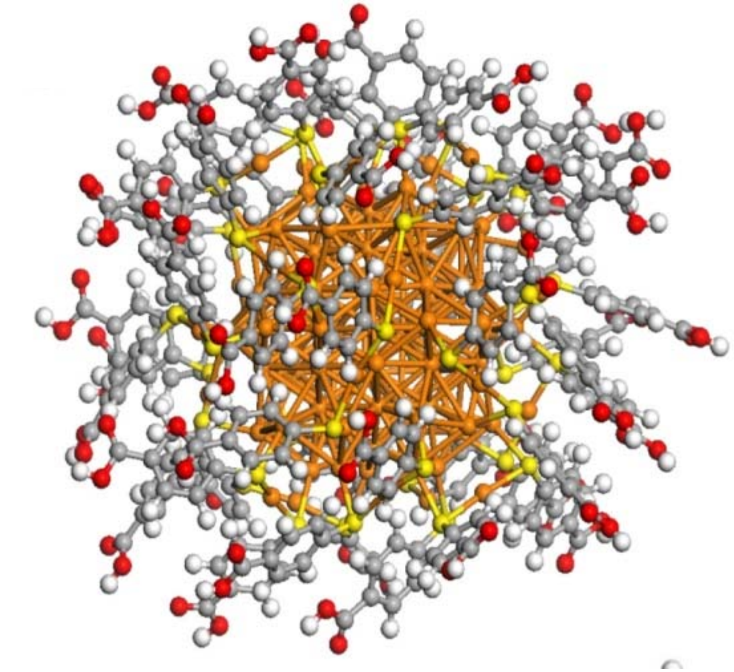

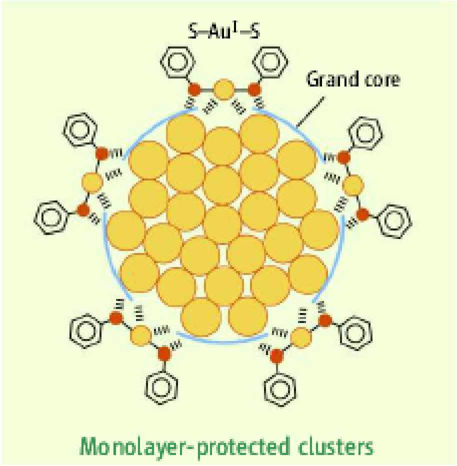

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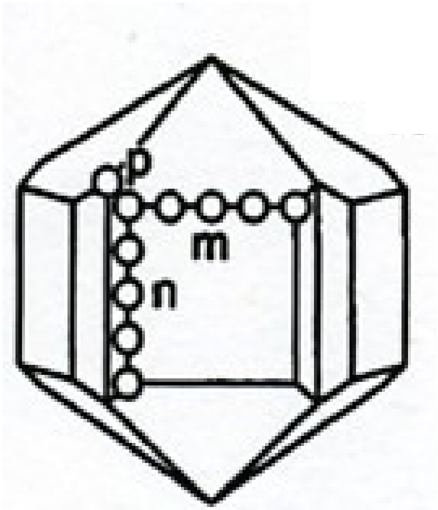


MD (m,n,p)

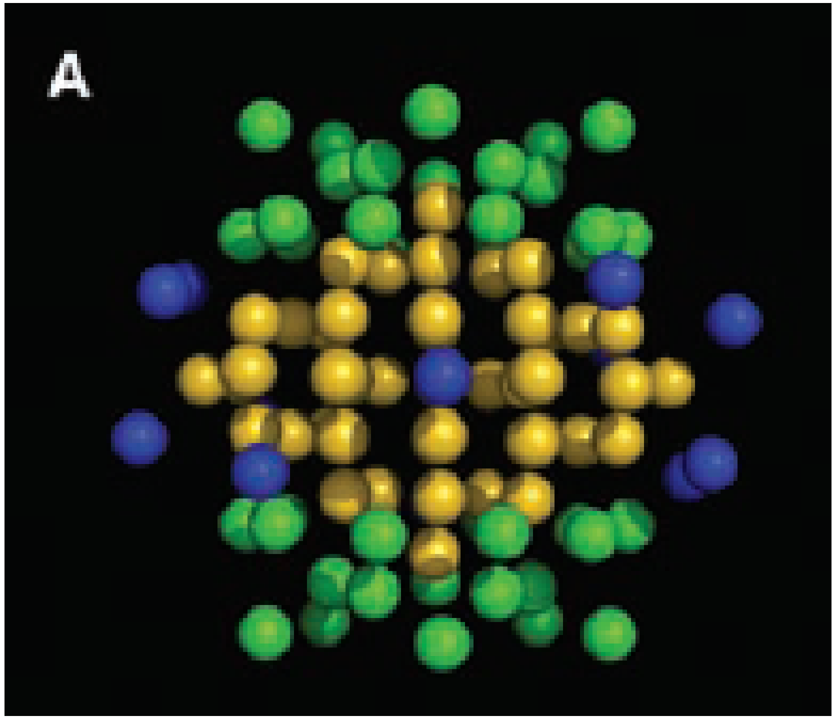
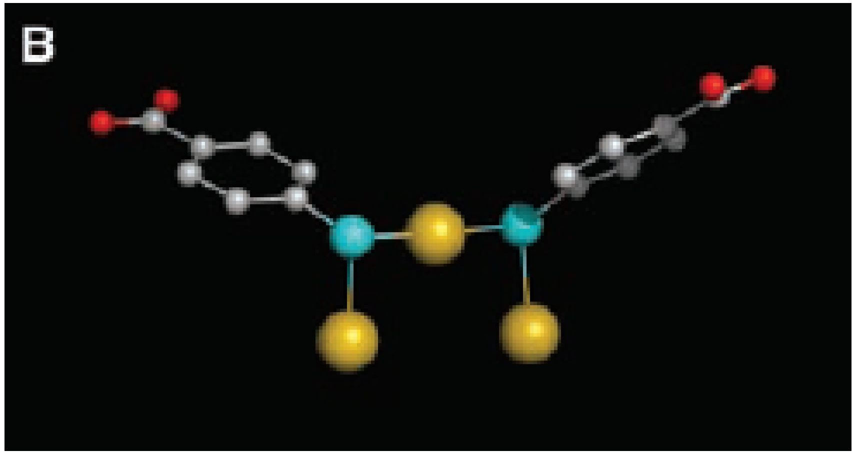
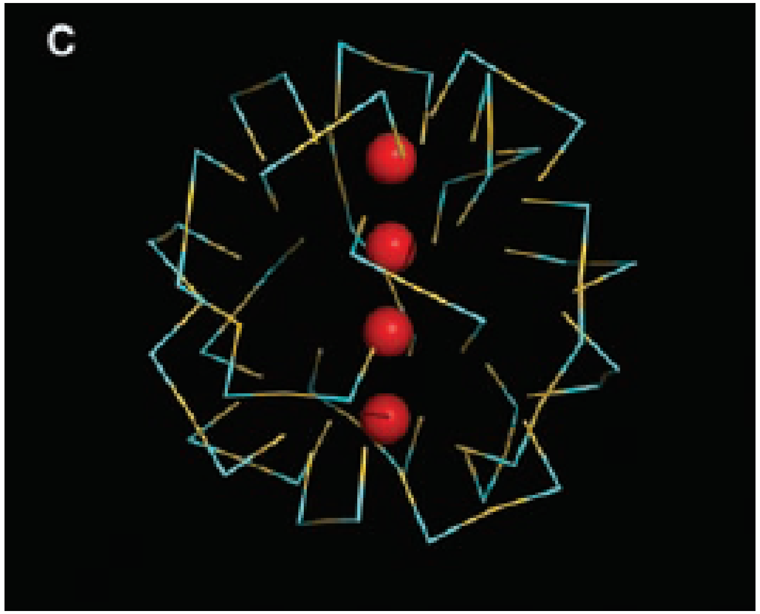


Fig.A: Packing of gold atoms in the nanoparticle. (A) MD (2,1,2) in yellow, two 20-atom“caps” at the poles in green, and the 13-atom equatorial band in blue.

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

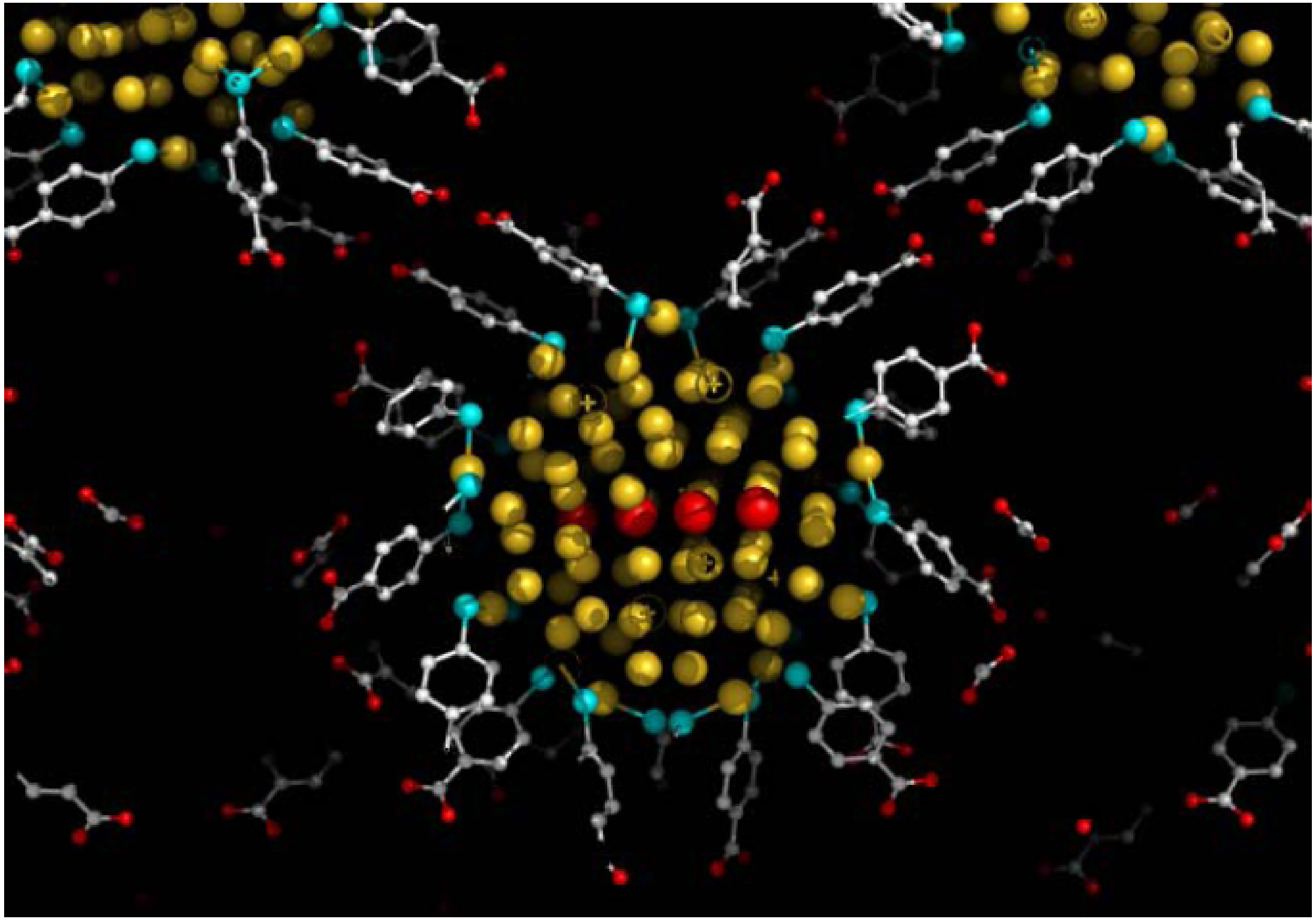


Example of two p-MBAs interacting with three gold atoms in a bridge conformation, here termed a staple motif. Gold atoms are yellow, sulfur atoms are cyan, oxygen atoms are red, and carbon atoms are gray.



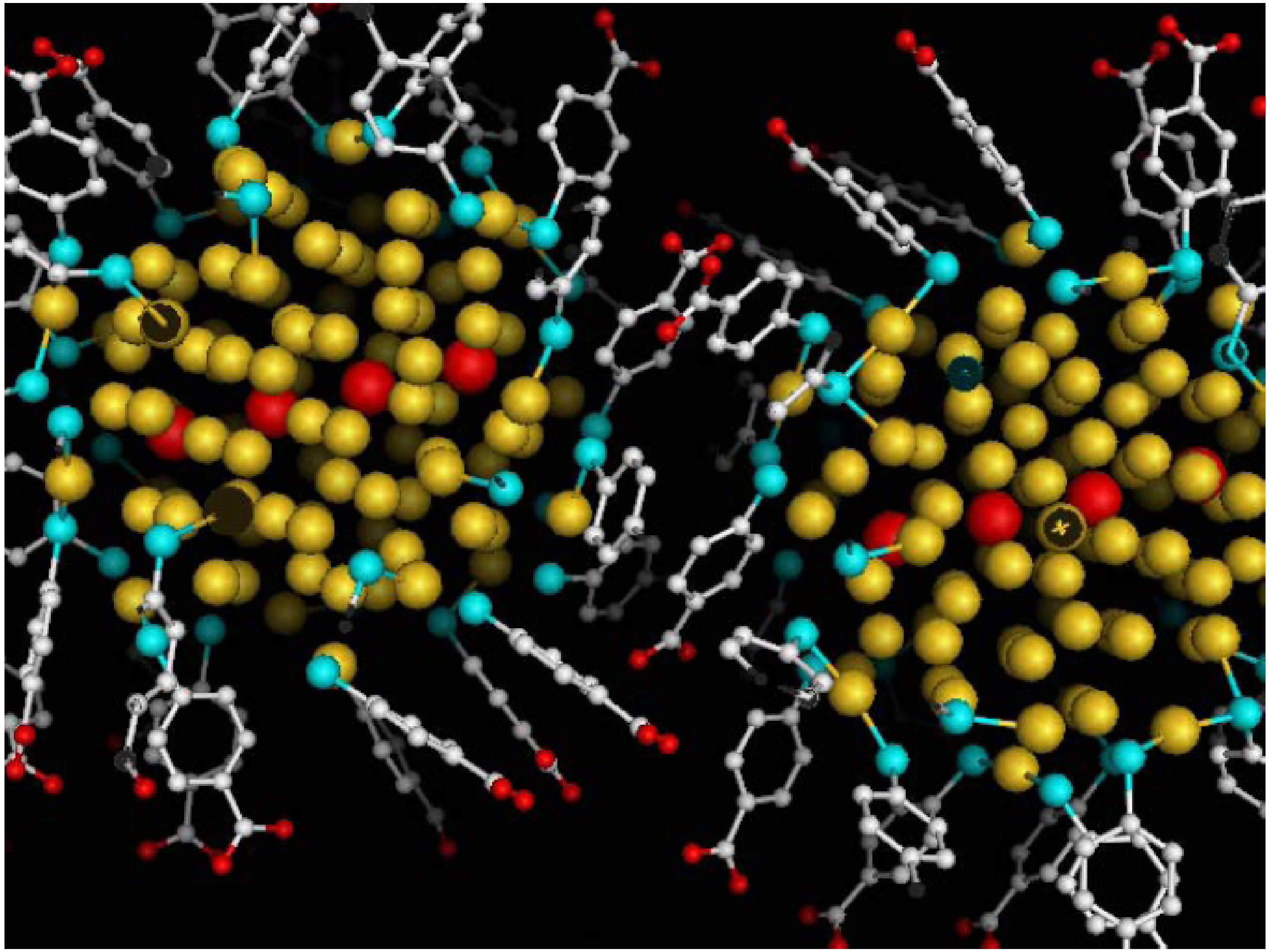
Distribution of staple motifs in the surface of the nanoparticle. Staple motifs are depicted symbolically, with gold in yellow and sulfur in cyan. Only the gold atoms on the axis of the MD are shown (in red).

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



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]

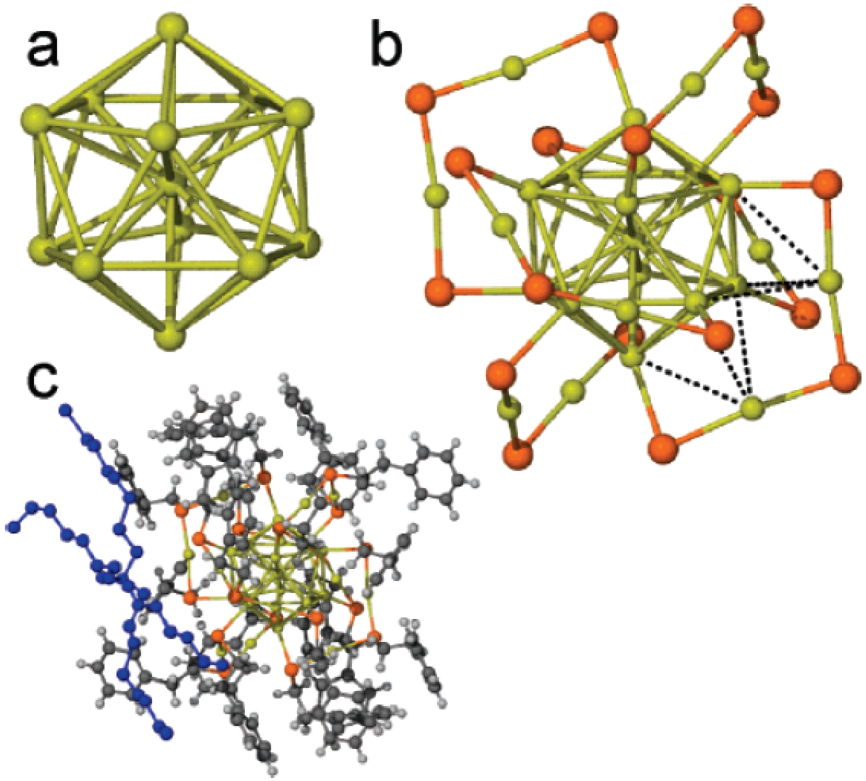


Figure 1. Breakdown of X-ray crystal structure of [TOA$^+$][Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}^-$] as seen from [001]. (a) Arrangement of the Au$_{13}$ core with 12 atoms on the vertices of an icosahedron and one in the center. (b) Depiction of gold and sulfur atoms, showing six orthogonal $-$Au$_2$(SCH$_2$CH$_2$Ph)$_3$$-$ "staples" surrounding the Au$_{13}$ core (two examples of possible aurophilic bonding shown as dashed lines). (c) [TOA$^+$][Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}^-$] 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