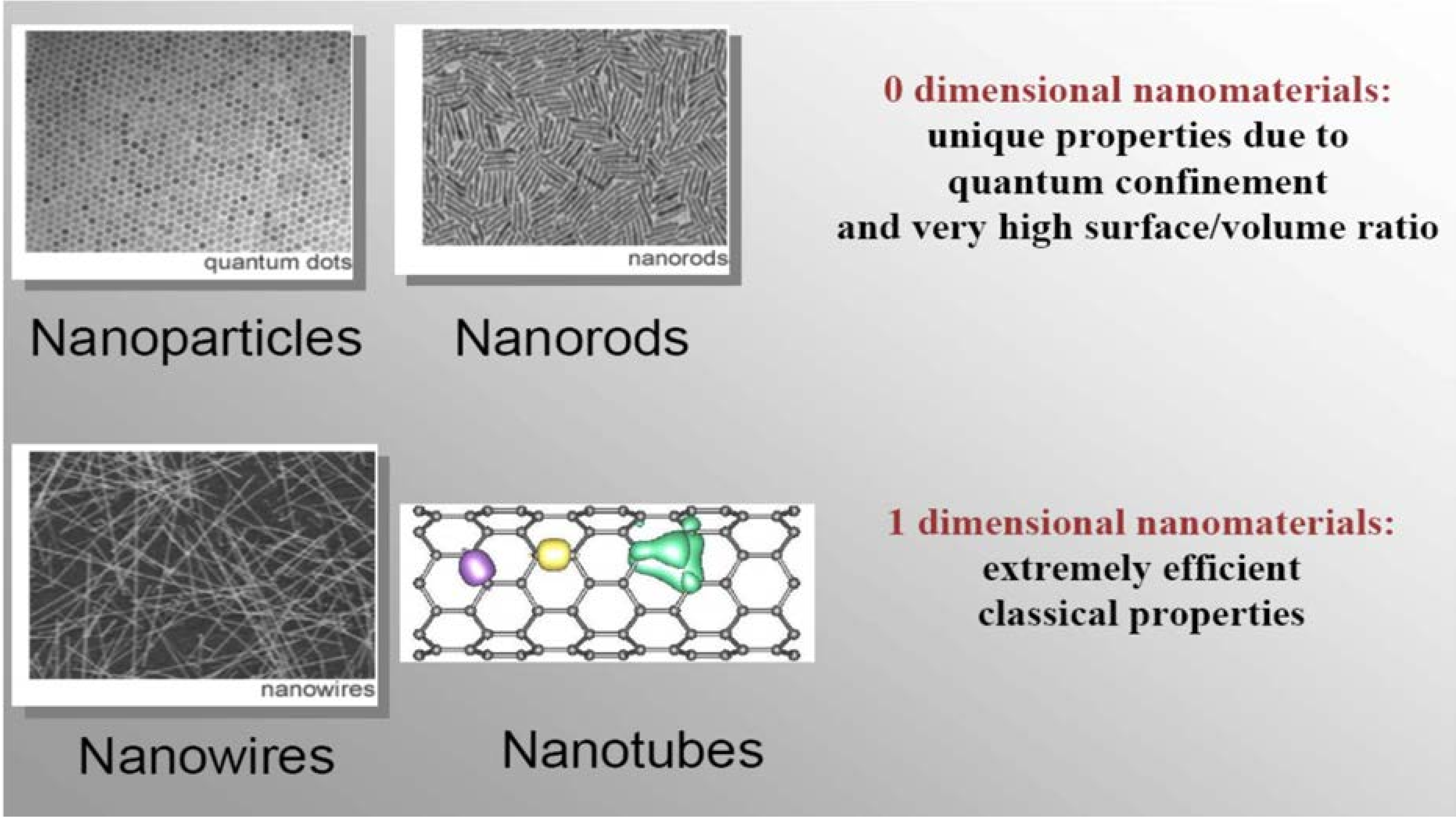
Metal Nanoparticles

- History and Culture
- How to make them
- Stabilization
- Plasmonic character
- Applications: SERRS

- Usually: Au, Ag, Cu, Pt, Pd, Ru, Re…
- but: Fe, Ni.. (very reactive, very explosive

What are they, and how they fit into nanoscience / colloidal science ??



Nanoparticles

Nanorods

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

Nanowires

Nanotubes

1 dimensional nanomaterials:
extremely efficient
classical properties

- the extraction of gold started in the 5th millennium B.C. near Varna (Bulgaria) and reached10 tons per year in Egypt around 1200-1300 B.C.when the marvelous statue of Touthankamon was constructed.

- it is probable that “soluble” gold appeared around the 5th or 4th century B.C. in Egypt and China.

- the Lycurgus Cup that was manufactured in the 5th to 4th century B.C. It is ruby red in transmitted light and green in reflected light, due to the presence of gold colloids.

Nanoparticles in ancient materials

Daylight

Light from inside

Lycurgus Cup in the British Museum

Roman pottery – 400 after Christ

Red color from nanosized gold!

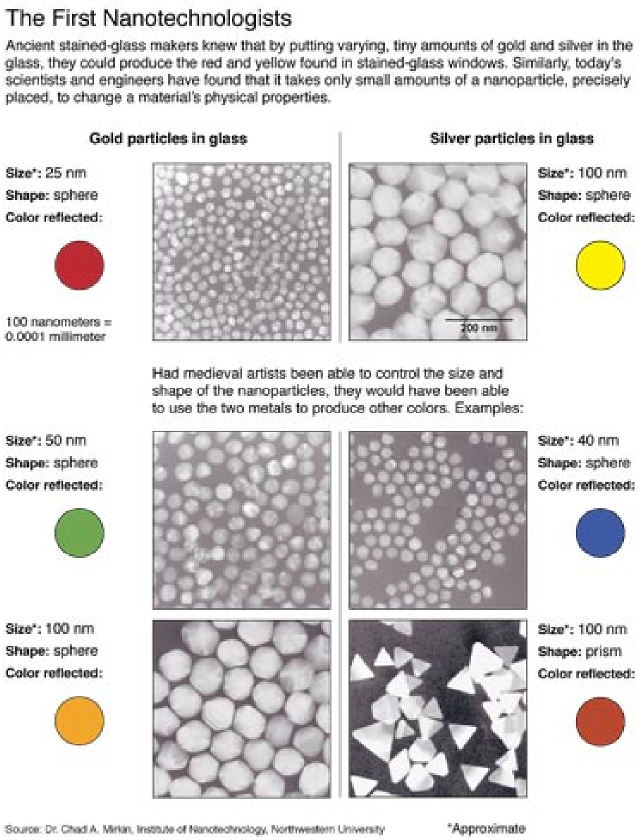
Nature **2000**, *407*, 691

Nanoparticles in ancient materials

15th and 16th centuries (Renaissance):

Pottery of Deruta (Umbria, Italy)

Glazes containing copper and silver nanoparticles



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: 🟠

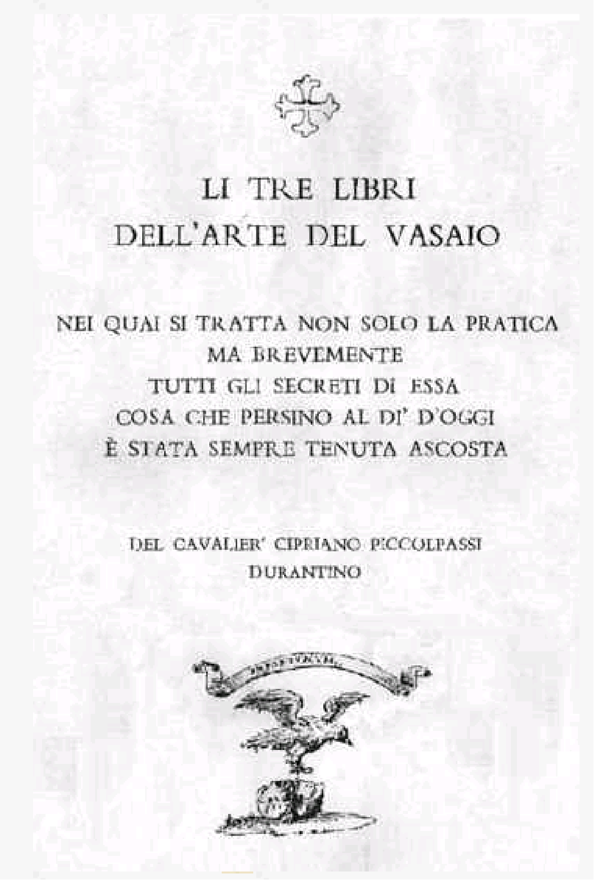
Size*: 100 nm
Shape: prism
Color reflected: 🟤

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

*Approximate

The New York Times, February 22, 2005

Nanoparticles in ancient materials



LI TRE LIBRI
DELL'ARTE DEL VASAIO

NEI QUAI SI TRATTA NON SOLO LA PRATICA
MA BREVEMENTE
TUTTI GLI SECRETI DI ESSA
COSA CHE PERSINO AL DI' D'OGGI
È STATA SEMPRE TENUTA ASCOSTA

DEL CAVALIER' CIPRIANO PICCOLPASSI
DURANTINO

16th century:

Cipriano Piccolpasso:

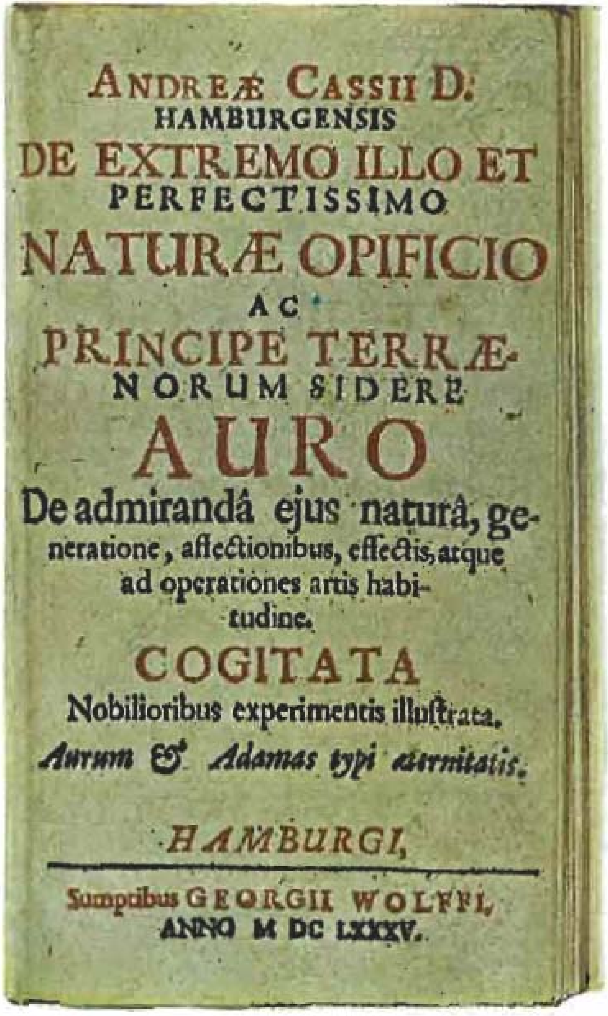
„Li tre libri dell'arte del vasaio“

Recipe for the nanoparticulate glazes:

Mix copper and silver salts with vinegar, ochre, and clay and apply them to the surface of already glazed pottery.

- **The reputation of soluble gold until the Middle Ages was to disclose fabulous curative powers for various diseases, such as heart and venereal problems, dysentery, epilepsy, and tumors, and for diagnosis of syphilis.**
- **the first book on colloidal gold, published by the philosopher and medical doctor Francisci Antonii in 1618. This book includes considerable information on the formationof colloidal gold sols and their medical uses, including successful practical cases.**
- **In 1676, the German chemist Johann Kunckels published another book, whose chapter 7 concerned "drinkable gold that contains metallic gold in a neutral, slightly pink solution that exert curative properties for several diseases". He concluded that "gold must be present in such a degree of communition that it is not visible to the human eye".**

History of Gold Colloids and their Application



ANDREÆ CASSII D.
HAMBURGENSIS
DE EXTREMO ILLO ET
PERFECTISSIMO
NATURÆ OPIFICIO
AC
PRINCIPE TERRÆNORUM SIDERE
AURO
De admirandâ ejus naturâ, generatione, affectionibus, effectis, atque ad operationes artis habitudine.
COGITATA
Nobilioribus experimentis illuſtrata.
Aurum & Adamas typi æternitatis.

HAMBURGI,

Sumptibus GEORGII WOLFFI,
ANNO M DC LXXXV.

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**

Gold Bull. **1976**, *9*, 134

Nanoparticles in ancient materials

1685: „Purple of Cassius“

In the seventeenth century, beautiful glass which came to be known as 'ruby glass' from its colour, was first made in Potsdam in Germany. The recipe for making the colouring pigment or stain was published in 1685 by Andreas Cassius, and ever since then the colour has been called Purple of Cassius.

The recipe was costly, for it involved dissolving fine gold powder in aqua regia, adding water, and then adding a piece of pure tin. After an hour or two, a brilliant purple precipitate formed, Purple of Cassius.

There is a story of another chemist or alchemist making the same colour by chance when he dissolved gold powder in aqua regia in a pewter vessel, and the the attack of the acid aqua regia on the pewter provided the necessary tin (pewter is an alloy that consists mainly of tin).

Purple of Cassius was used in some of the most world-famous porcelain from Meissen, and Sevres, and the art of making it travelled to China where it was used from 1723 in Chinese Famille Rose porcelain.

The presence of gold explains its extremely high cost, but it has immense colouring power and is still used today in very high quality tableware.

Many famous chemists in the eighteenth and nineteenth centuries attempted to understand the nature of Purple of Cassius, but it was a Viennese chemist, Richard Zsigmondey, who finally found the answer: the gold is in colloidal form, adsorbed on a base of stannous hydroxide. For his work on the nature of colloids, Zsigmondey was awarded the Nobel Prize in 1925.

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

Glauber

Tea pot with the red colour by Kunckel

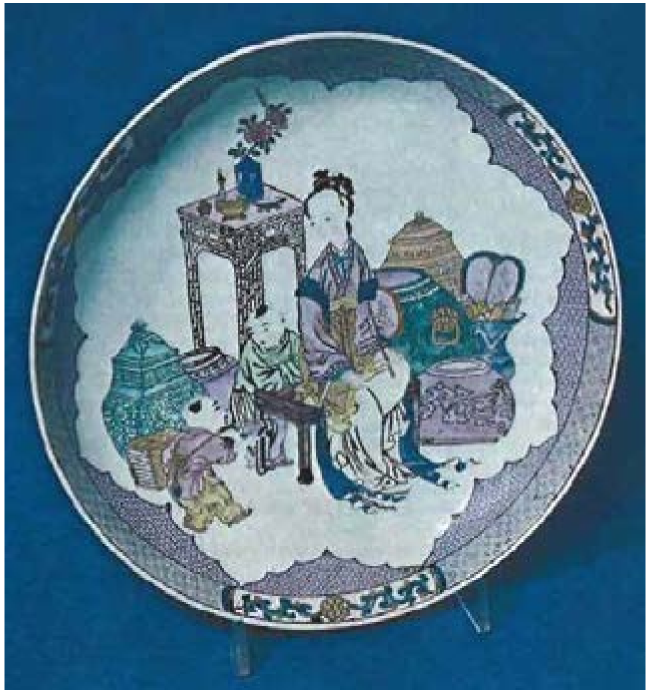
Gold Bull. **1976**, *9*, 134

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

- A colorant in glasses, “Purple of Cassius”, is a colloid resulting from the heterocoagulation of gold particles and tin dioxide, and it was popular in the 17th century.
- A complete treatise on colloidal gold was published in 1718 by Hans Heinrich Helcher. In this treatise, this philosopher and doctor stated that the use of boiled starch in its drinkable gold preparation noticeably enhanced its stability.
- These ideas were common in the 18th century, as indicated in a French dictionary, dated 1769, under the heading “or potable”, where it was said that “drinkable gold contained gold in its elementary form but under extreme sub-division suspended in a liquid”.
- In 1794, Mrs. Fuhlame reported in a book that she had dyed silk with colloidal gold.
- In 1818, Jeremias Benjamin Richters suggested an explanation for the differences in color shown by various preparation of drinkable gold: pink or purple solutions contain gold in the finest degree of subdivision, whereas yellow solutions are found when the fine particles have aggregated.

- **In 1857, Faraday reported the formation of deep red solutions of colloidal gold by reduction of an aqueous solution of chloroaurate ($AuCl_4^-$) using phosphorus in CS_2 (a two-phase system) in a well known work.**

- **He investigated the optical properties of thin films prepared from dried colloidal solutions and observed reversible color changes of the films upon mechanical compression (from bluish-purple to green upon pressurizing).**

- **The term “colloid” (from the French, *colle*) was coined shortly thereafter by Graham.**

Marie-Christine Daniel and Didier Astruc, *Chem. Rev.* **2004,** *104,* 293-346

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.

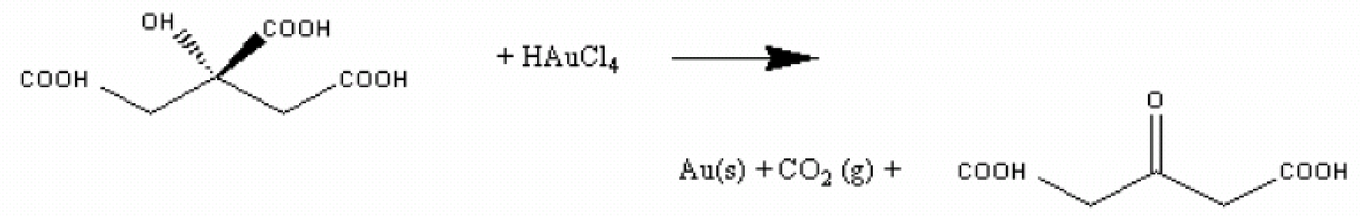
Around 1897, almost 250 years after its discovery, Richard Zsigmondy, a chemist working on gold colloids at the Schott Glassworks in Jena, showed that Purple of Cassius consisted of colloidal gold and stannic acid.
He was awarded the Nobel Prize in Chemistry in 1925.

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.

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

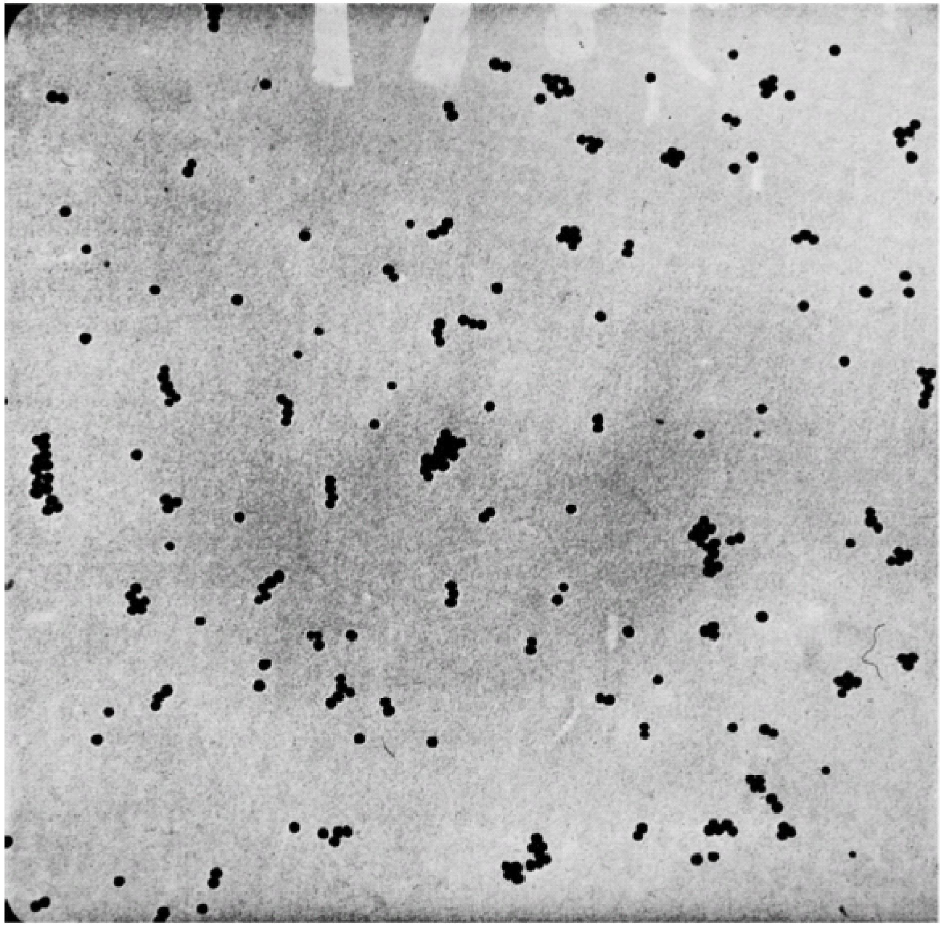


FIG. 3.—Electron micrograph of a gold sol reduced with sodium citrate (standard citrate sol) magnification 50,000 diameters.

Gold colloids with uniform diameters of about 20 nm

Size dependent on citrate concentration

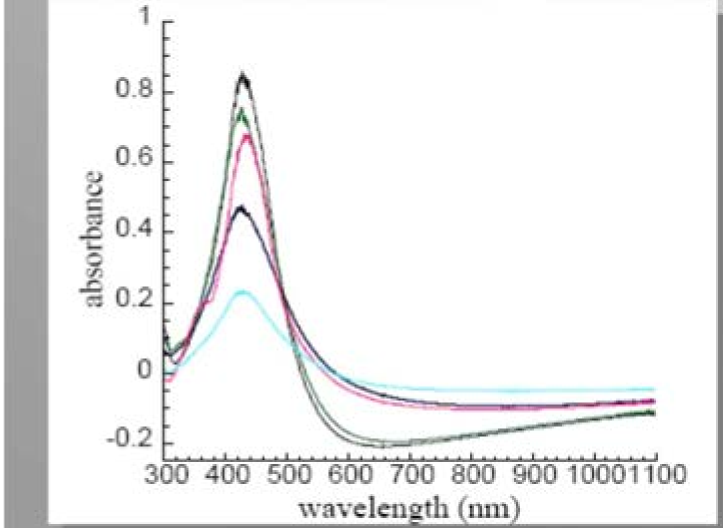
$$Ag^{+} + RSH \longrightarrow (RSAg)_n$$

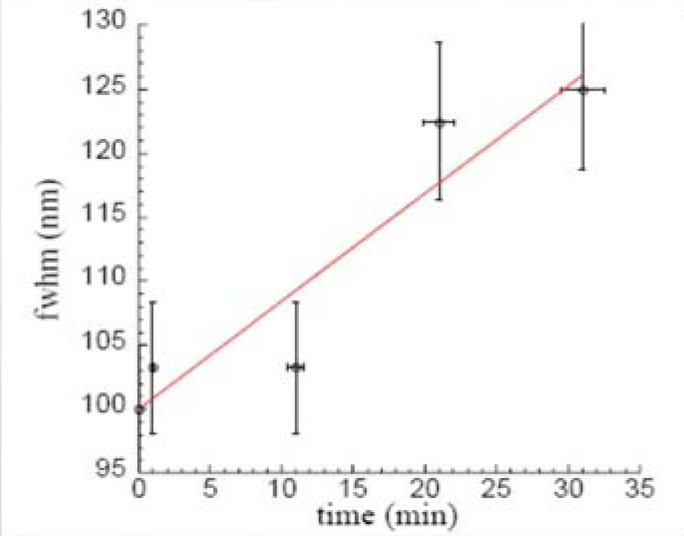
$$(RSAg)_n + Ag^{+} \xrightarrow{NaBH_4} (RS)_n\, Ag_{m'}$$

$m' > n$

$$(RS)_n\, Ag_{m'} + Ag^{+} \xrightarrow[h\nu]{Dye} (RS)_n\, Ag_{m''}$$

$m'' > m'$





Brust,et. al. ***Chem Commun.****, 1655, 1995.*   *Kim et al.,* ***Langmuir*** *14,226, 1998*

Synthesis by galvanic Exchange Reactions

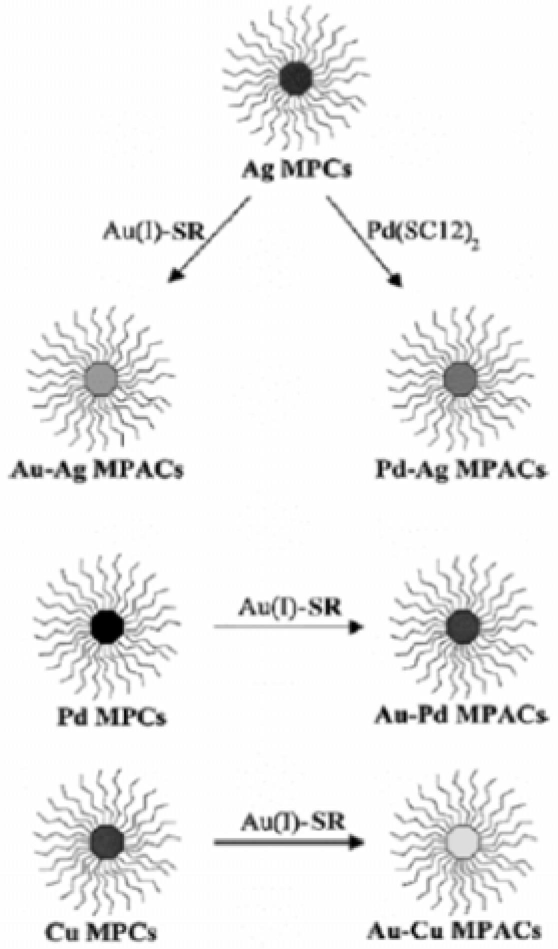
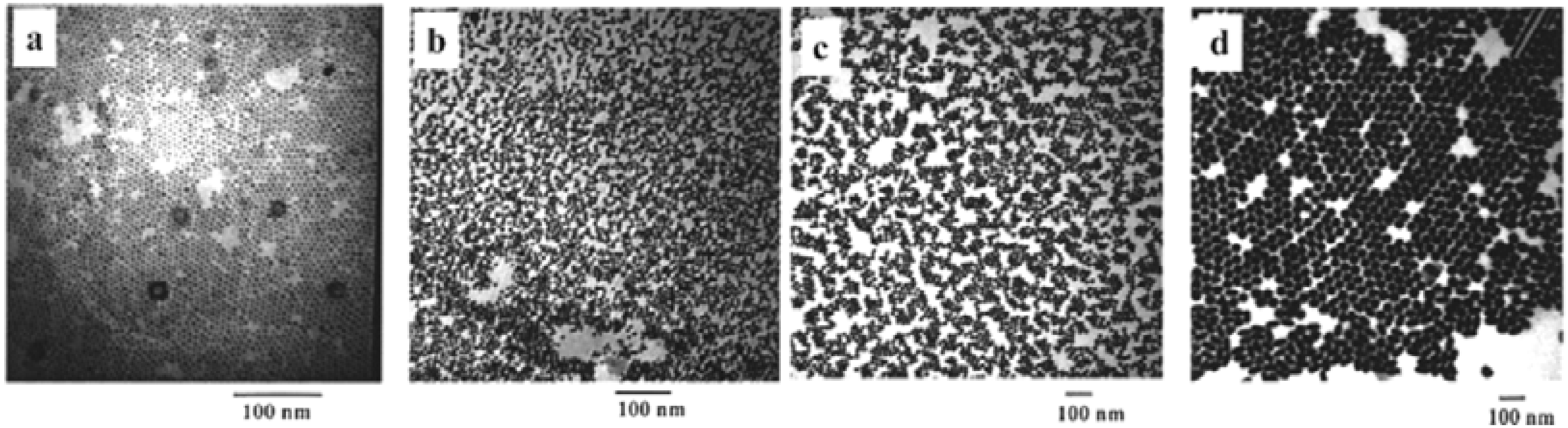
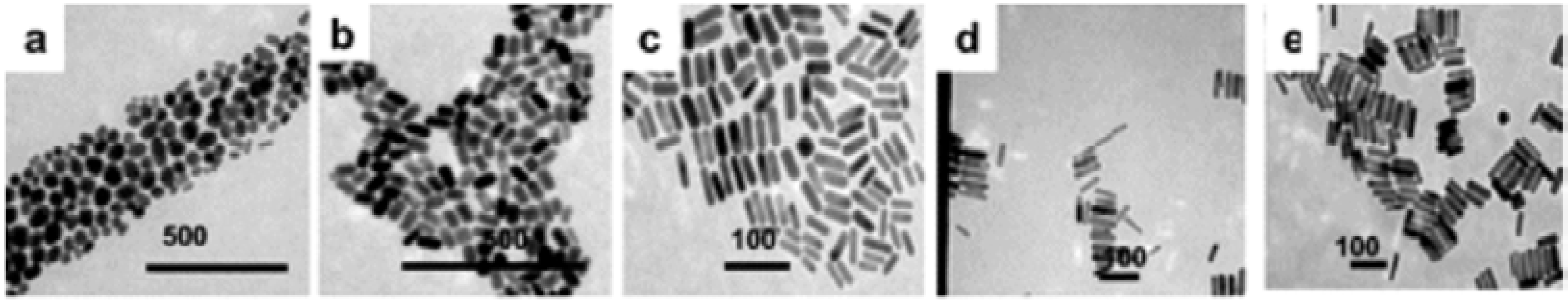


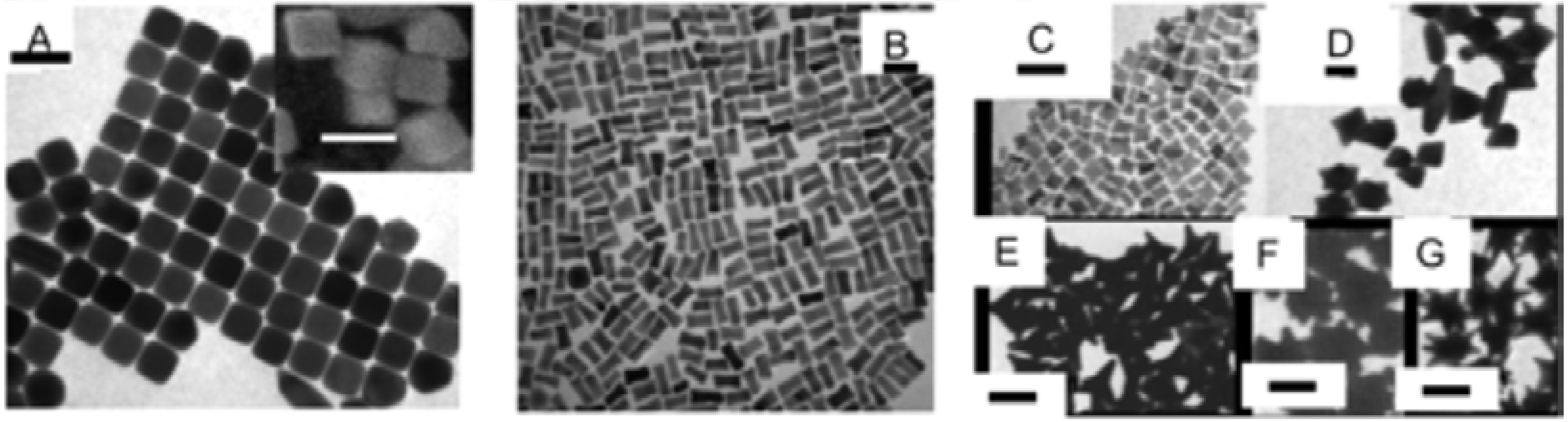
Figure 16. Cartoon diagram of core metal galvanic exchange reactions. MPC, monolayer-protected cluster; MPAC, monolayer-protected alloy cluster; SC12, $S(CH_2)_{11}$-CH_3. Reprinted with permission from ref 166a (Murray's group). Copyright 2002 American Chemical Society.

Synthesis of Gold Colloids

Excellent control over size and shape

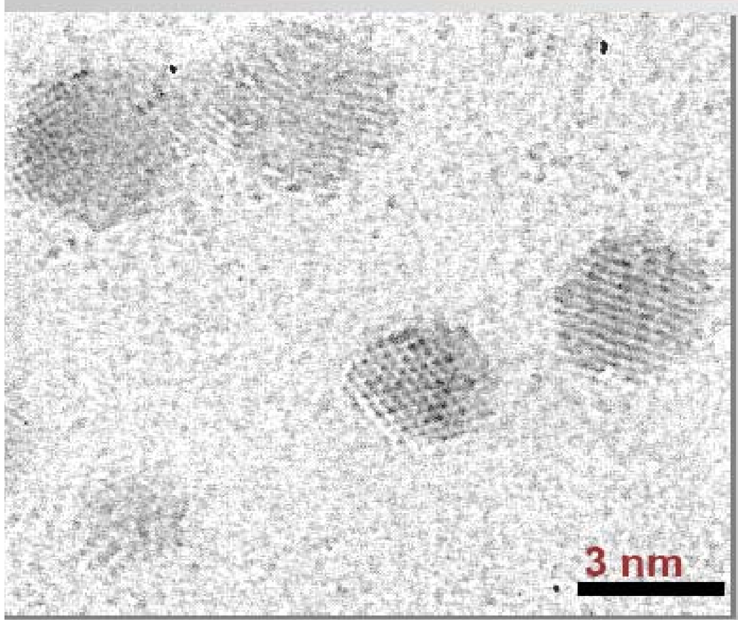


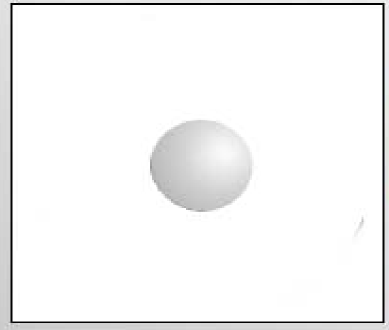


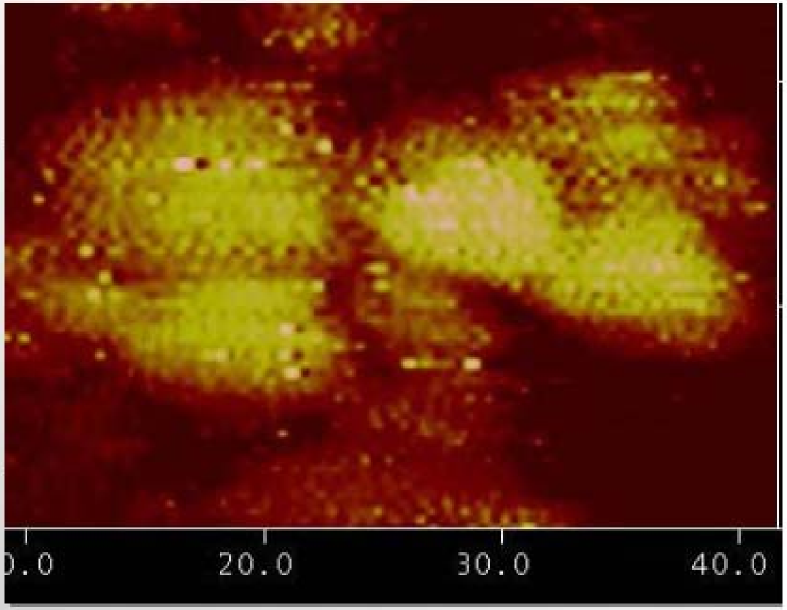


Characterizing Metal Nanoparticles

SuNMaG

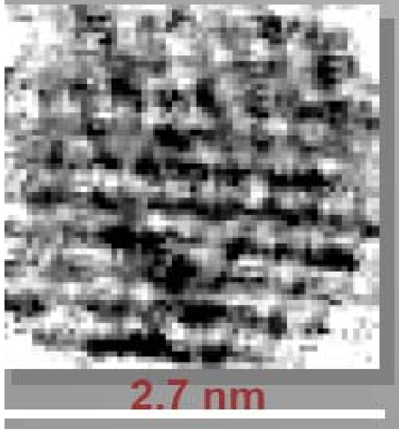


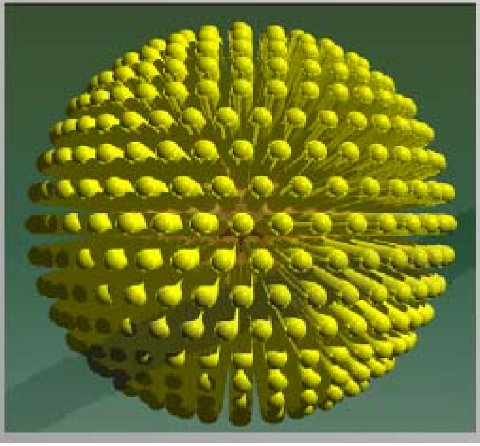


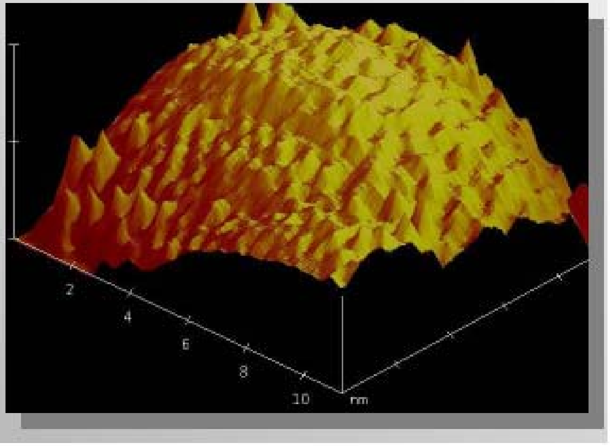


TEM shows atoms in the core

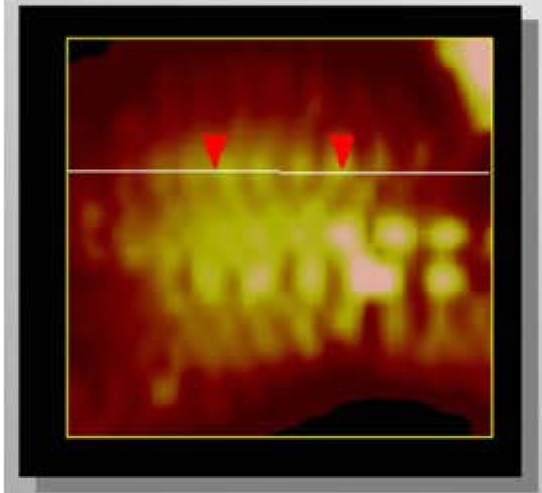
STM shows ligands in the shell

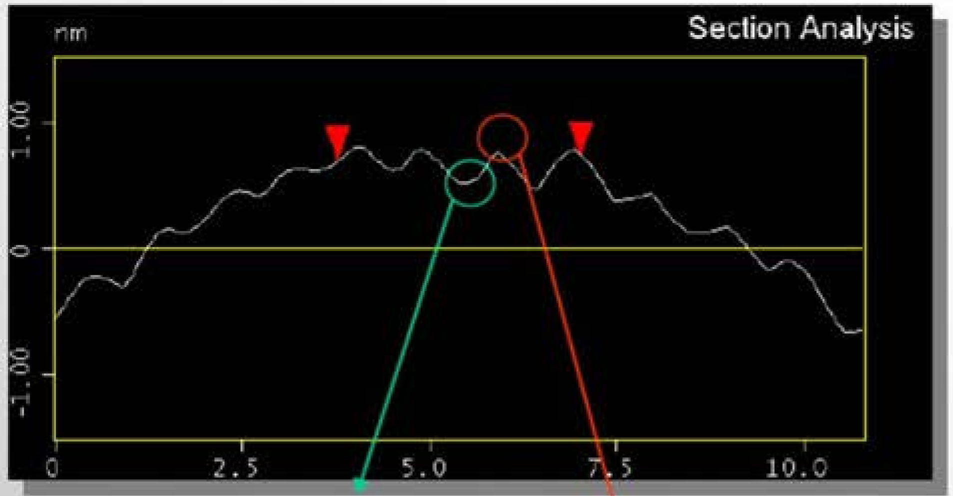






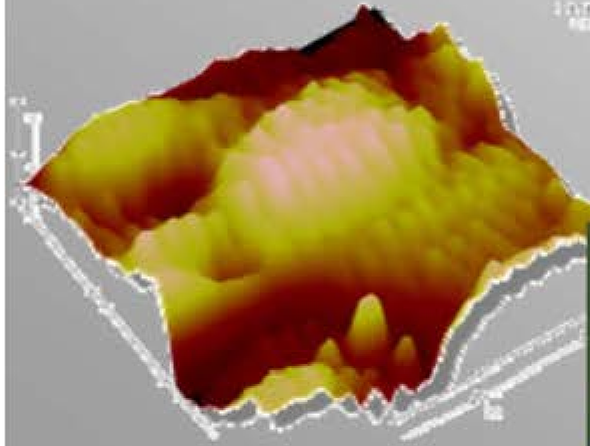
Hydrophobic/Hydrophilic Ripples

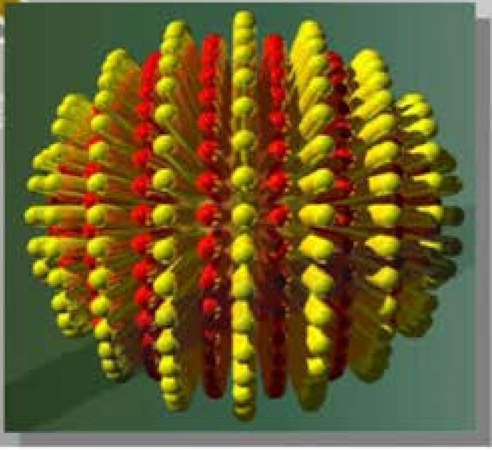




Hydrophilic Region:

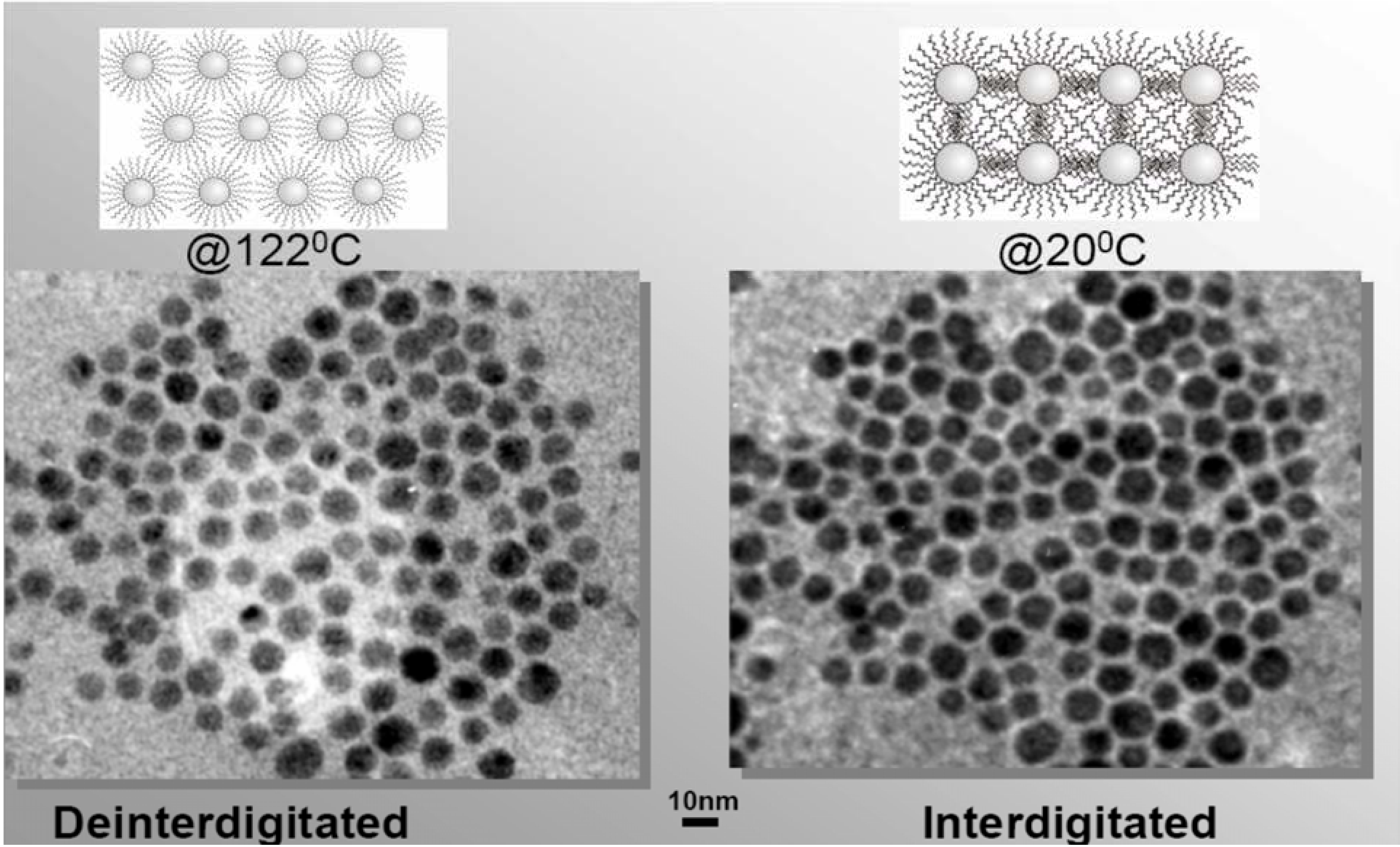
Carboxylic Acid Terminated Molecules





Hydrophobic Region:

Methyl Terminated Molecules


@122⁰C
@20⁰C
10nm
Deinterdigitated
Interdigitated

The stability of nanoparticles: the DLVO theory

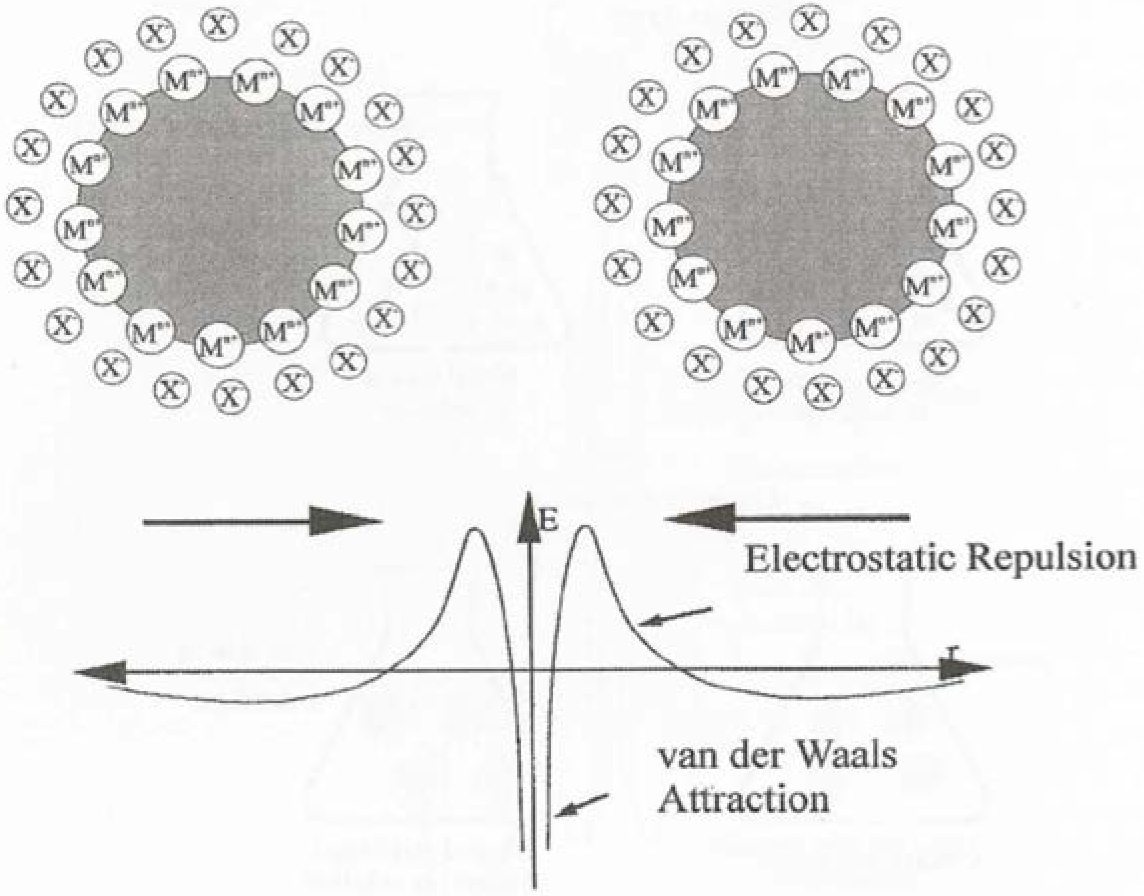


FIGURE 2.24 Electrostatic stabilization of metal colloids. Van der Waals attraction and electrostatic repulsion compete with each other.[27]

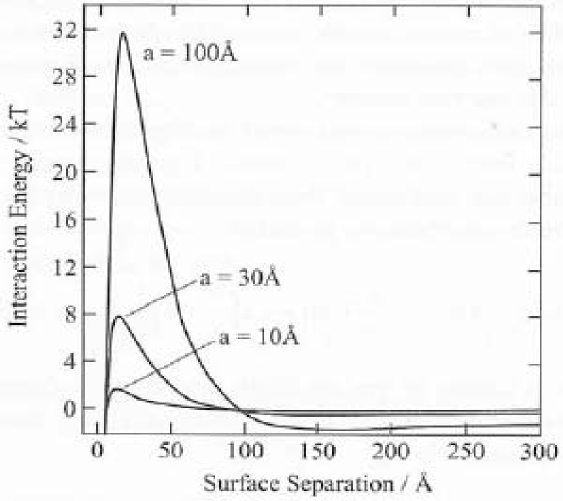


FIGURE 5.4 Plot of the interaction energy between two spherical gold particles in aqueous solution as a function of the particle separation, for several particle radii. Hamaker constant = 25×10^{-20} J, $I = 1$ mM, $\psi_0 = 0.10$ V, $a = 1.0$ nm, 3.0 nm, and 10.0 nm, Debye length = 10 nm. Note that the secondary minimum is negligible for nanoparticles, but becomes important above 10 nm.

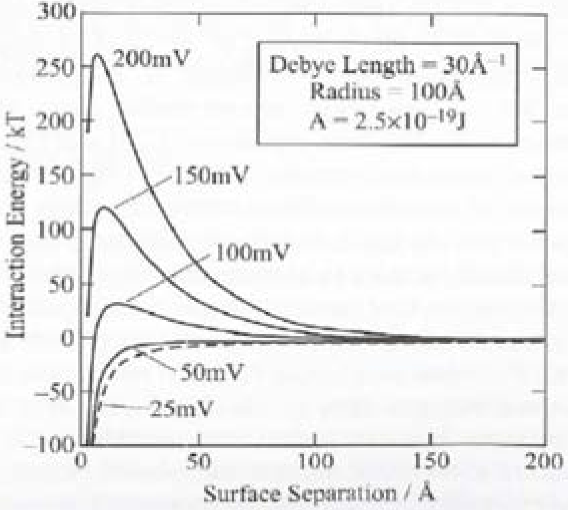


FIGURE 5.5 Plot of the interaction energy between two spherical gold particles in aqueous solution as a function of the particle separation for several surface potentials. Hamaker constant = 25×10^{-20} J, $I = 10$ mM, $a = 10$ nm, Debye length = 3 nm. Note that a zeta potential, $|\zeta| > 50$ mV, is necessary for colloid stability because of the high Hamaker constant.

Other synthetic approach: flame pyrolysis

Comparison of wet- & dry-technology

Dry-technology (aerosol):

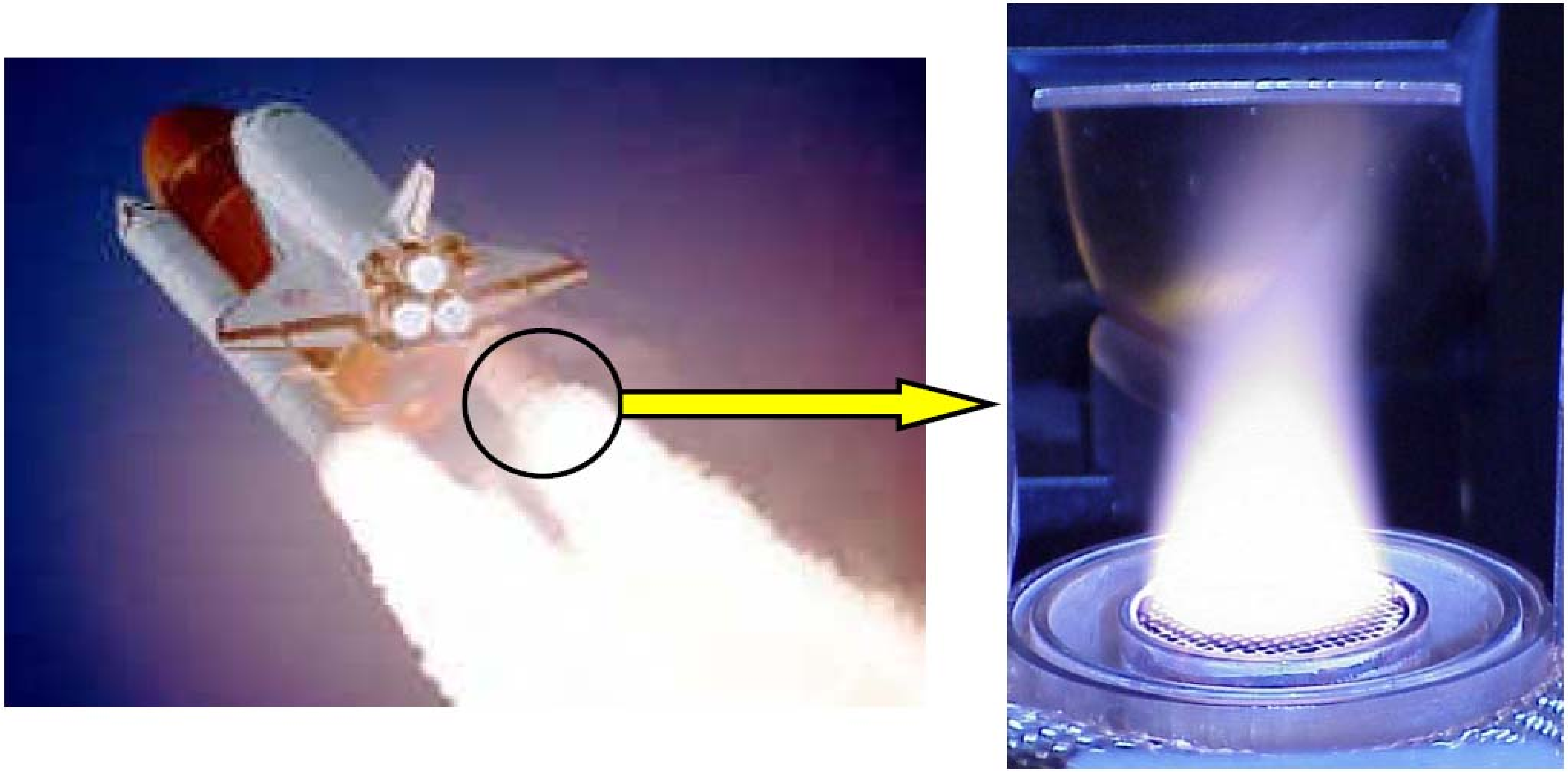
- Mix precursor
- Dry flame conversion
- Filtration
- Milling

Wet-technology:

- Dissolve
- Add precipitation agent
- Temperature/Pressure treatment
- Filtration
- Washing
- Drying
- Calcination
- Milling

Short process chains, very short process time:
Reduced costs, green processes

A rough analogy to flame aerosol reactors



… just well attached to the ground !

AEROSOL MANUFACTURING OF NANOPARTICLES

Wegner, Pratsinis *Chem. Eng. Sci.* **58**, 4581-9 (2003).

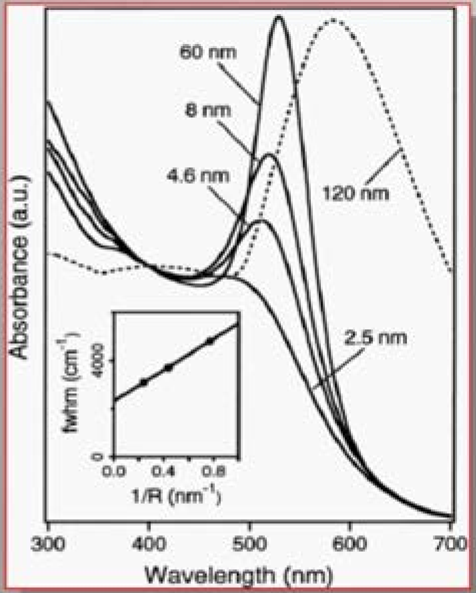
Product Particles	Volume t/y	Value \$/y	Process	Coagulation Coalescence	Surface Growth
Carbon black	8 M	8 B	Flame, C_xH_y	X	X
Titania	2 M	4 B	Flame, $TiCl_4$	X	?
Fumed Silica	0.2 M	2 B	Flame, $SiCl_4$	X	-
Zinc Oxide	0.6 M	0.7B	Hot –Wall, Zn	X	X
Filamentary Ni	0.04M	~0.1B	Hot-Wall, $Ni(CO)_4$	X	X
Fe, Pt, Zn_2SiO_4/Mn	~0.02M	~0.3B	Hot-Wall, Spray…	X	X

Optical Properties of metal nanoparticles

Mie Theory(1908)

$$\sigma_{abs}(\omega) = \frac{9\omega V_0 \varepsilon_m^{3/2}}{c} \frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2}$$

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$



J.H. Hodak, et al. ; **J. Phys Chem. B**, 104(43), 9954, **2000**.

Drude free electron model

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 - i\gamma\omega}$$

Empirically

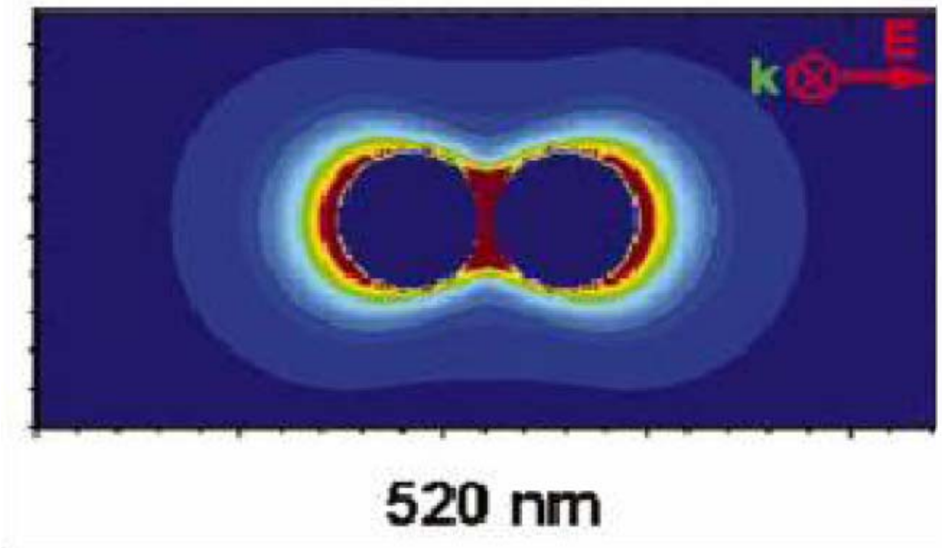
$$\gamma(r) = \gamma_0 + \frac{a}{r}$$

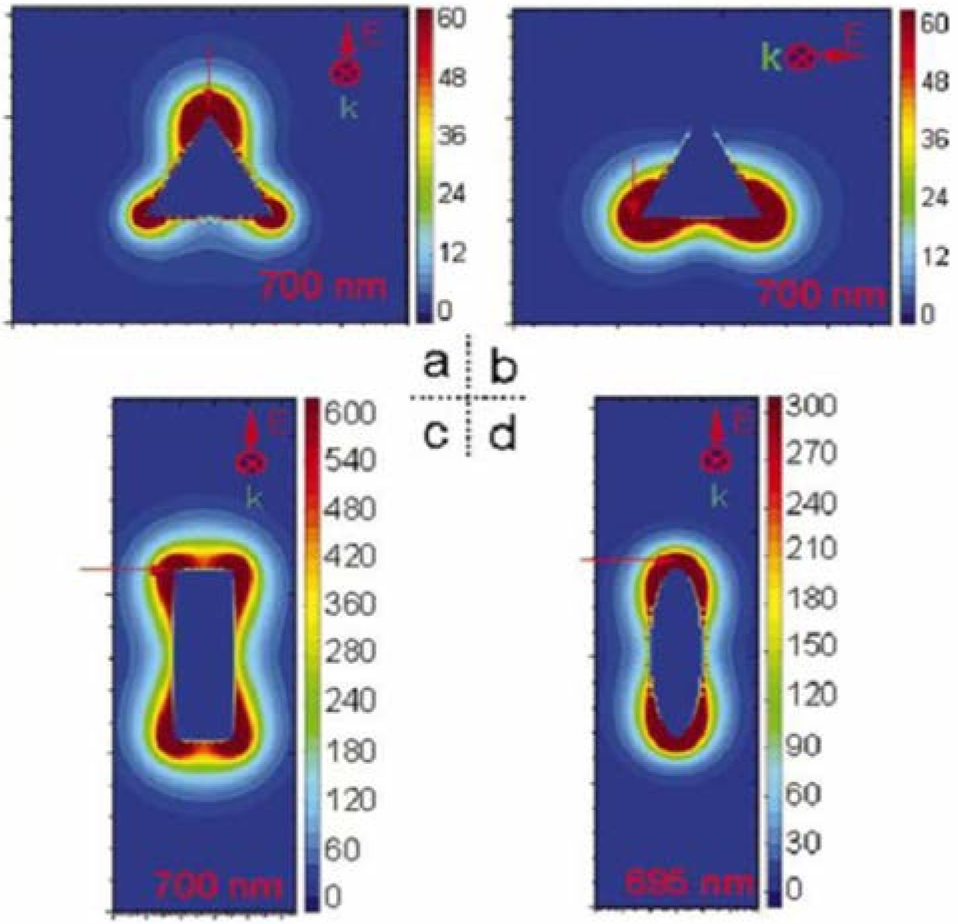
Surface Plasmon Resonance is invariant with respect to the size on the nanoparticle.

The FWHM scales with the radius of the particles.

- **Assumes spherical particle**
- **Particle diameter << λ/10**

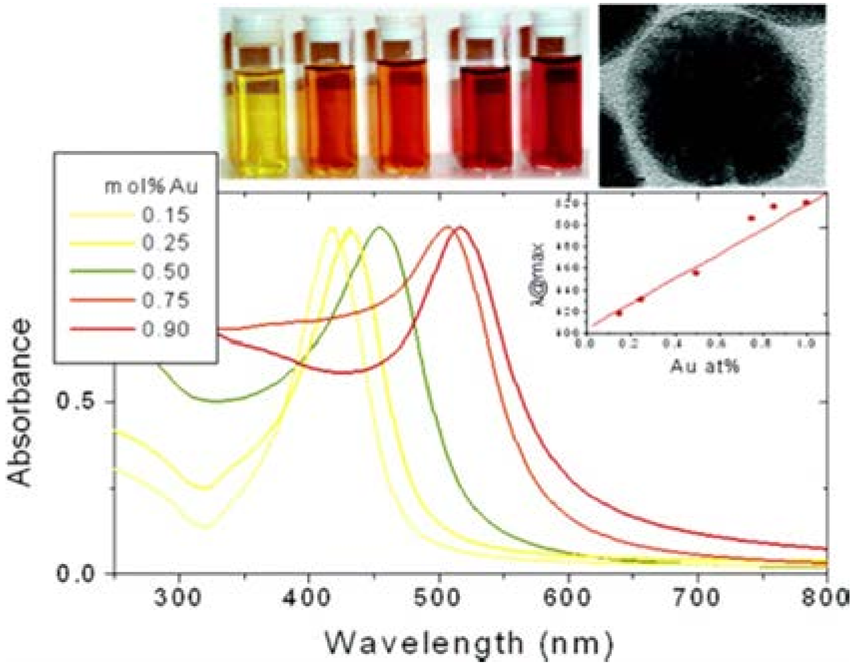
Some pictures of plasmon modes



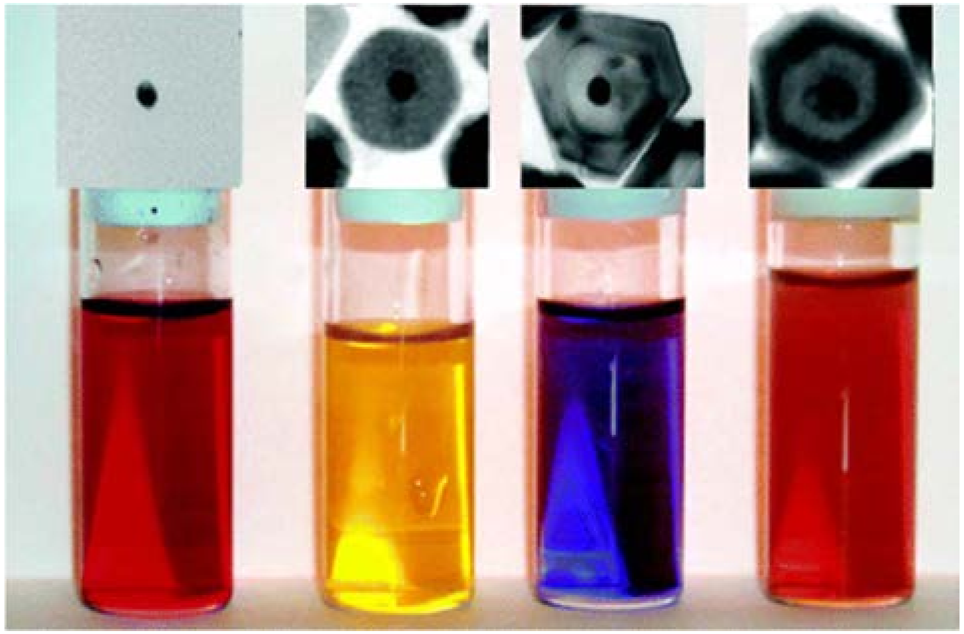


Tailoring of the Optical Properties of Gold Colloids

AuAg Bimetallic Nanoparticles: Alloys vs. Core-Shells



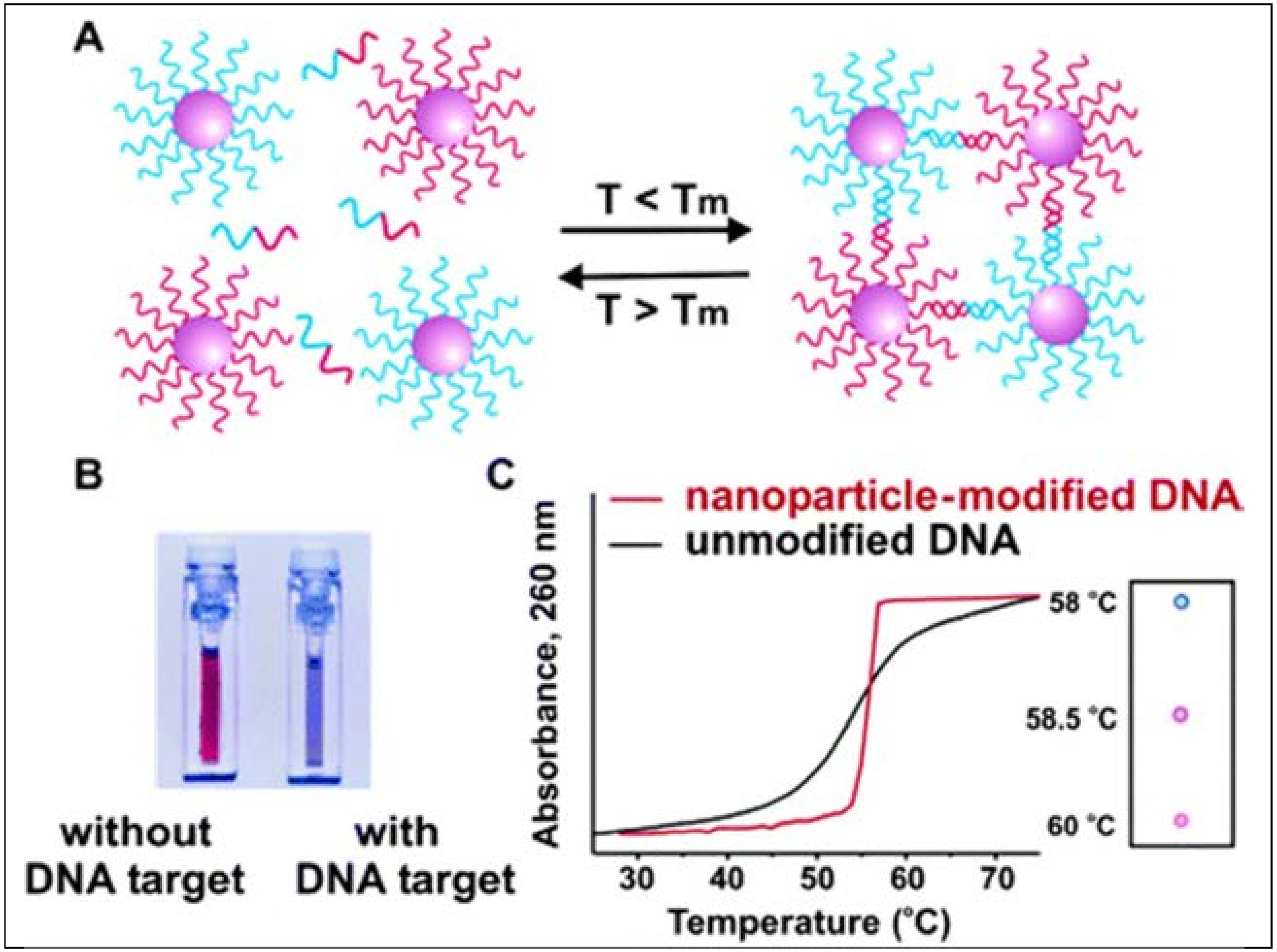
Variation in optical properties (UV-vis spectra and color) for AuAg alloy nanoparticle colloids with varying compositions.



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.

„Modern“ Applications of Gold Colloids

Example: Optical Sensing of DNA

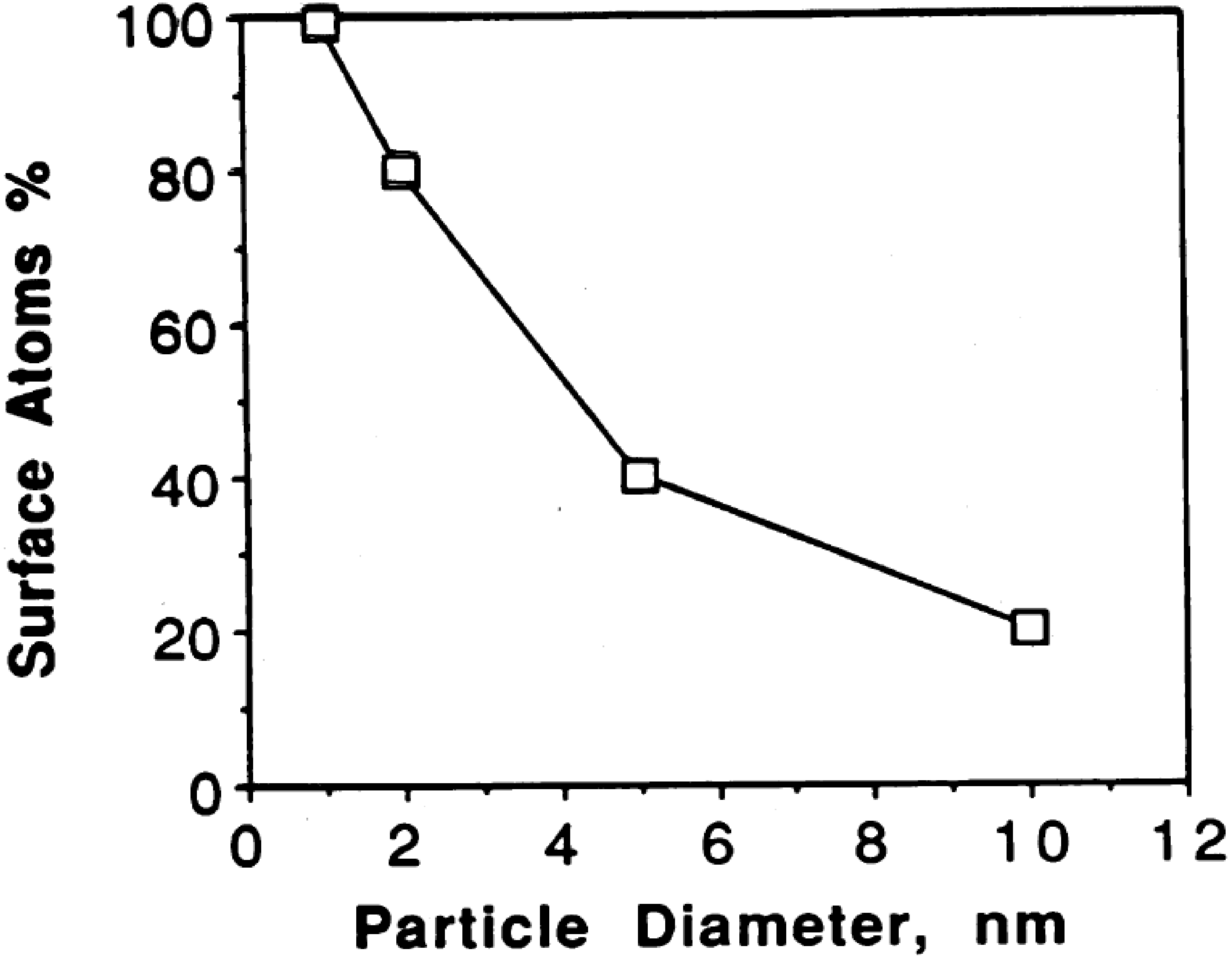


Oligonucleotide-functionalized gold nanoparticles aggregate in the presence of complementary DNA:

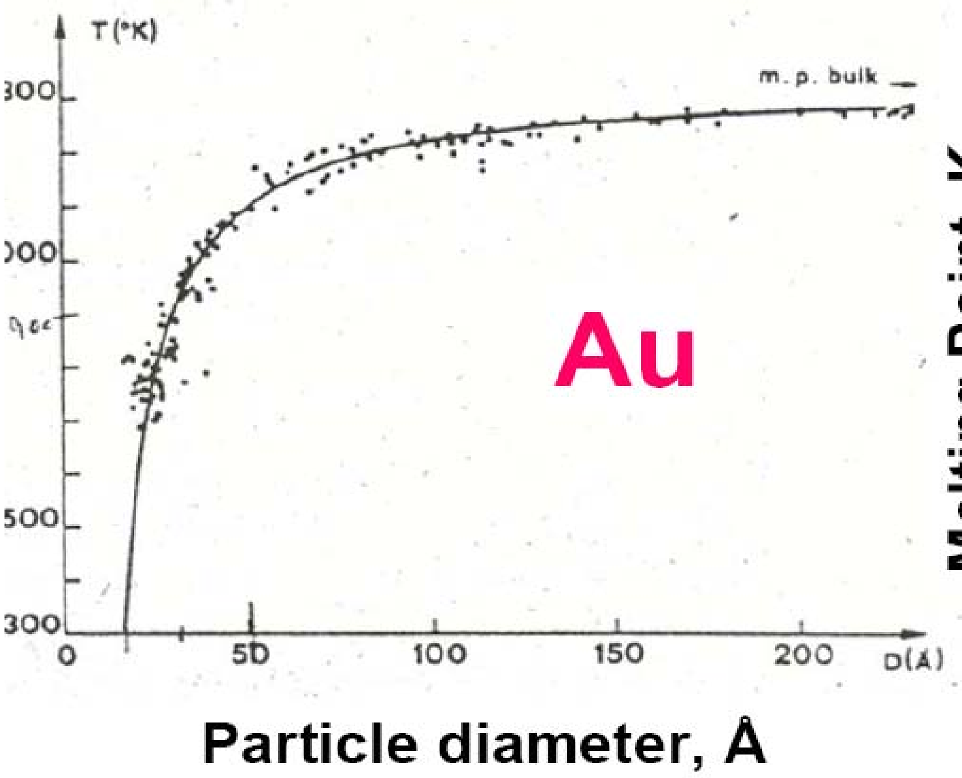
Change in colour from red to blue!

Science **1997**, *277*, 1078

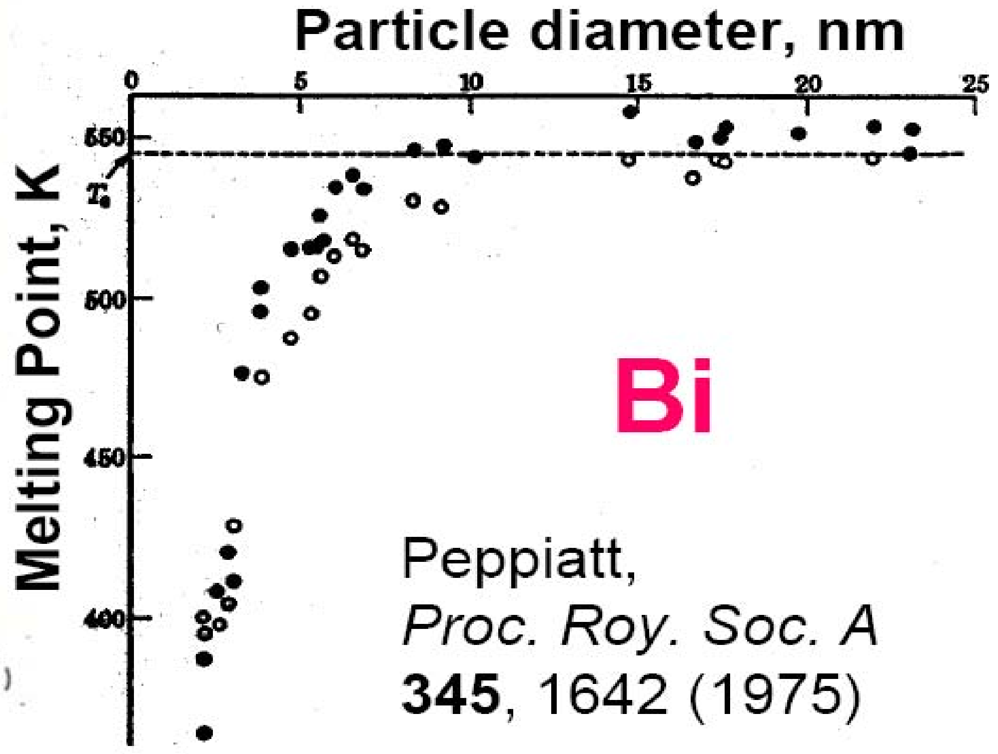
Ratio of Surface Atoms to Total Atoms in a Single Particle (Ichinose et al., 1992)



The Melting Point Decreases with Decreasing Nanoparticle Size



uffat and Borel,
hys. Rev. A **13**, 2287 (1976)



Peppiatt,
Proc. Roy. Soc. A
345, 1642 (1975)

Applications of Nanoparticles

- Large area per gram (adsorbents, membranes)
- Stepped surface at the atomic level (catalysts)
- Easily mix in gases and liquids (reinforcers)
- Superfine particle chains (recording media)
- Easily carried in an organism (new medicine)
- Superplasticity
- Cosmetics that last way into the night ...

Some people believe that nanoparticles are a new state of matter!

A special application: Surface Enhanced Resonant Raman Scattering

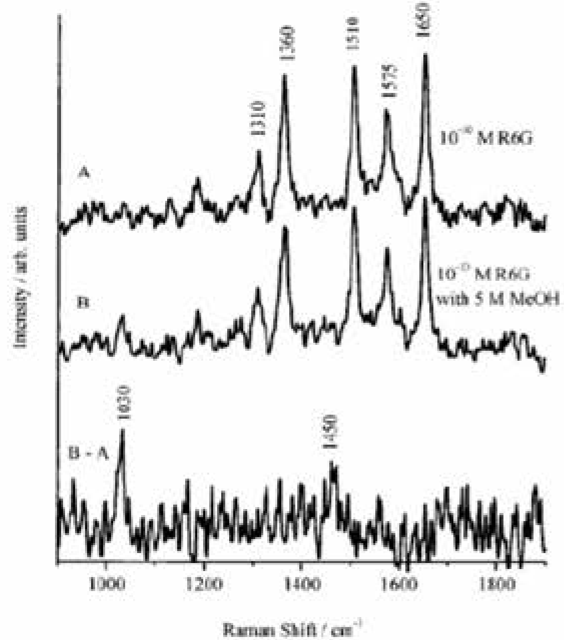


Figure 4. SERRS spectrum from 8×10^{-11} M rhodamine 6G in silver colloidal solution (top), with addition of 5 M methanol (middle). Spectra were measured using 514.5 nm resonant excitation; laser intensity was ca. 10^3 W/cm^2. No fluorescence was obtained at such low concentration because all dye molecules can find a place on the colloidal silver particles where the fluorescence is quenched. The bottom curve depicts the exact subtraction of the top curve from the middle one and shows only the methanol lines. The methanol Raman signal is not enhanced on colloidal silver and shows a Raman cross section on the order of 10^{-30} cm^2/molecule.[133]

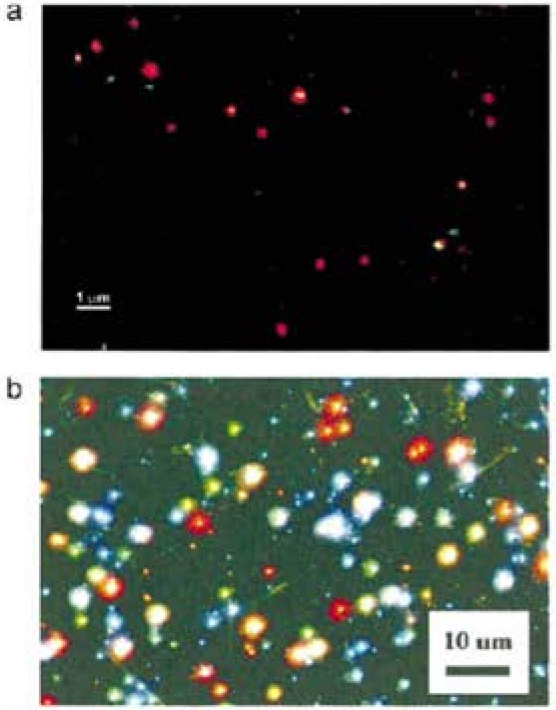


Figure 8. (a) Multicolor Raman image of Ag nanoparticles excited with a mercury lamp at 490 and 570 nm. The probe molecule is bis(4-bipyridyl)ethylene (BPE). The green, red, and yellow signals correspond to 70 nm particles (excited at 490 nm), 140 nm particles (excited at 570 nm), and intermediate-sized particles or nanoaggregates (excited at both 490 and 570 nm), respectively. (b) Multicolor Rayleigh image of Ag nanoparticles excited with a tungsten lamp. For rough orientation, the blue particles correspond to spherical Ag particles with a size of approximately 50 nm or to smaller nonspherical particles and red images come from particles with very high axial ratios, such as rods. (Reprinted with permission from refs 85 and 87. Copyright 1998 American Chemical Society.)

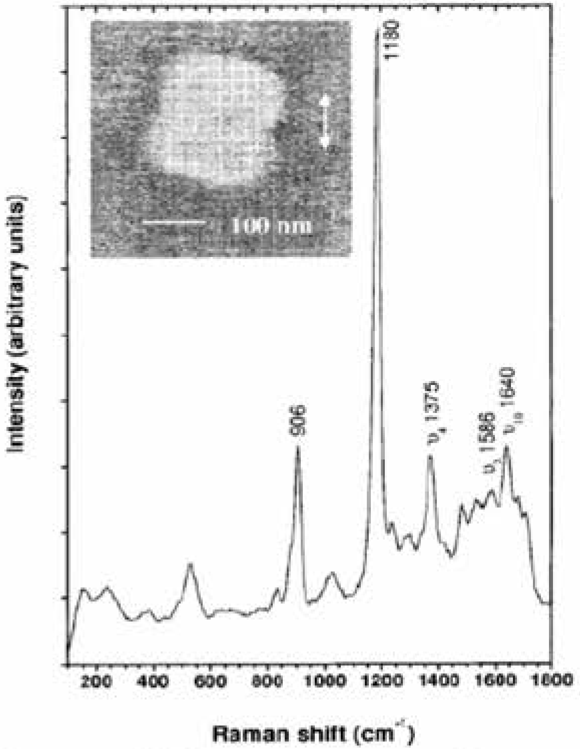


Figure 14. SERS spectrum of a single Hemoglobin molecule on an optically "hot" silver nanoparticle (see inset). A 100× microscope objective was used to illuminate this pair and also to collect the scattered light. The laser wavelength was 514.5 nm, laser power was ~20 μW, laser focus radius was ~1 μm, and integration time was 200 s. (Reprinted with permission from ref 86.)

the end

Thanks !