



Colloidal Gold

Markus Niederberger

Email: Markus.Niederberger@mpikg.mpg.de

22.11.2006



Outline

- 1) Definition
- 2) History
- 3) Synthesis
- 4) Chemical and Physical Properties
- 5) Applications
- 6) References



Definition

Colloidal gold:

Stable suspension of sub-micrometer-sized particles of gold in a liquid



Short History of Gold

- 4000 B.C.:** A culture in Eastern Europe begins to use gold to fashion decorative objects
- 2500 B.C.:** Gold jewelry was found in the Tomb of Djer, king of the First Egyptian Dynasty
- 1200 B.C.:** The Egyptians master the art of beating gold into leaf as well as alloying it with other metals for hardness and color variations
- 1091 B.C.:** Little squares of gold are used in China as a form of money
- 300 B.C.:** Greeks and Jews of ancient Alexandria start to practice Alchemy, the quest of turning base metals into gold
- 200 B.C.:** The Romans gain access to the gold mining region of Spain
- 50 B.C.:** The Romans begin issuing a gold coin called the Aureus
- 1284 A.D.:** Venice introduces the gold Ducat, which soon becomes the most popular coin in the world



History of Gold Colloids and their Application

History: Gold in Medicine

Humankind has linked the lustre of gold with the warm, life-giving light of the sun. In cultures, which deified the sun, gold represented its earthly form.

The earliest records of the use of gold for medicinal and healing purposes come from Alexandria, Egypt. Over 5000 years ago the Egyptians ingested gold for mental and bodily purification.

Gold was mainly used in medicine for its magico-religious powers and played almost no role in rational therapeutics until late Middle Age.

Why? There was no way to dissolve gold. The special characteristics of gold made it difficult to use medicinally.



History of Gold Colloids and their Application

History: Gold in Medicine

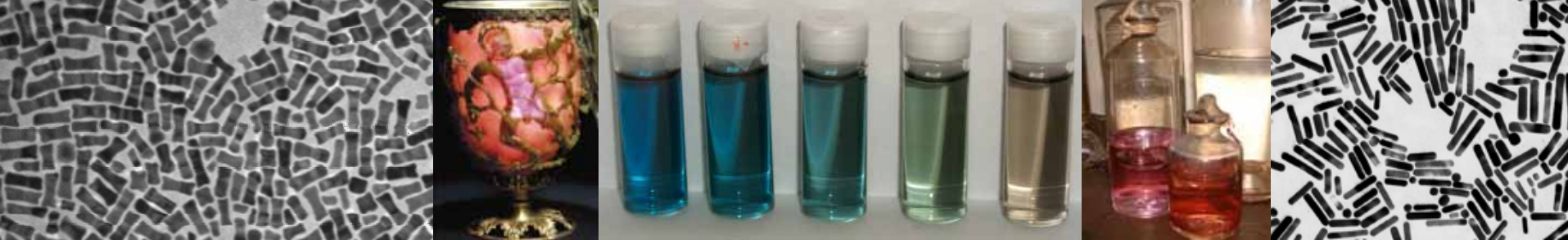
Around 1300 Geber (pseudonym for Islamic alchemist Jabir ibn Hayan) published his „*Summa Perfectionis Magisterii*“, presenting the preparation of aqua regia, a mixture of hydrochloric and nitric acid, which is able to dissolve gold. Through aqua regia alchemists hoped to learn the secrets locked within the „purest earthly substance“, and perhaps extract the elixir that could turn any metal into gold or could restore lost youth to an aged man.

Now that gold was soluble, it became more important for medicine.

Arnald of Villanova (1235-1311): „Gold is a miracle of nature. It cleanses the substance of the heart and the fountain of life.“



Relation between sun, gold and heart: Gold represents the power of the sun on earth, and the heart was the physiological equivalent of the sun, warming the body!



History of Gold Colloids and their Application

History: Gold in Medicine

The discovery of aqua regia inspired the European alchemists to search for the fifth element (in addition to earth, air, fire and water), the „quint essence“ which contained the characteristics of a substance.

Through dissolution and distillation processes the alchemist tried to isolate this quint essence from earthly elements like blood or gold.

However, potable gold did not become a common medicine until Paracelsus (1493-1541): Aurum potable for the treatment of melancholy („it made one's heart happy“).

In the early 17th century gold seriously began to enter the official drug compendia, however there was always a big controversy about its value.



History of Gold Colloids and their Application

History: Gold in Medicine

In the 18th and early 19th century the use of gold in medicine almost disappeared.

In the mid-19th century gold was used in syphilis therapy.

Around 1880: Keeley Institute in the USA used gold for healing alcoholism.

1890: Robert Koch discovers the *in vitro* bacteriostatic properties of gold.

Nowadays the medicinal use of gold is almost entirely limited to the treatment of rheumatoid arthritis.



History of Gold Colloids and their Application



Gold in Dentistry

Ca. 700 B.C.:

First clear evidence for the application of gold in prosthetic dentistry in the Etruscan culture



History of Gold Colloids and their Application

Gold-Based Enamel Colours

1659: Johann Rudolf Glauber prepared colloidal gold as purple by reduction of gold salts by tin chloride (Purple of Cassius)

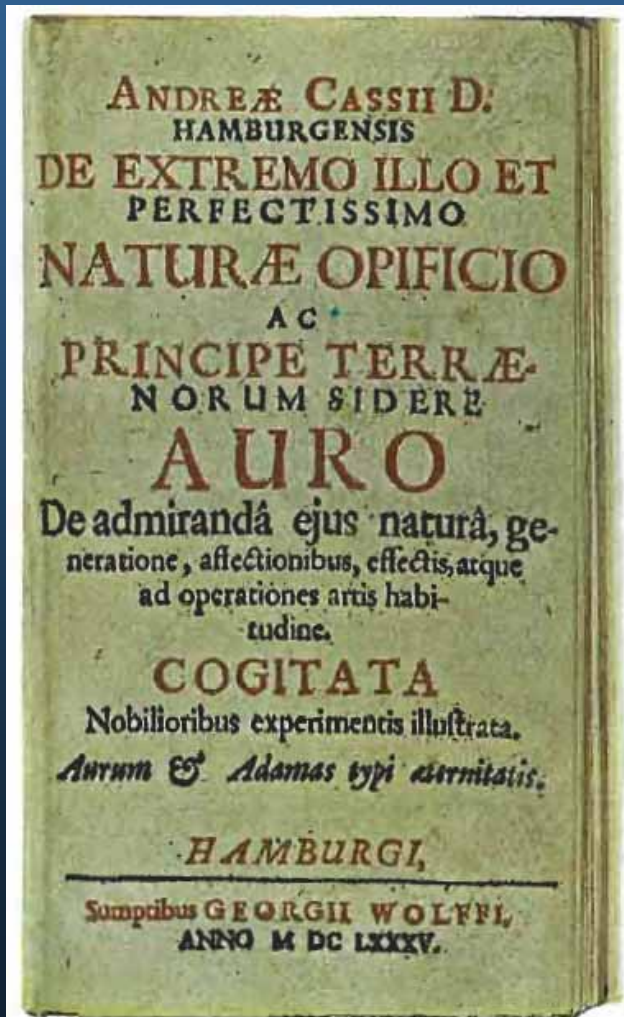
1679-1689: Johann Kunckel used the purple for his glass works in Potsdam



Tea pot with the red colour by Kunckel



History of Gold Colloids and their Application



Gold-Based Glass and Enamel Colours

1685: Andreas Cassius published *De Auro*

„Thoughts concerning that last and most perfect work of Nature and chief of metals, gold, its wonderful properties, generation, affections, effects and fitness for the operations of art; illustrated by experiments“



Purple of Cassius



History of Gold Colloids and their Application

Gold-Based Glass and Enamel Colours

- 1719: Purple of Cassius was used in the Meissen porcelain factory
 Ca. 1720: Purple of Cassius reached China, where it was used in *Famille Rose* porcelain



Meissen jug, 1740



Famille Rose, 1723



History of Gold Colloids and their Application

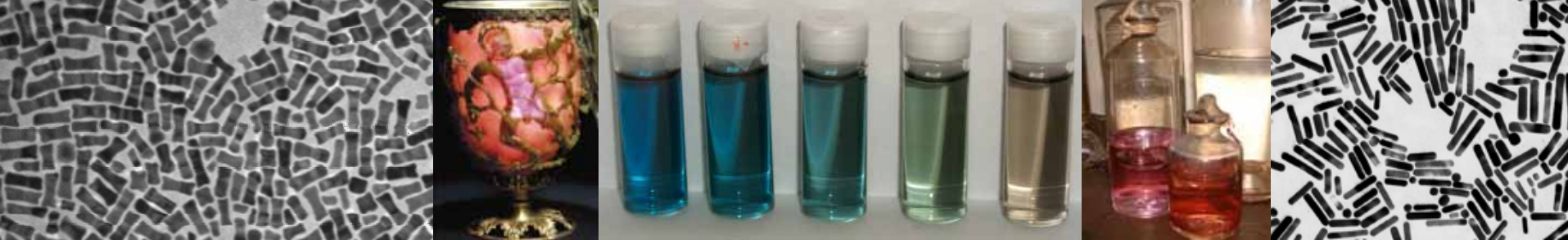
Purple of Cassius became, until today, the most popular enamel colour for pottery and porcelain.

However, its chemical nature was a challenge for the scientists of the 19th century.

Around 1897, almost 250 years after its discovery, Richard Zsigmondy, a chemist working on gold colloids at the Schott Glassworks in Jena, showed that Purple of Cassius consisted of colloidal gold and stannic acid. He was awarded the Nobel Prize in Chemistry in 1925.

Ca. 1850s: Michael Faraday prepared pure colloidal gold using phosphorus to reduce gold chloride. He recognized that the colour was due to the small size of the colloids.





History of Gold Colloids and their Application

Gold Colloids in Glass



Lycurgus Cup in the British Museum

Roman pottery – 400 after Christ

Red color from nanosized gold!

Illuminated from outside (green) and from inside (red)

Nature **2000**, 407, 691

Stained glass in Gothic churches: A colored “stain” is achieved when colorless metaldoped glass is heated at high temperatures. Annealing of gold-doped glass results in the formation of colloidal gold, which gives rise to a characteristic ruby red.



The First Nanotechnologists

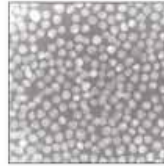
Ancient stained-glass makers knew that by putting varying, tiny amounts of gold and silver in the glass, they could produce the red and yellow found in stained-glass windows. Similarly, today's scientists and engineers have found that it takes only small amounts of a nanoparticle, precisely placed, to change a material's physical properties.

Gold particles in glass

Size*: 25 nm
Shape: sphere
Color reflected:

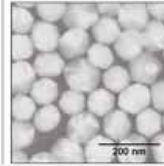


100 nanometers =
0.0001 millimeter



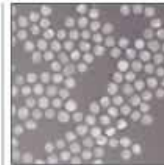
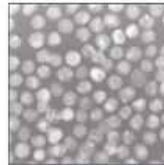
Silver particles in glass

Size*: 100 nm
Shape: sphere
Color reflected:



Had medieval artists been able to control the size and shape of the nanoparticles, they would have been able to use the two metals to produce other colors. Examples:

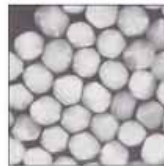
Size*: 50 nm
Shape: sphere
Color reflected:



Size*: 40 nm
Shape: sphere
Color reflected:



Size*: 100 nm
Shape: sphere
Color reflected:



Size*: 100 nm
Shape: prism
Color reflected:



Source: Dr. Chad A. Mirkin, Institute of Nanotechnology, Northwestern University

*Approximate



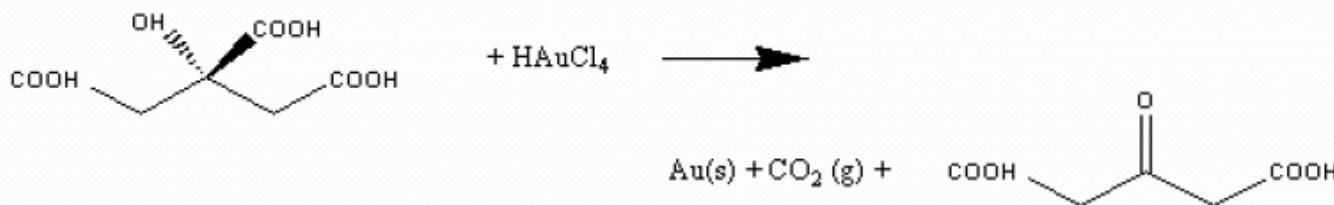


Synthesis of Gold Colloids

1951: **Method by Turkevich** *et al.* (Reduction by citrate)

A STUDY OF THE NUCLEATION AND GROWTH PROCESSES IN THE SYNTHESIS OF COLLOIDAL GOLD by J. Turkevich, P. C. Stevenson, J. Hillier
DISCUSSIONS OF THE FARADAY SOCIETY (11): 55 (1951)

Times Cited: 436



Gold chloride is dissolved in water while heating and stirring
 Trisodium citrate dihydrate is dissolved in a small amount of water then added
 Reflux for one hour, as citrate reduces Gold(III).

Citrate as reducing and stabilizing agent



Synthesis of Gold Colloids

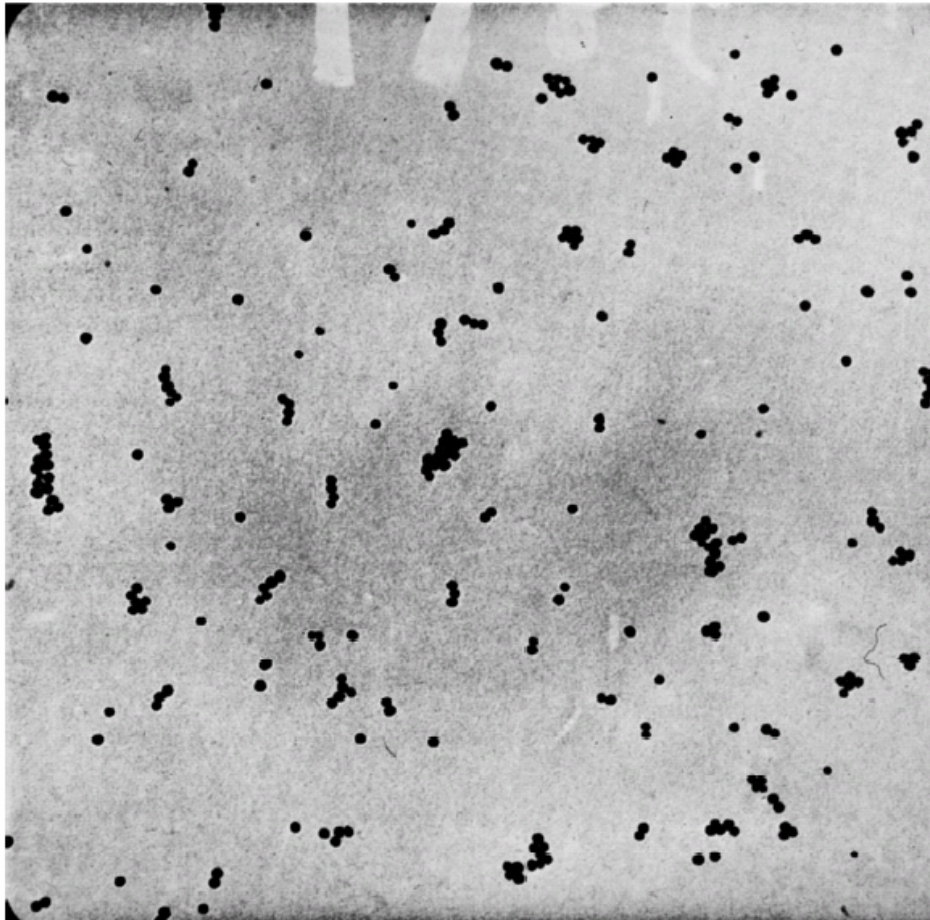


FIG. 3.—Electron micrograph of a gold sol reduced with sodium citrate (standard citrate sol) magnification 50,000 diameters.

Gold colloids with
uniform diameters of
about 20 nm

Size dependent on
citrate concentration



Synthesis of Gold Colloids

1994: The Brust-Schiffrin Method (Two-Phase Synthesis and Stabilization by Thiols)

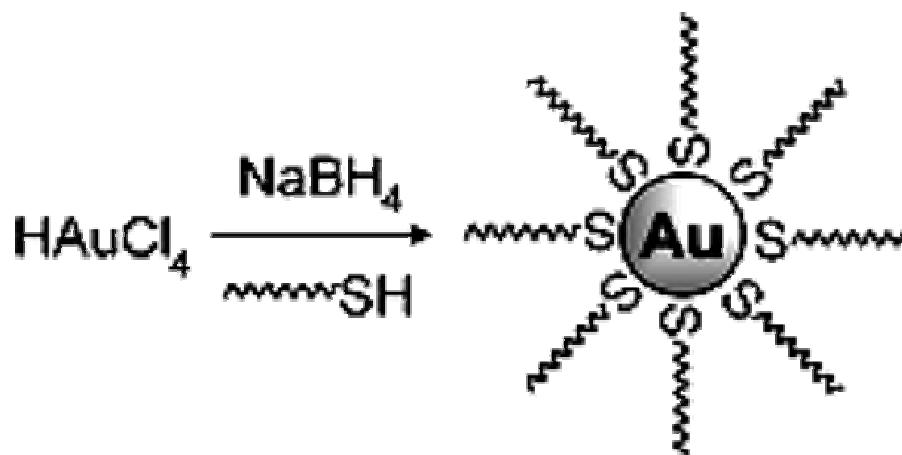
Synthesis of Thiol-Derivatized Gold Nanoparticles in a Two-Phase Liquid-Liquid System

By M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. J. Whyman

J. Chem. Soc., Chem. Commun. **1994**, 801-802.

Times Cited: 1386

AuCl_4^- is transferred to toluene using tetraoctylammonium bromide as the phase-transfer reagent and reduced by NaBH_4 in the presence of dodecanethiol. The organic phase changes color from orange to deep brown within a few seconds upon addition of NaBH_4 :





Synthesis of Gold Colloids

Nowadays: In addition to Citrate Reduction and Brust-Schiffrin Method many other approaches based on the use of sulfur, phosphine, phosphine oxide, amine and carboxylate ligands

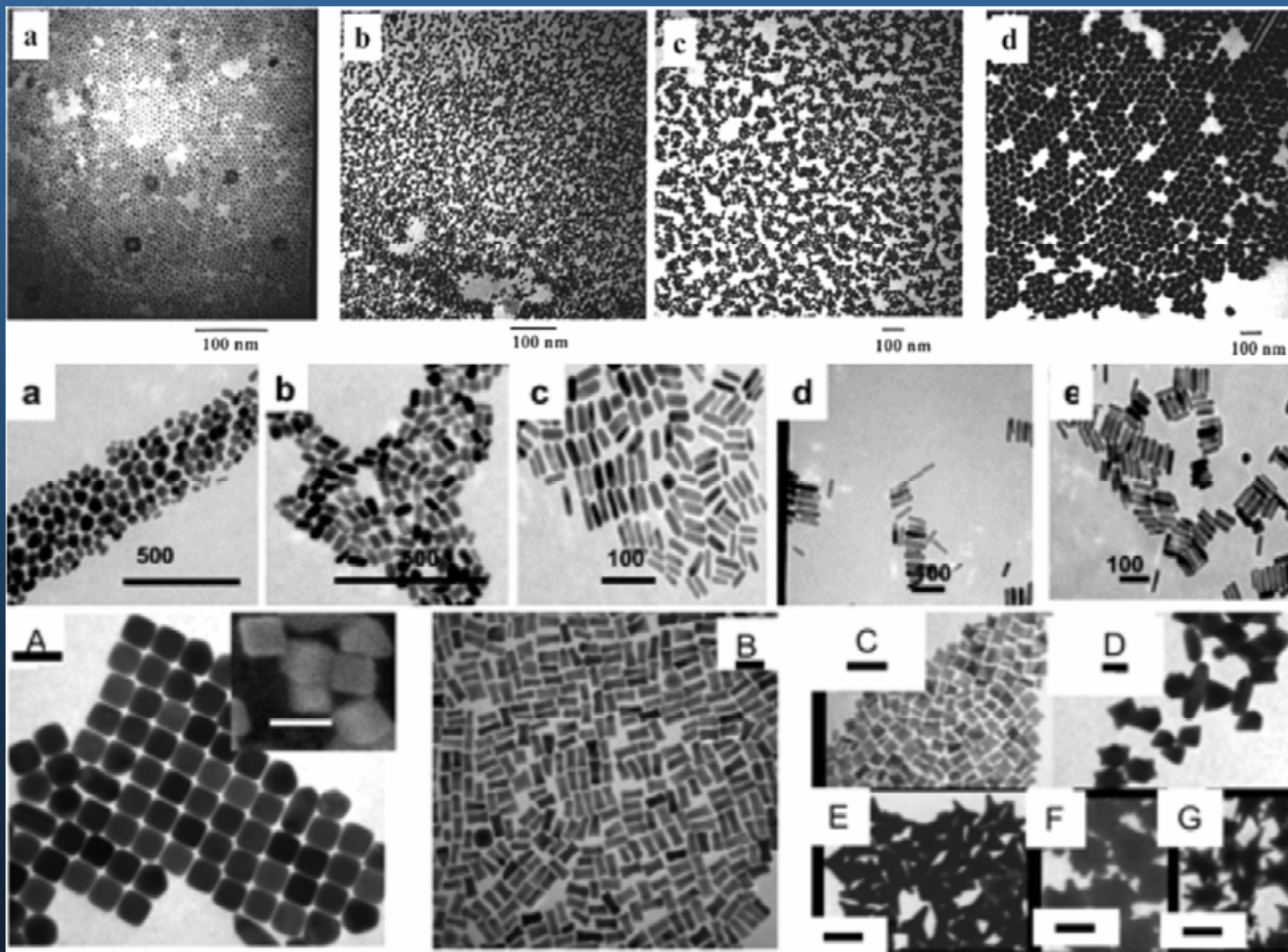
Microemulsion, Reversed Micelles

Seeding Growth (variation of seed-to-metal salt ratio)

Physical methods (photochemistry, sonochemistry, radiolysis, thermolysis,...)

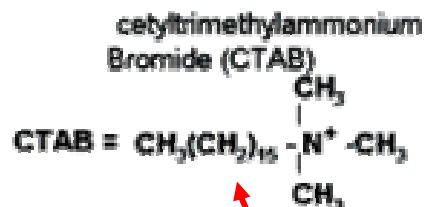
Synthesis of Gold Colloids

Excellent control over size and shape



Synthesis of Gold Colloids

Seed-mediated growth for controlling the aspect ratio:



I. Synthesis of seed

2.5×10^{-4} M HAuCl_4 +
 2.5×10^{-4} M Na-citrate



+

0.6 mL 0.1 M
Ice-cold aq NaBH_4



Gold nanoparticle seeds
(~ 4nm diameter)

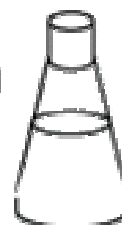
II. Stock solution

Stock solution
 2.5×10^{-4} M HAuCl_4
+ 0.1 M CTAB

=

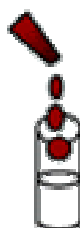


Addition of
Ascorbic acid



Reduction
of Au^{3+} to
 Au^{1+} results
in disappearance
of color

II. Three step protocol for nanorod synthesis



Step A

Add 1mL
of A

Step B



Step C

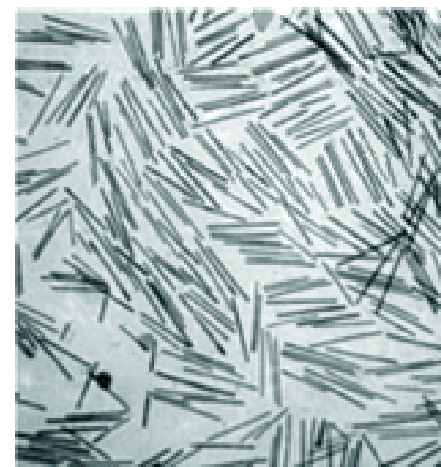


=

1 mL seed +
9 mL of stock
solution

1 mL A +
9 mL of stock
solution

10 mL B +
90 mL stock



Growth Mechanism of Gold Nanorods

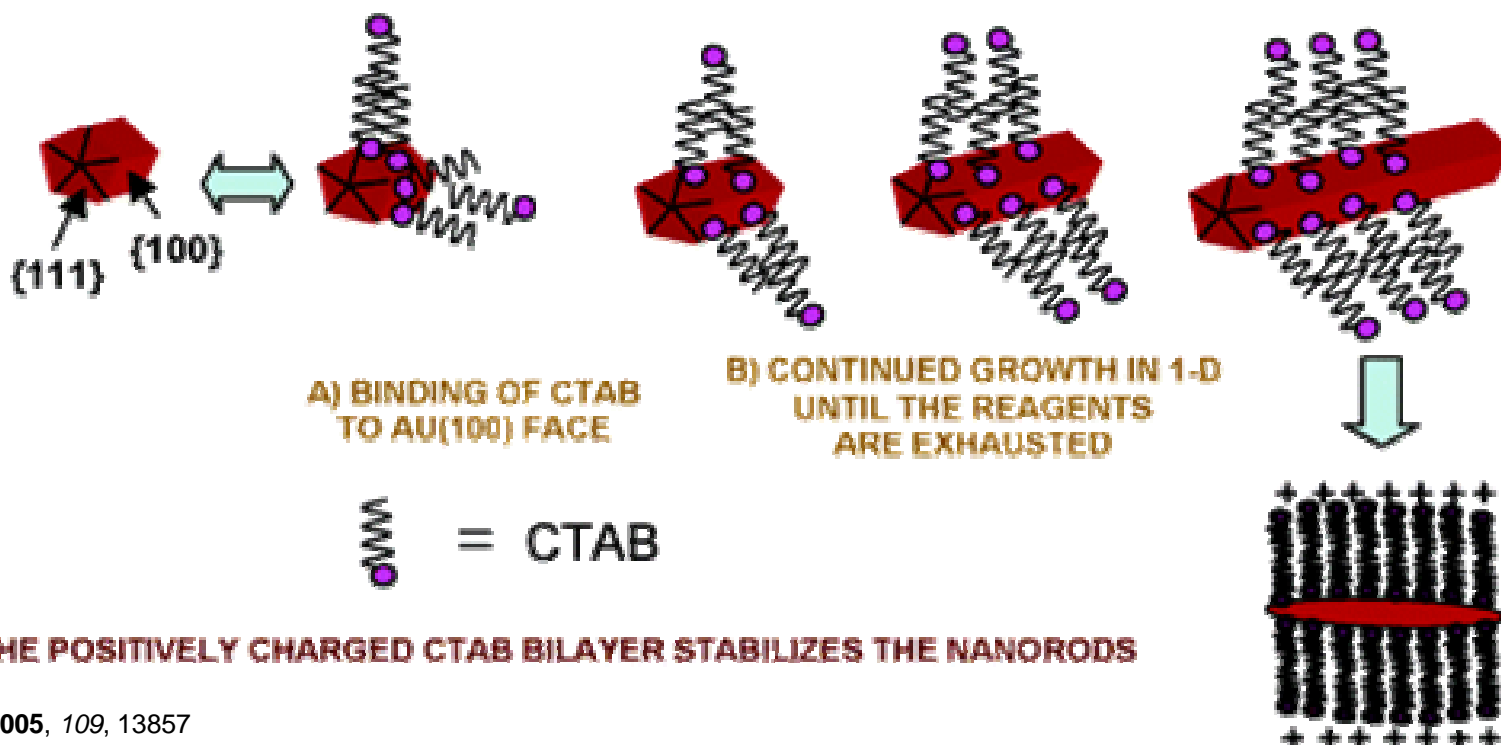
STEP 1: SYMMETRY BREAKING IN FCC METALS

A) NUCLEATION

B) GROWTH

C) DEVELOPMENT OF FACETS

STEP 2: PREFERENTIAL SURFACTANT BINDING TO SPECIFIC CRYSTAL FACES

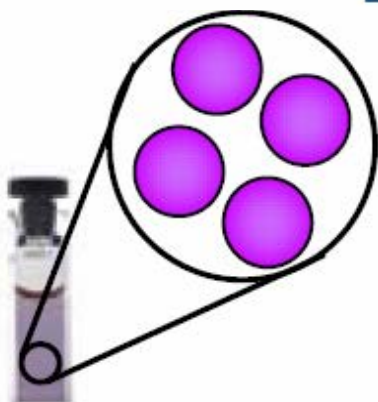


Properties of Gold Colloids

Size-dependent Properties of Gold



Bulk Gold
mp = 1064 °C
Color = gold

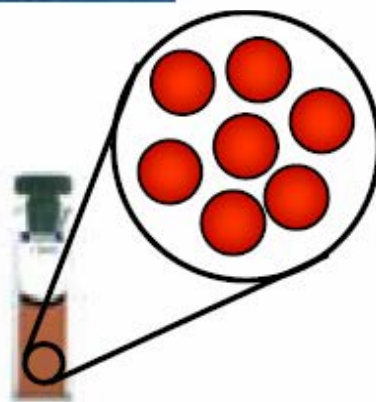


100 nm gold particles

mp = ~1000 °C

$\lambda_{\text{abs}} = 575 \text{ nm}$ (**yellow**)

Color = purple-pink

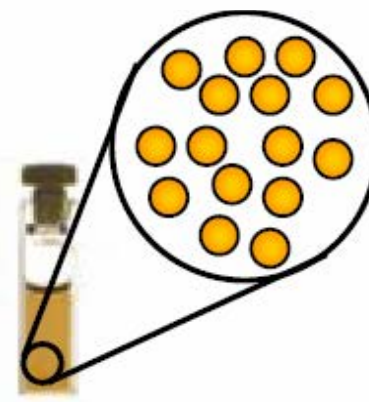


20 nm gold particles

mp = ~1000 °C

$\lambda_{\text{abs}} = 521 \text{ nm}$ (**green**)

Color = red



1 nm gold particles

mp = 700 °C

$\lambda_{\text{abs}} = 420 \text{ nm}$ (**purple**)

Color = brown-yellow

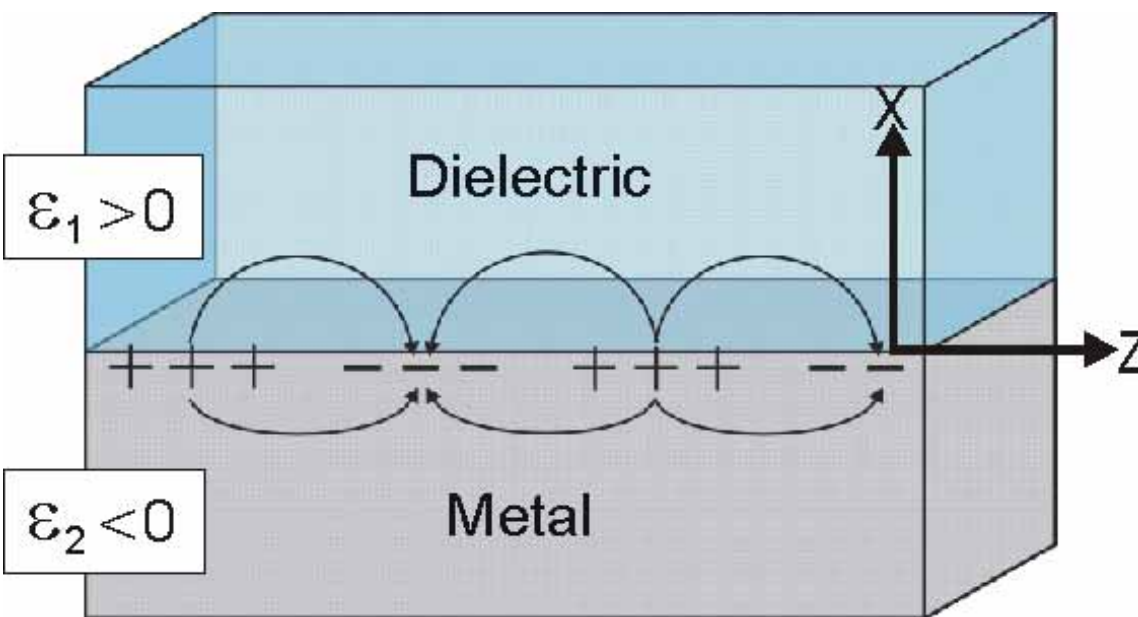


Optical Properties of Gold Colloids

Definitions

Plasmons: Collective oscillations of the free electron gas at optical frequencies

Surface plasmons: Oscillation of the electrons in the conduction band at the surface of the nanoparticles upon excitation with incident radiation



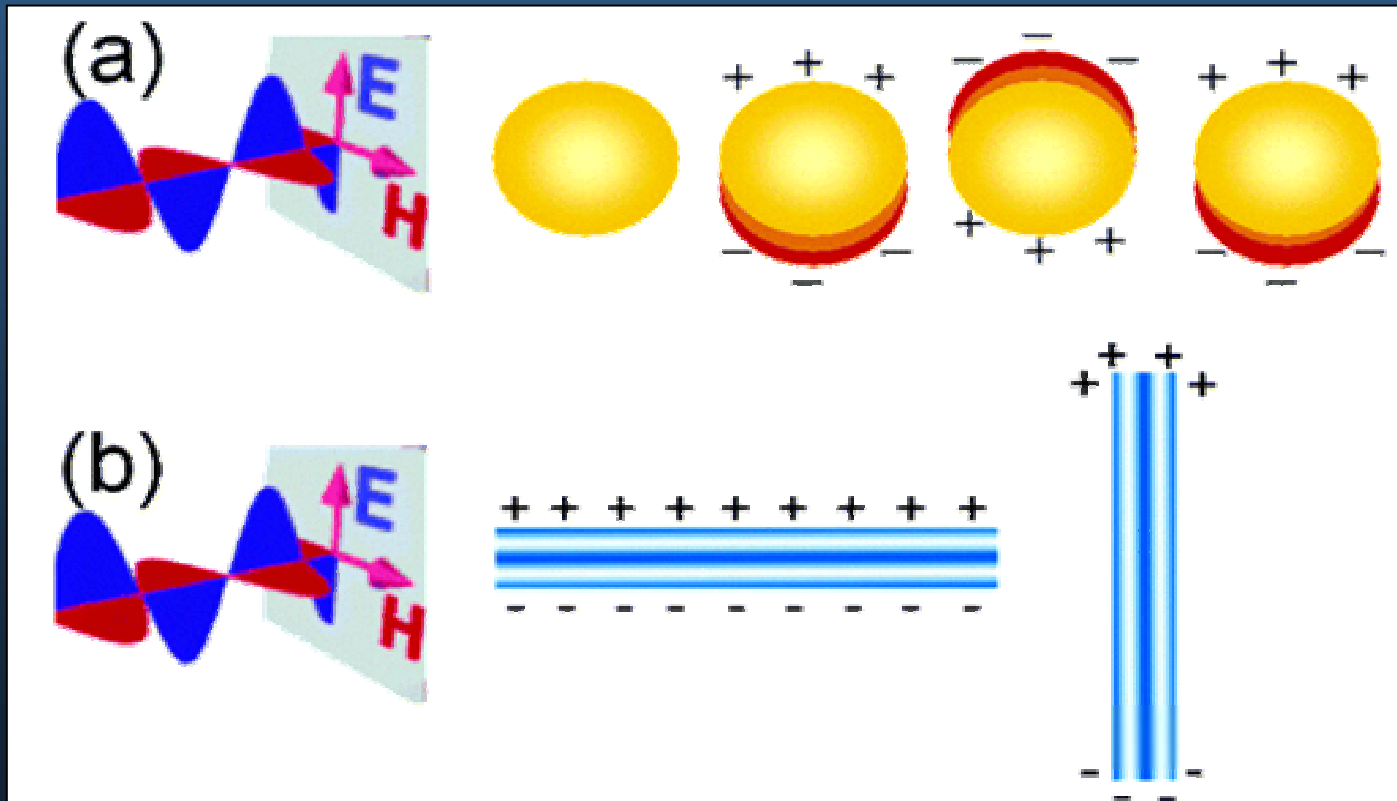
Surface plasmons exist only at the interface of two media with dielectric constants of opposite sign, for example:

This condition is met in the IR-visible wavelength region for air/metal and water/metal interfaces (where the dielectric constant of a metal is negative and that of air or water is positive).

Optical Properties of Gold Colloids

- 1) Electric field of incoming radiation induces the formation of a dipole in the NP
- 2) Restoring force tries to compensate it
- 3) Unique resonance frequency matches this electron oscillation

(a) Interaction of an electromagnetic radiation (light) with a metal nanosphere. A dipole is induced, which oscillates in phase with the electric field of the incoming light. (b) **Transversal** and **longitudinal** oscillation of electrons in a metal nanorod.





Optical Properties of Gold Colloids

For many metals like Pb, In, Hg, Sn and Cd the plasma frequency is in the UV:
No colour effects.

For Au, Ag and Cu the plasma frequency is in the visible part of the spectrum:
Colour effects.

The plasmon absorption is highly dependent on nanoparticle **shape, size, aggregation state and dielectric constant** of the surrounding medium.

Accordingly, the optical properties of gold nanoparticles can be controlled by adjusting these parameters!

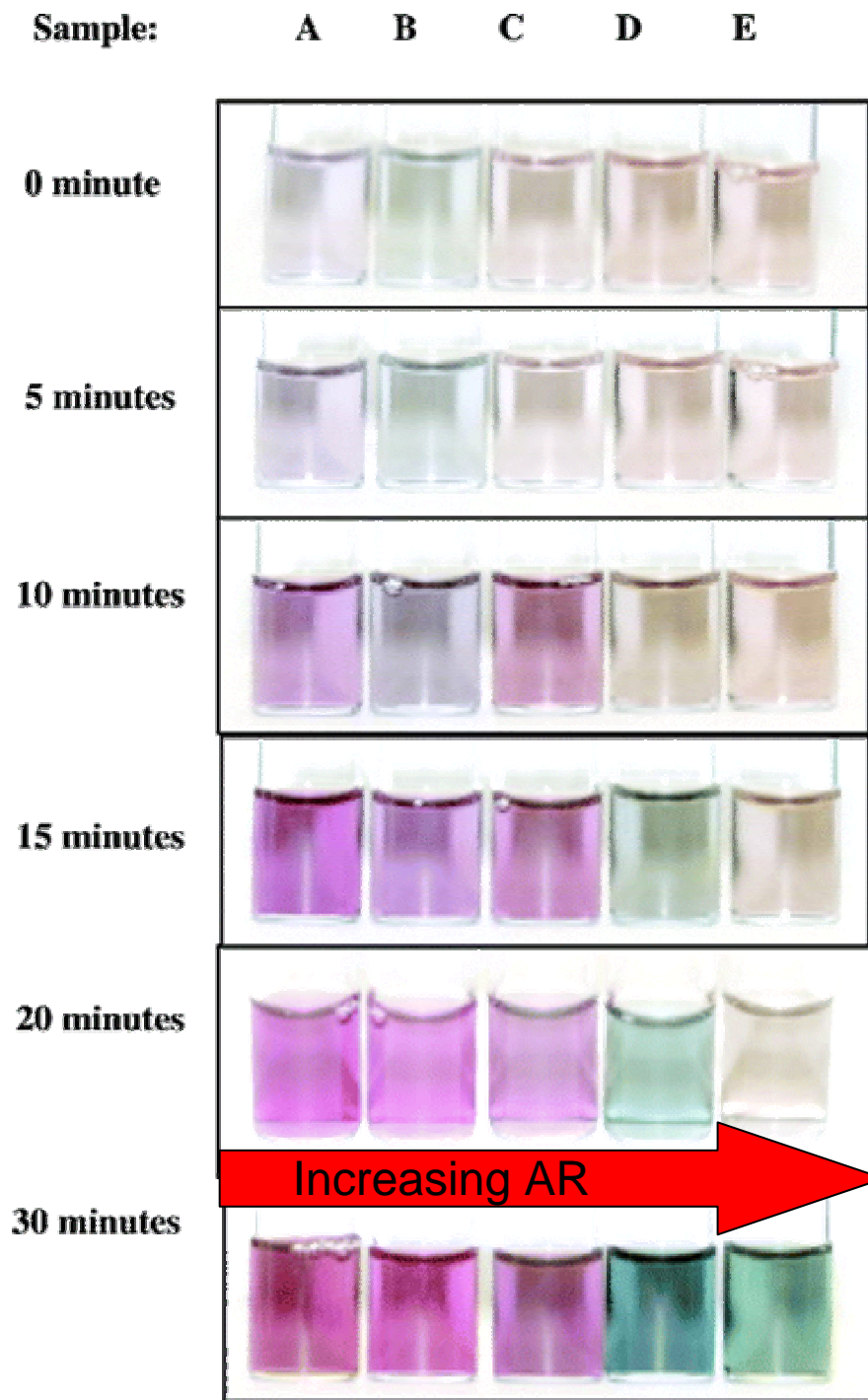


Table 1. Dimensions and Aspect Ratios of Gold Nanorods before and after Heating at 100 °C for 30 min, As Measured by TEM

sample	initial length (nm)	final length (nm)	initial width (nm)	final width (nm)	initial AR	final AR
A	48 ± 5	47 ± 5	22 ± 5	47 ± 5.0	2.2	1
B	50.9 ± 5	45.4 ± 5	18 ± 0.5	21.6 ± 0.5	2.8	2.1
C	57.6 ± 3	58.5 ± 3	14.8 ± 0.5	19.6 ± 0.5	3.9	3
D	54.8 ± 3	55.5 ± 3	11.9 ± 0.5	16.7 ± 0.5	4.6	3.3
E	57.3 ± 3	54.4 ± 3	10.7 ± 0.5	16.5 ± 0.5	5.4	3.3



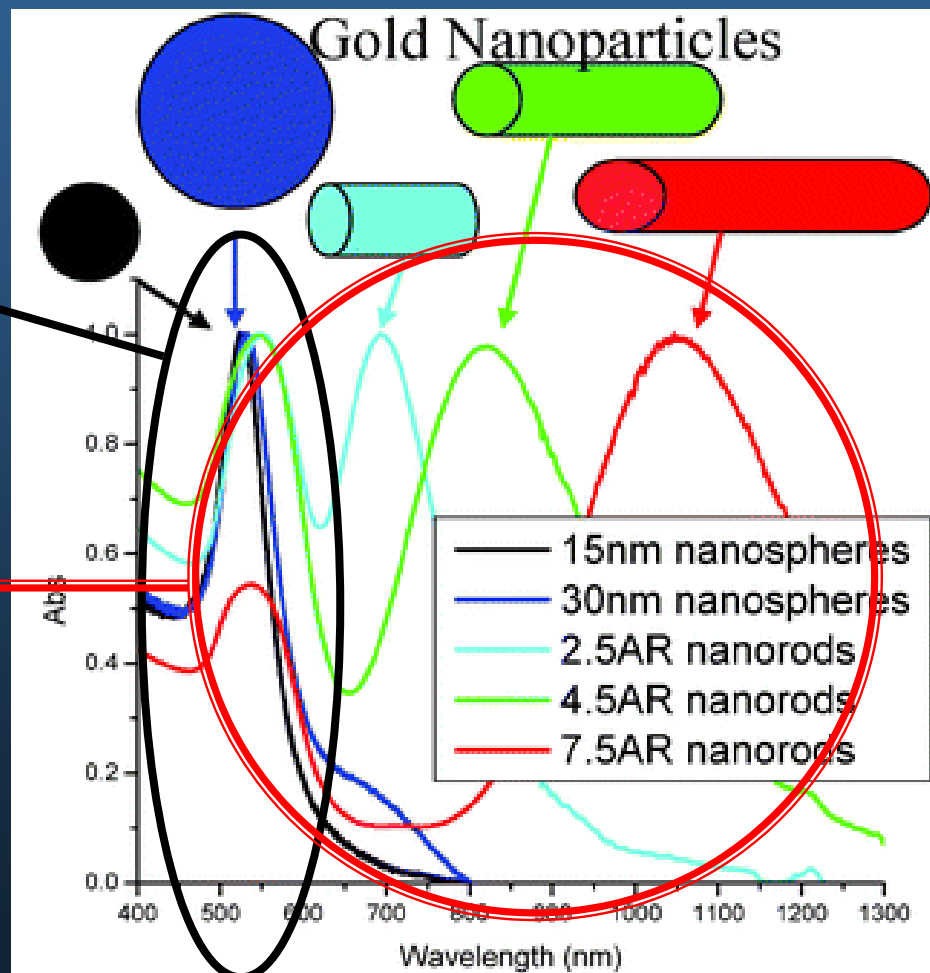
Optical Properties of Gold Colloids

Transverse oscillation at
around 520 nm:

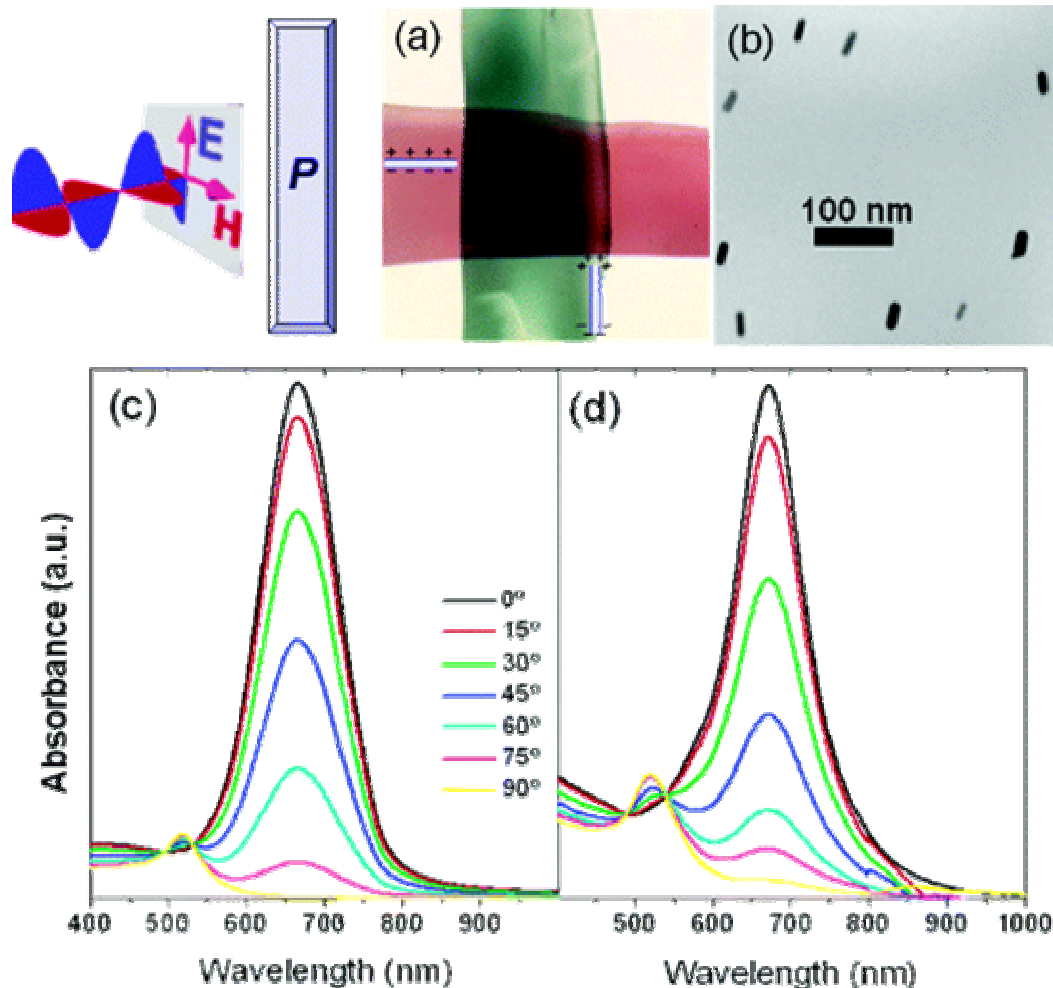
Independent of AR

Longitudinal surface
plasmon resonance:

Increases with larger
aspect ratios!



Optical Properties of Gold Colloids



(a) Photograph of PVA films containing Au nanorods aligned parallel (blue film) and perpendicular (red film) to the electric field of polarized incoming light.

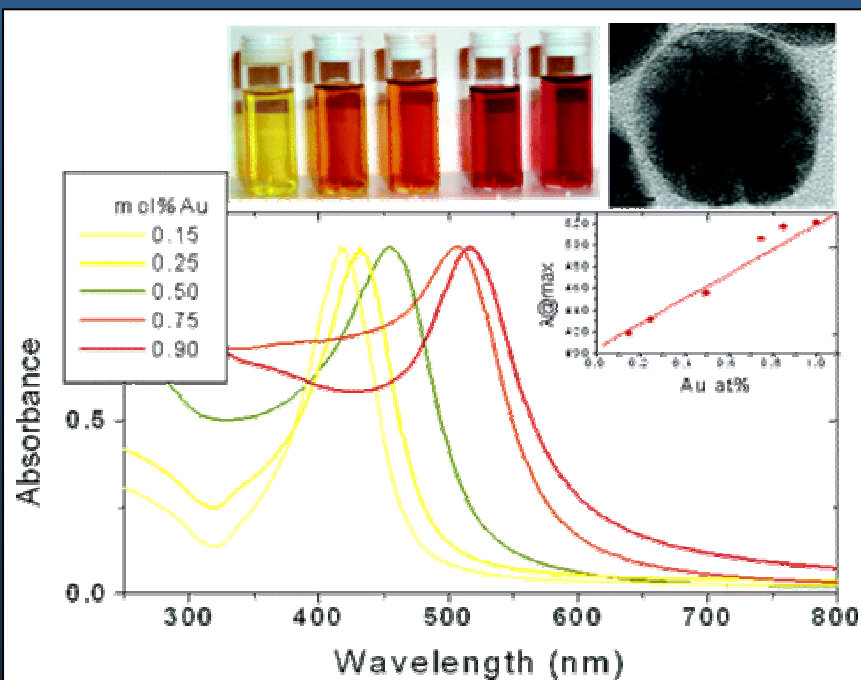
(b) TEM image showing the preferential alignment of nanorods in a stretched PVA film.

(c) Calculated and (d) experimental UV-vis-NIR spectra of PVA films containing aligned Au nanorods (aspect ratio 2.23) for varying polarization angles as indicated.

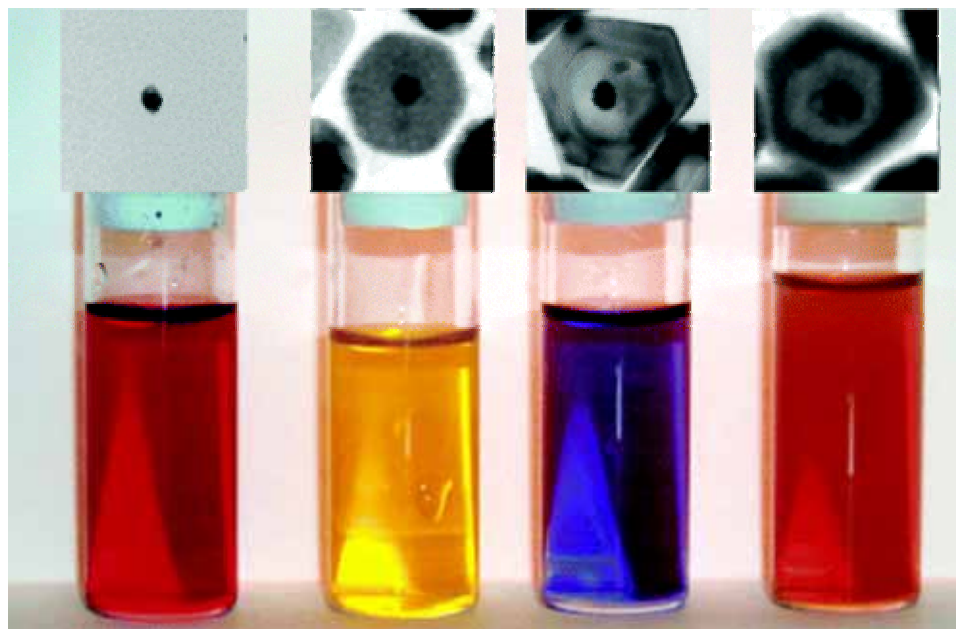


Tailoring of the Optical Properties of Gold Colloids

AuAg Bimetallic Nanoparticles: Alloys vs. Core-Shells



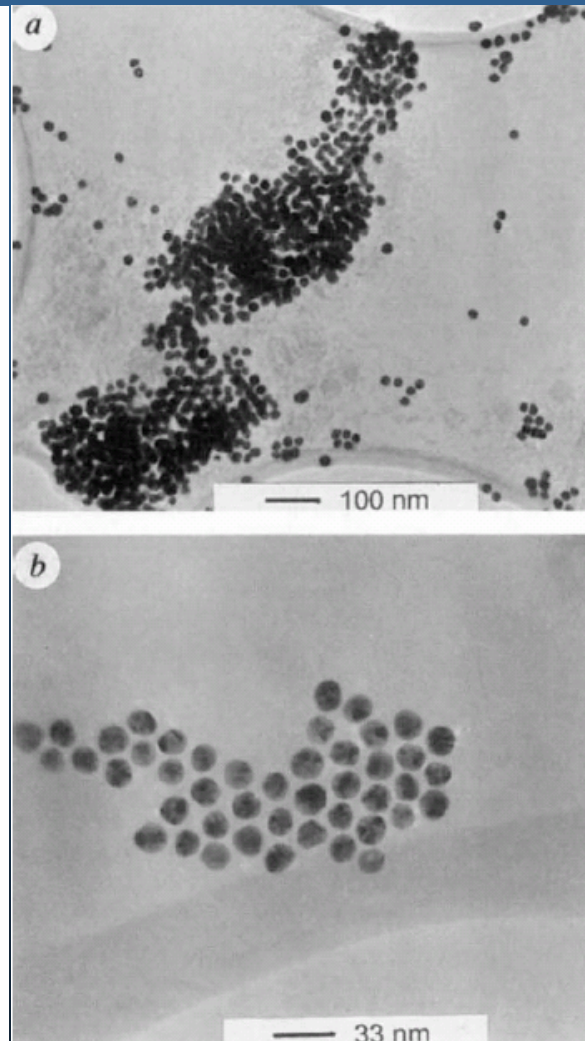
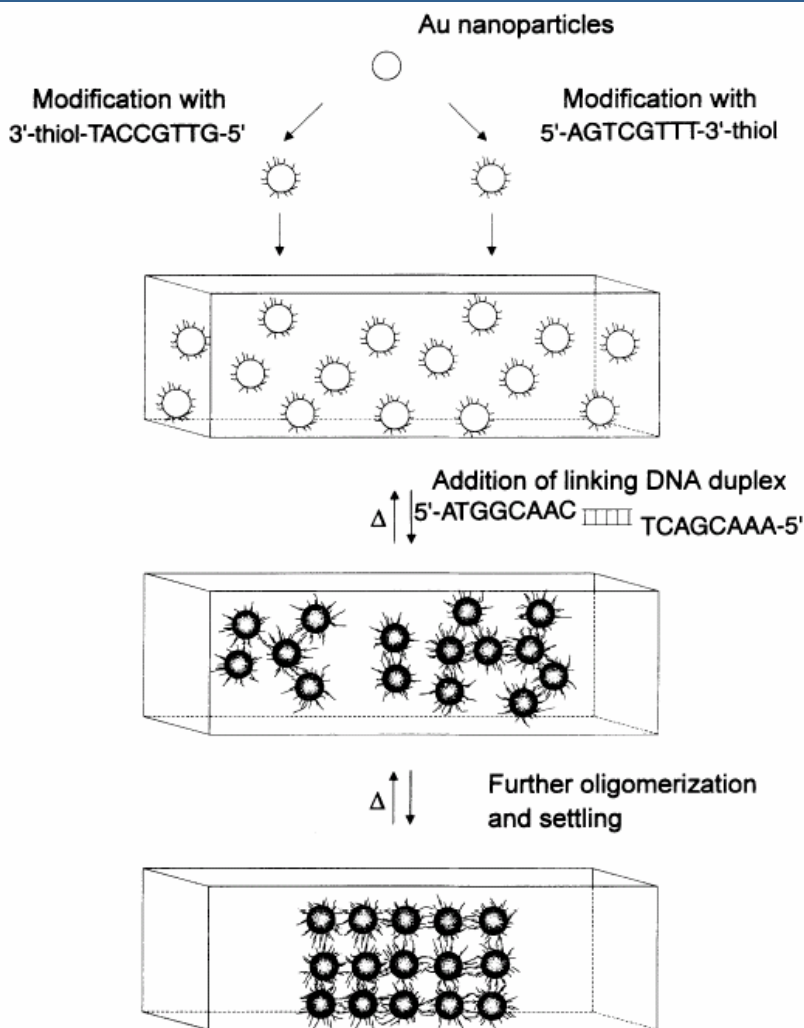
Variation in optical properties (UV-vis spectra and color) for AuAg alloy nanoparticle colloids with varying compositions.



Photographs of aqueous dispersions of (from left to right) Au, Au@Ag, Au@Ag@Au, and Au@Ag@Au@Ag nanoparticles, and the corresponding TEM images. Au core size: 16 nm.



A ssembly of Gold Colloids



Two batches of 13 nm gold particles with non-complementary DNA oligonucleotides

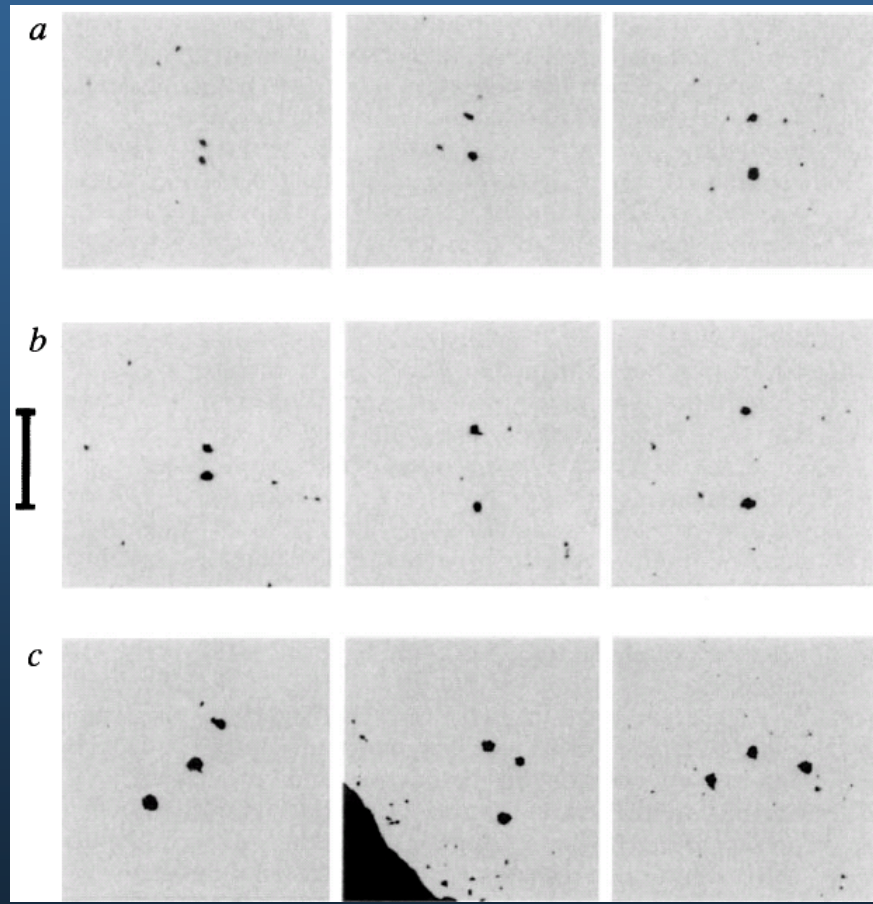
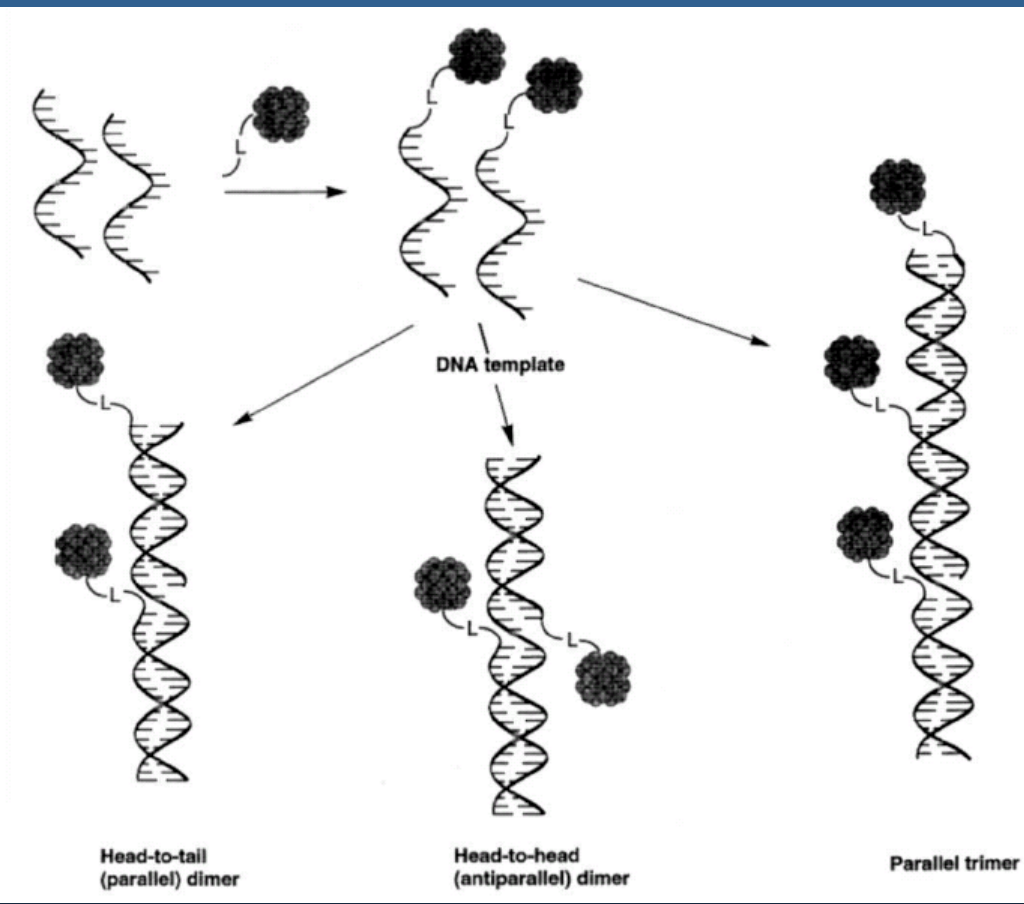
Controlled assembly upon addition of complementary oligonucleotides

Assembly reversible by thermal denaturation

Control of optical, electronic and structural properties



A ssembly of Gold Colloids



Single-stranded DNA oligonucleotides attached to gold (1.4 nm)

Assembly into dimers and trimers on addition of complementary DNA template

Nature **1996**, 382, 609

An assembly of Gold Colloids

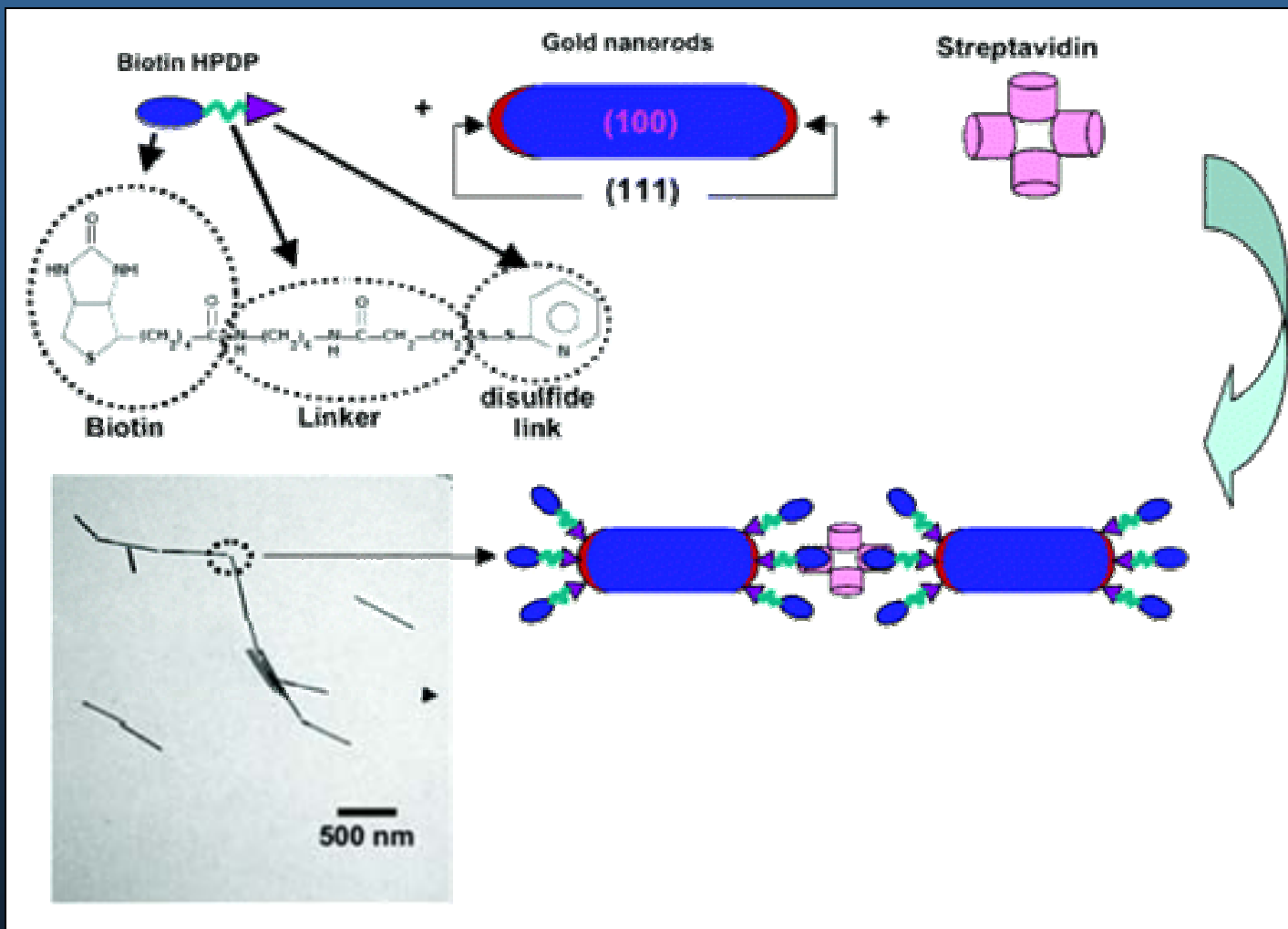
Principle: Biotin binds tightly to the protein streptavidin.

Biotin-streptavidin assembly of gold nanorods:

A biotin disulfide is added to biotinylate the rods, and subsequent addition of streptavidin causes noncovalent assembly.

Inset: transmission electron micrograph of gold nanorod-streptavidin assemblies.

{100} faces along the rod are protected by CTAB





„Modern“ Applications of Gold Colloids

Sensing

Two important features:

The plasmon absorption of gold nanoparticles is highly sensitive to the local environment, i.e., molecules chemically bonded to gold nanoparticles induce a colour change by shifting the surface plasmon absorption maximum.

—————→ Optical Sensors

Surface-Enhanced Raman-Scattering (SERS): The spectral signal for a molecule is intensified by a nearby metal nanoparticle, i.e., molecules adsorbed to the surface of gold nanoparticles undergo surface-enhanced Raman-scattering due to the coupling of the plasmon band of the irradiated metal with the electronic states of the molecules.

Raman vibrations of molecules are in general very weak. But in the presence of copper, gold and silver nanoparticles the molecular Raman vibrations excited by visible light are enhanced by orders of magnitude.

—————→ Single Molecule Detection



„Modern“ Applications of Gold Colloids

Surface-Enhanced Raman-Scattering (SERS)

Two mechanisms: **Electromagnetic and chemical enhancement**

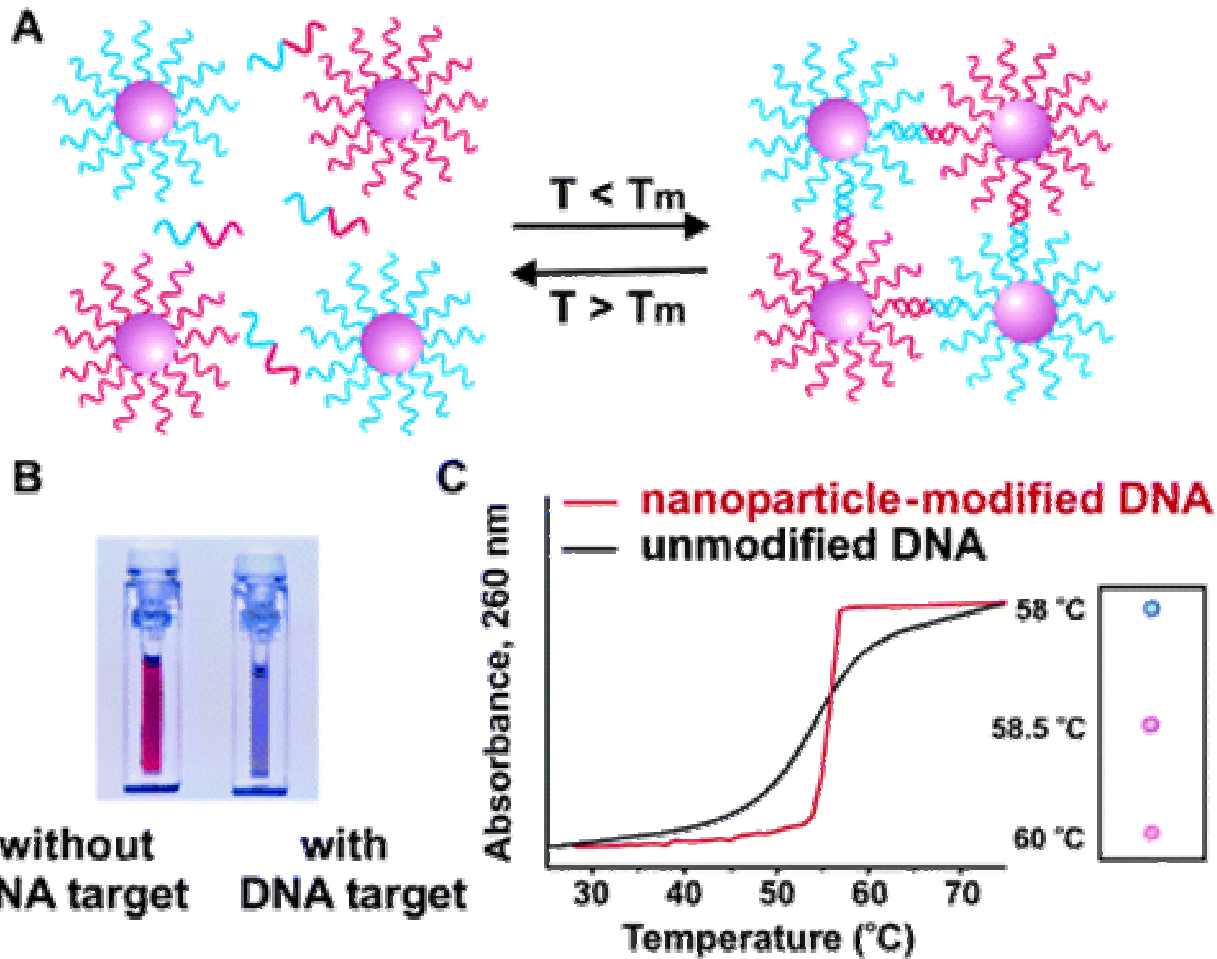
In general, there are two traditional operational mechanisms to describe the overall SERS enhancement: the electromagnetic (EM) and chemical (CHEM) enhancement mechanisms.

EM enhancement is due to the increased local electric field incident on an adsorbed molecule at a metallic surface, due to visible light absorption by the metal.

CHEM enhancement results from electronic resonance/charge transfer between a molecule and a metal surface, which leads to an increase of the polarizability of the molecule.

„Modern“ Applications of Gold Colloids

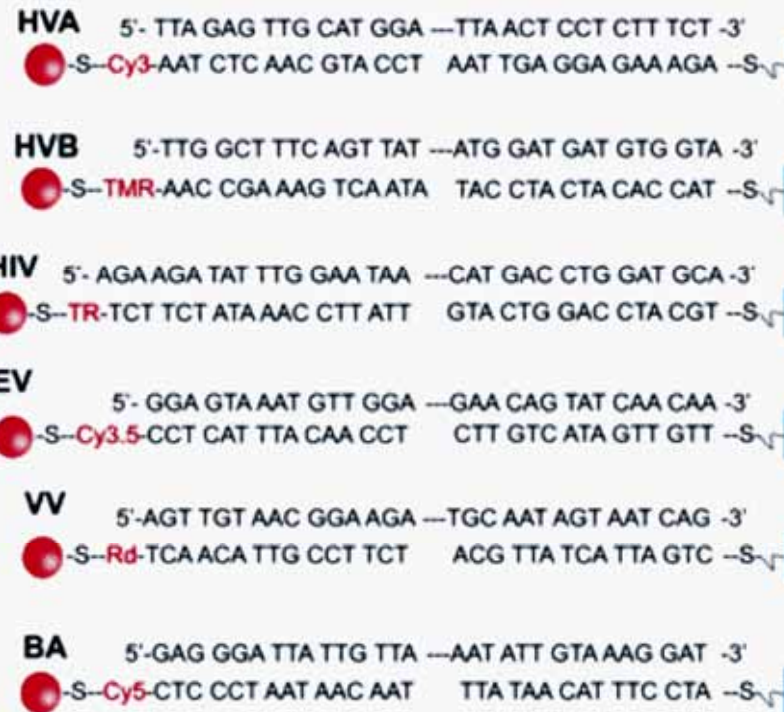
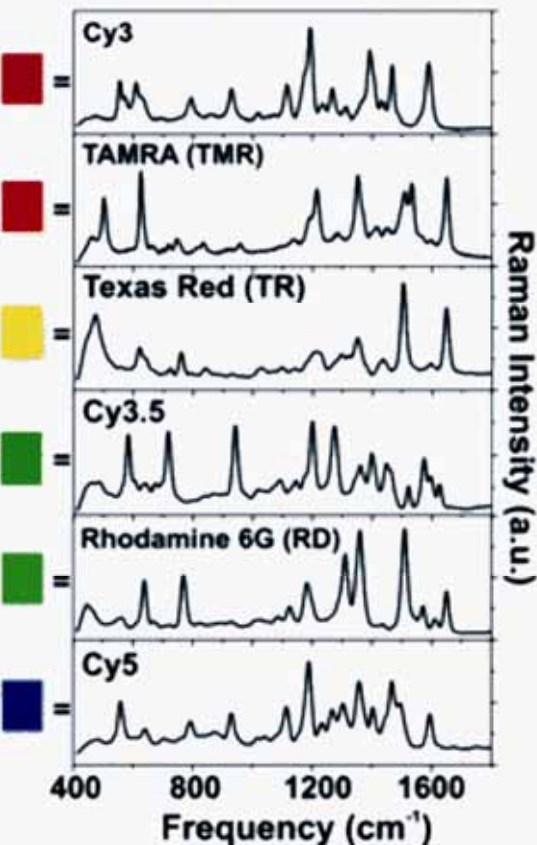
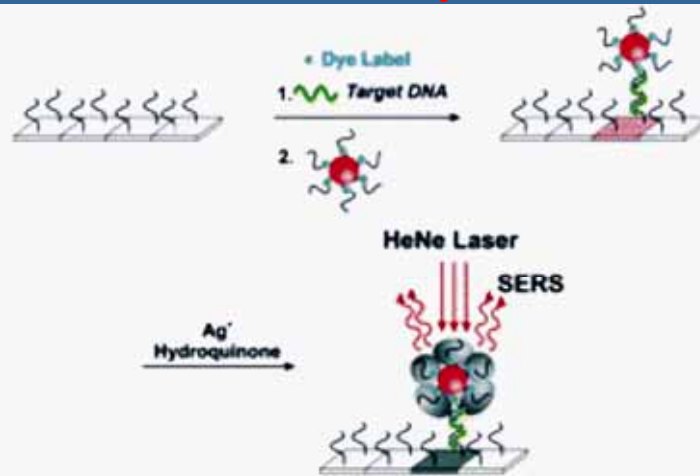
Example: Optical Sensing of DNA



Oligonucleotide-functionalized gold nanoparticles aggregate in the presence of complementary DNA:

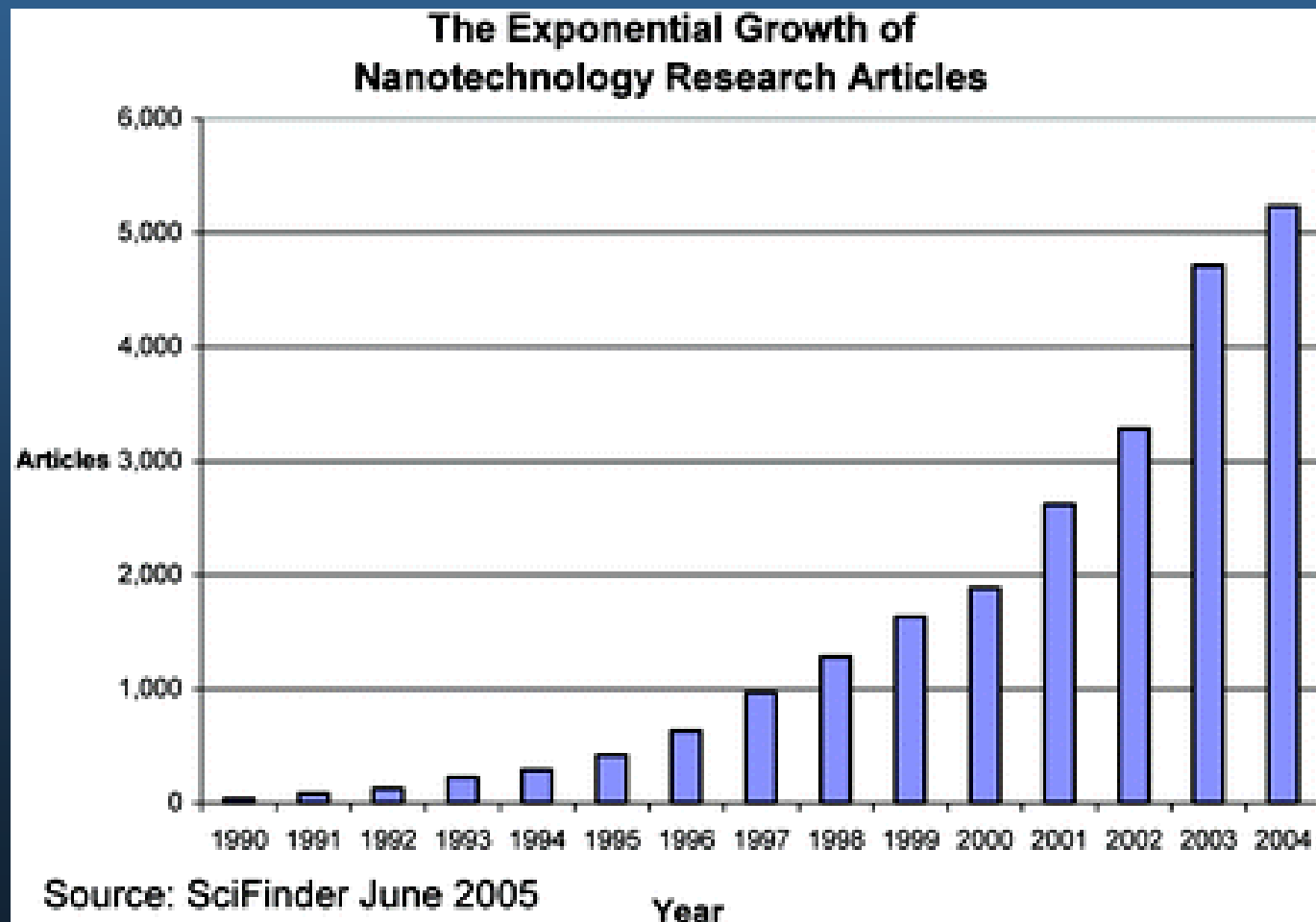
Change in colour from red to blue!

Example: DNA detection by Surface-Enhanced Raman Scattering





Gold Nanoparticles in Literature





L iterature

- Chem. Rev. **2004**, 104, 293:

Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology

- Chem. Soc. Rev. **2006**, 35, 209:

Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes

- J. Phys. Chem. B **2005**, 109, 13857:

Anisotropic Metal Nanoparticles: Synthesis, Assembly, and Optical Applications

- Langmuir **2006**, 22, 32:

Tailoring Surface Plasmons through the Morphology and Assembly of Metal Nanoparticles