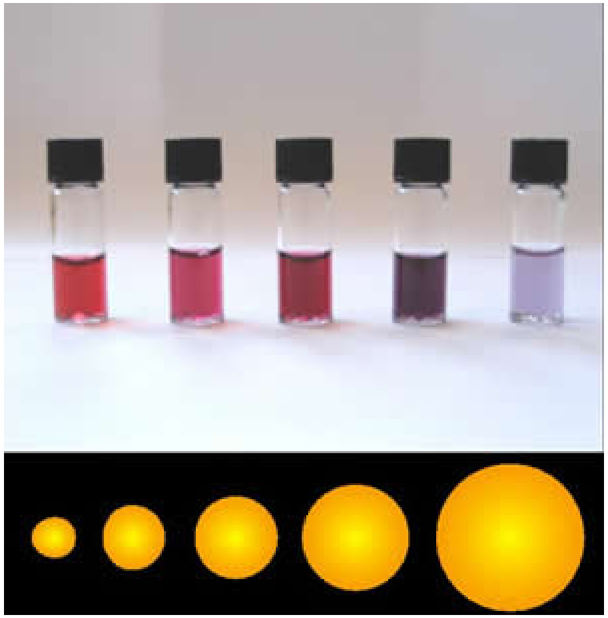
METALLIC NANOPARTICLES



DRAGOMIR MIRELA

UNIVERSITY OF NOVA GORICA

DOCTORAL STUDY, PROGRAMME PHYSICS

INTRODUCTION TO THE NANOWORLD

- WHAT IS NANO?

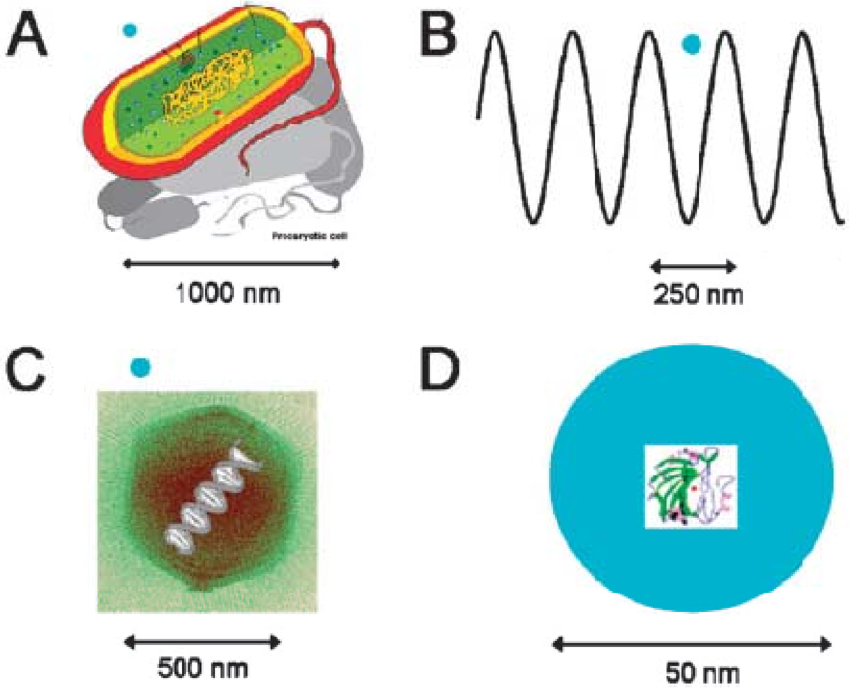
The prefix ***nano-*** is variously said to derive from the Greek word *νάνος* or the Latin word *nannus,* both meaning *dwarf*. It was adopted as an official SI prefix, meaning 10^{-9} of an SI base unit, at the 11th Conférence Générale des Poids et Mesures (CGPM) in 1960 (although it had informal status before that).

- ***Nanoscience*** → the study of the phenomena at 1-100 nm
- ***Nanomaterials*** → *those which have structured components with at least one dimension less than 100 nm*

Zero-Dimensional Nanostructures → Nanoparticles
One-Dimensional Nanostructures → Nanowires and Nanorods
Two-Dimensional Nanostructures → Thin Films

- ***Nanoparticles*** are nanosized structures in which at least one of its phases has one or more dimensions (length, width or thickness) in the nanometer size range (1 to 100 nm) as depicted in figure 1.

Figure 1. Depiction of the size regime of nanoparticles related to common ˝nano˝ scale objects; A-prokaryotic cell, B-ultraviolet wave, C-virus, D-enzyme. Blue spheres represent a 50 nm metal nanoparticle [Robin J. White-Chem. Soc. Rev, 2009, 38].



2. METALLIC NANOPARTICLES

- The term ***metal nanoparticle*** is used to described nanosized metals with dimensions (length, width or thickness) within the size range 1-100 nm.
- **The existence** of metallic nanoparticles in solution was first recognized by **Faraday in 1857** and a quantitative explanation of their colour was given by **Mie in 1908**.

Figure 2. The growth of number of publications dealing with metal nanoparticles [Juan M. Campelo – ChemSusChem 2009,2]

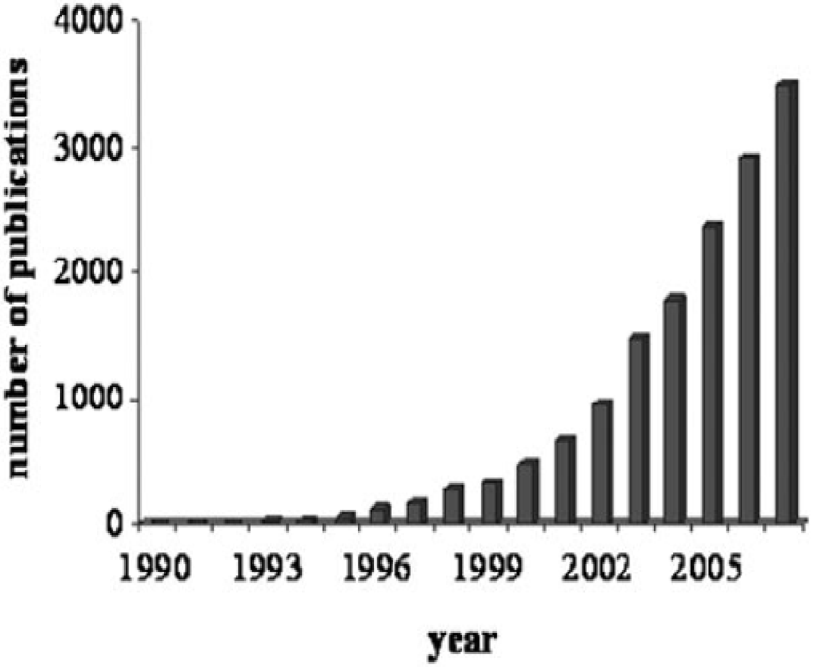
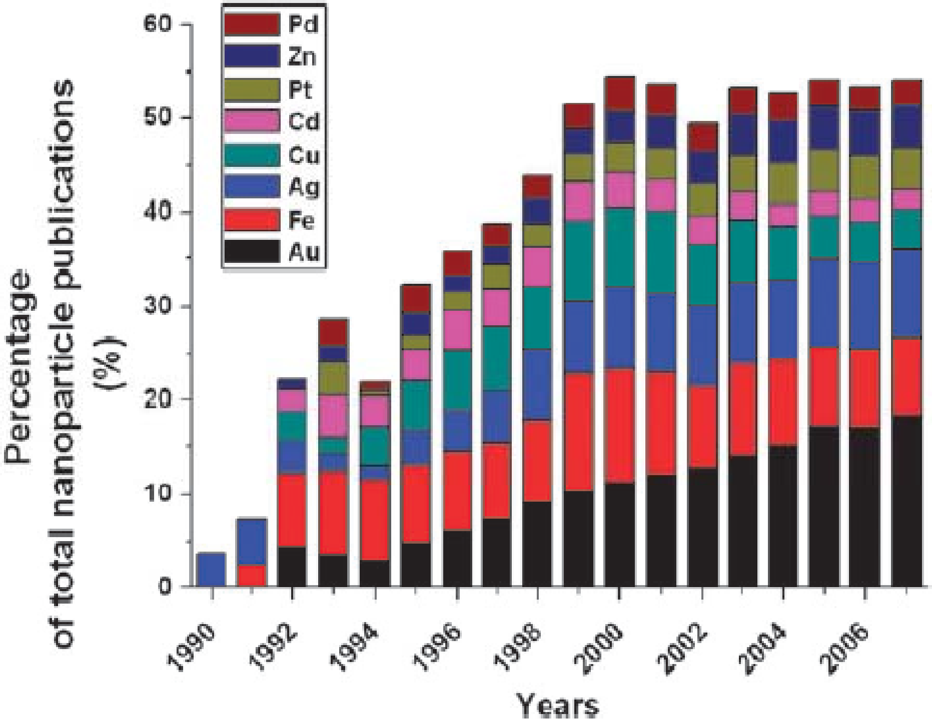


Figure 3. Interest in specific elements in the preparation of nanoparticles over the past 17 years [J Robin J. White-Chem. Soc. Rev, 2009,38]

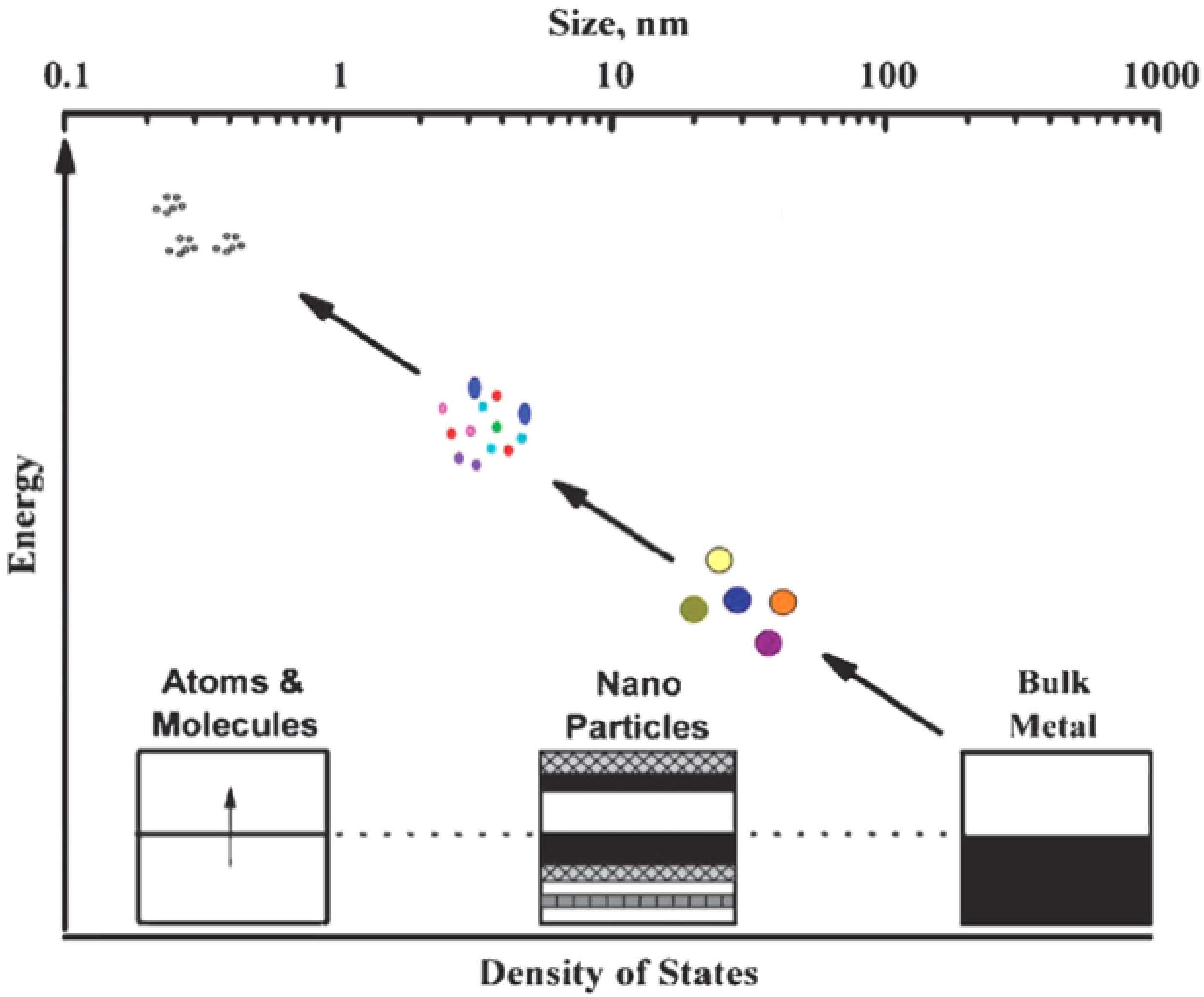


The main characteristics of MNPs

- large surface-area-to-volume ratio as compared to the bulk equivalents;
- large surface energies
- the transition between molecular and metallic states providing specific electronic structure (local density of states LDOS);
- plasmon excitation;
- quantum confinement;
- short range ordering;
- increased number of kinks;
- a large number of low-coordination sites such as corners and edges, having a large number of ˝dangling bonds˝ and consequently specific and chemical properties and the ability to store excess electrons.

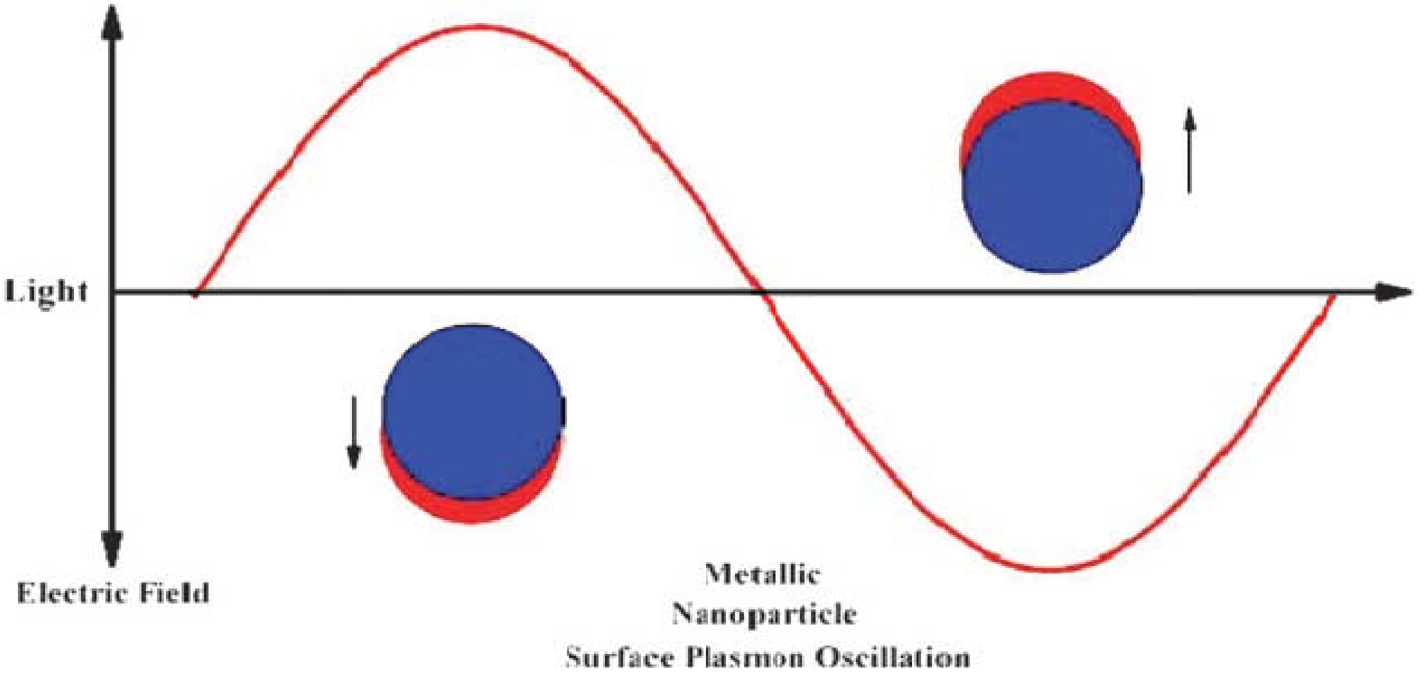
Density of States

Figure 4. Relationship between nanoparticle size, energy and the principle of energy of states [Robin J. White-Chem. Soc. Rev, 2009, 38].



Surface Plasmon Resonance

Figure 5. Oscillation of a metallic nanoparticle´s electron cloud (red) relative to the metal core (blue) in response to the electromagnetic field; the basis for the surface plasmon resonance effect observed in nanoparticles [Robin J. White-Chem. Soc. Rev, 2009, 38].



Local field factor

- The SPR can be simply formalized, in a first approach, by solving Laplace's equation in the case of a single conducting sphere surrounded by a homogeneous transparent medium, with the appropiate continuity relations at the metal-dielectric interface and assuming that the sphere radius is much lower than the wavelength (quasistatic approximation). The homogeneous local electric field inside the particle, $\boldsymbol{E_l}$:

Eq. 1:

$$\mathbf{E}_\mathrm{l} = \frac{3\varepsilon_d}{\varepsilon_m + 2\varepsilon_d}\mathbf{E}_\mathbf{0}$$

where:

- E_0 is the applied field
- ε_m = dielectric function of metal
- ε_d = dielectric function of the host medium

The local field factor is defined as the ratio of the local field to the applied one:

Eq.2:

$$f = E_l/E_0$$

SYNTHESIS METHODS

A. CHEMICAL METHODS

- A.1. Chemical reduction of metal salts
  - A.1.1. The alcohol reduction process
    - A.1.2. The polyol process
- A.2. Microemulsions
- A.3. Thermal decomposition of metal salts
- A.4. Electrochemical synthesis

B. PHYSICAL METHODS

- B.1. Exploding wire technique
- B.2. Plasma
- B.3. Chemical vapour deposition
- B.4. Microwave irradiation
- B.5. Pulsed laser ablation
- B.6. Supercritical fluids
- B.6. Sonochemical reduction
- B.7. Gamma radiation

Goals and Problems in Metallic Nanoparticles Synthesis

- Ideally, metallic nanoparticles should be prepared by a method which:

- is reproducible
- may control the shape of the particles
- yields monodisperse metallic nanoparticles
- is easy, cheap
- use less toxis precursors: in water or more environmentally benign solvents (e.g. ethanol)
- use the least number of reagents
- use a reaction temperature close to room temperature
- with as few synthetic steps as possible (one-pot reaction)
- minimizing the quantities of generated by-products and waste.

A.1. Chemical reduction of metal salts

- In 1857 Michael Faraday reported a systematic study of the synthesis and colors of colloidal gold.
- In 1951, J. Turkevich reproduced standard protocols for the preparation of metal colloids (was refined in 1970 by G. Frens)

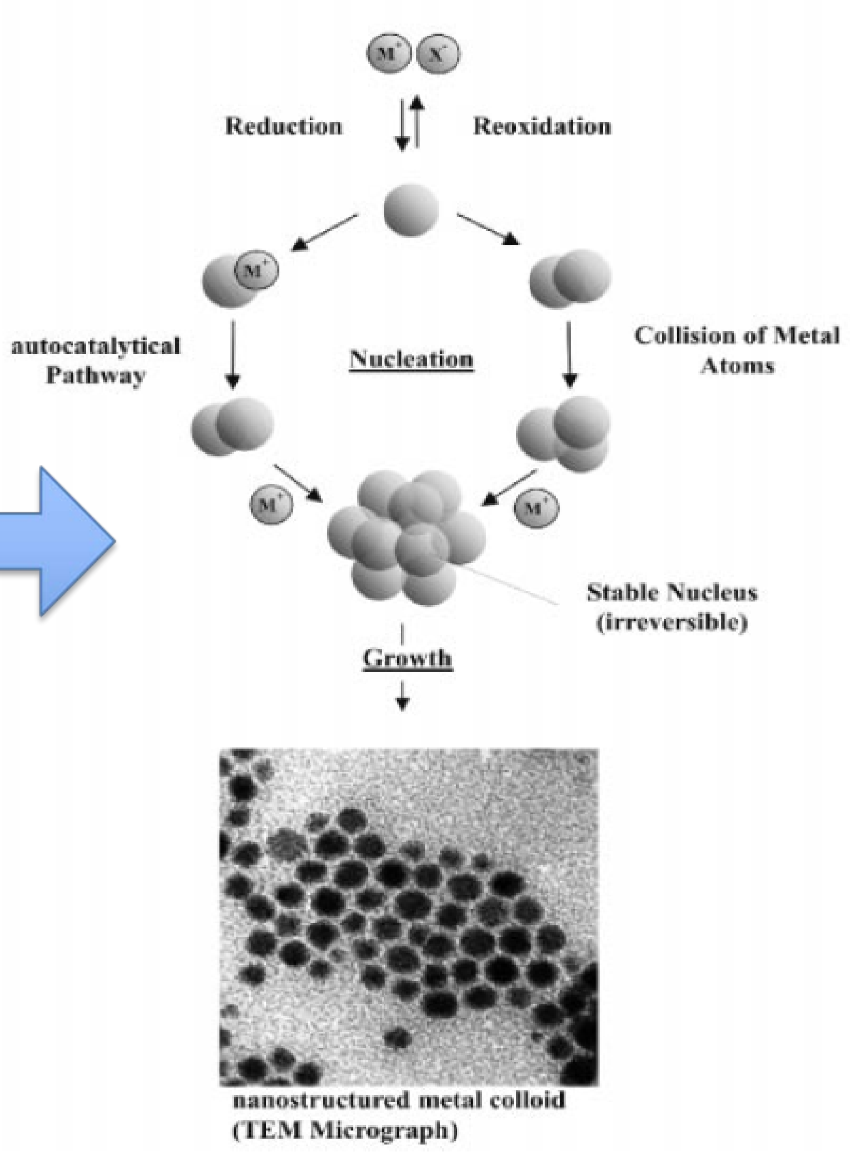


Figure 6. The formation of metal colloids by the salt reduction method [Helmut Boennemann – Eur.J.Inorg.Chem, 2001].

Nucleation and Growth (La Mer)

1. **Nucleation** → takes place because the supersaturated solution is thermodynamically unstable. For the nucleation process to occur, the solution must be supersaturated in order to generate an extremely small size ″sol″ particle.

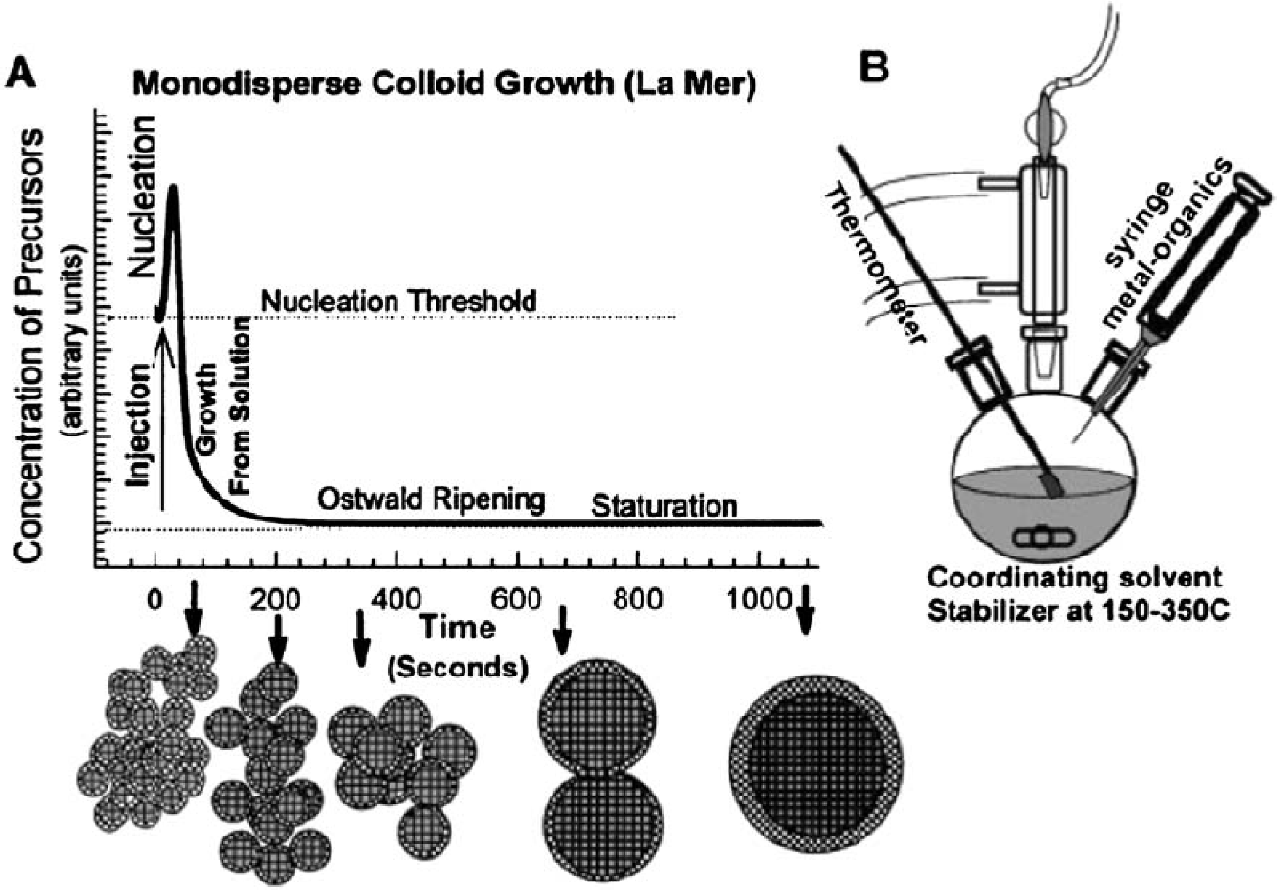


Figure 7. The concept of monodisperse colloid growth of la Merr model (A) and typically synthetic apparatus (B) [John A. Blackman - *Metallic nanoparticles*, Elsevier, 2009].

Nucleation and Growth (La Mer)

2. **Growth** → After the nuclei are formed from the solution, they grow via deposition of the soluble species onto the solid surface (molecular addition).

- The relative rates of growth of small and large particles are different when the reactants are depleted due to particle growth.

- Secondary growth → the growth of particles by aggregation
  → is faster than that by molecular addition
  → it occurs by stable particles combining with smaller unstable nuclei

Stabilizing Metallic Nanoparticles

- by **placing them in an inert environment**
  - an inorganic matrix or
  - polymer
- by **adding surface-protecting reagents**
  - organic ligands – figure 9
  - inorganic capping materials – figure 8

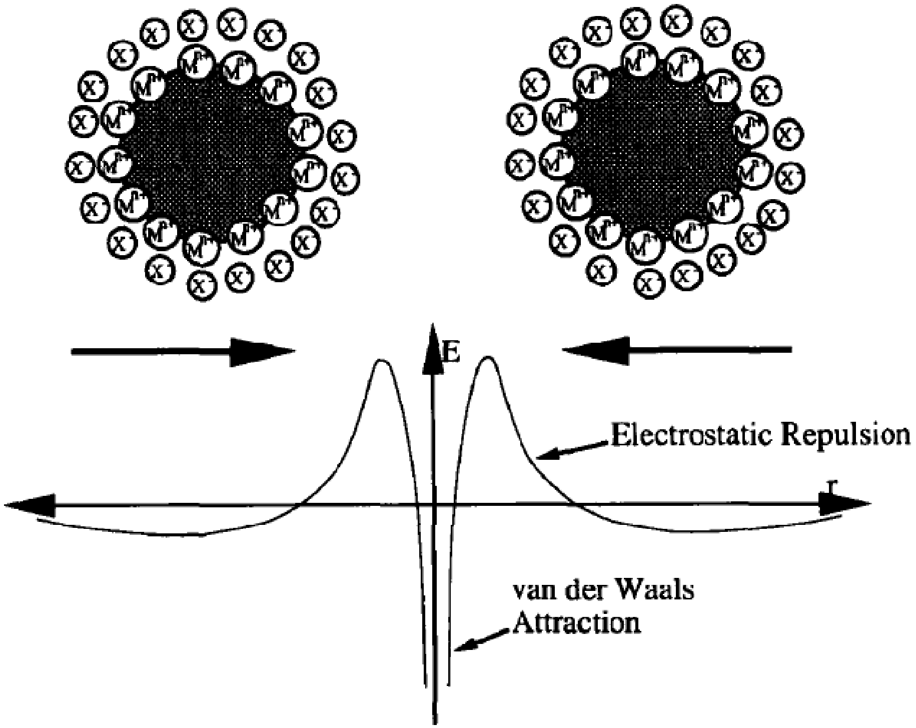


Figure 8. Electrostatic stabilization of metal colloid particles. Attractive van der Waals forces are outweighed by repulsive electrostatic forces between adsorbed ions and associated counterions at moderate interparticle separation [Gunter Schmid - **Clusters and Colloids,** VCH, 1994]

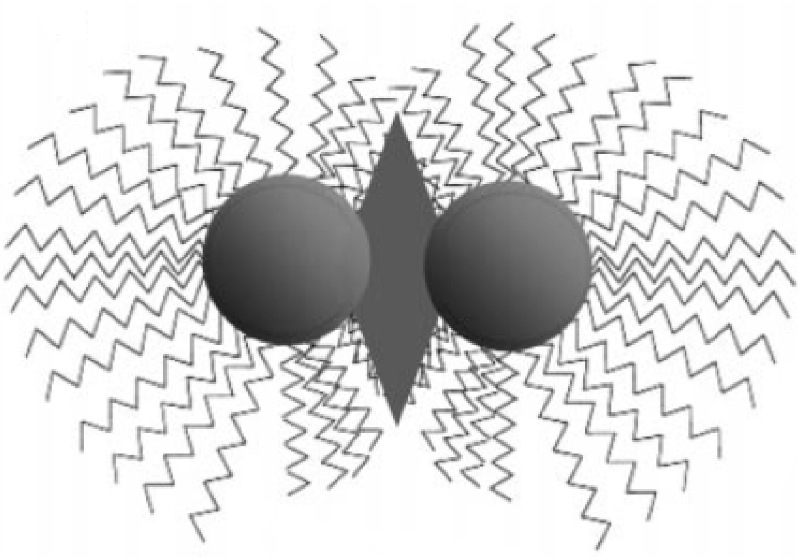
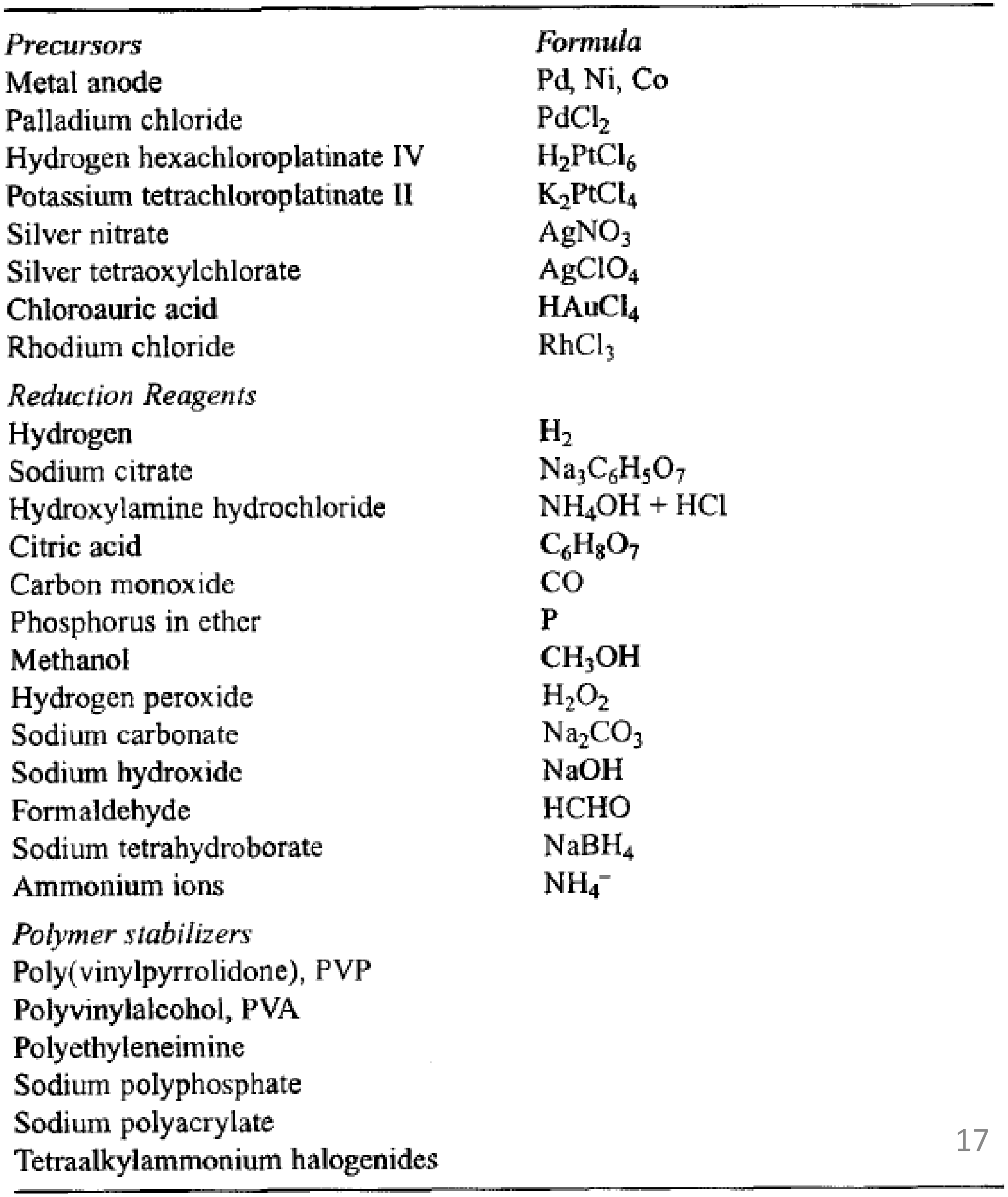


Figure 9 . Steric stabilization of nanostructured metal colloids [Helmut Boennemann – Eur.J.Inorg.Chem.2001]

A.1. Chemical reduction of metal salts

Table 1. Summary of precursors, reduction agents and polymer atabilizers
[Guozong Chao - *NANOSTRUCTURES AND NANOMATERIALS*, Imperial College Press, 2004]

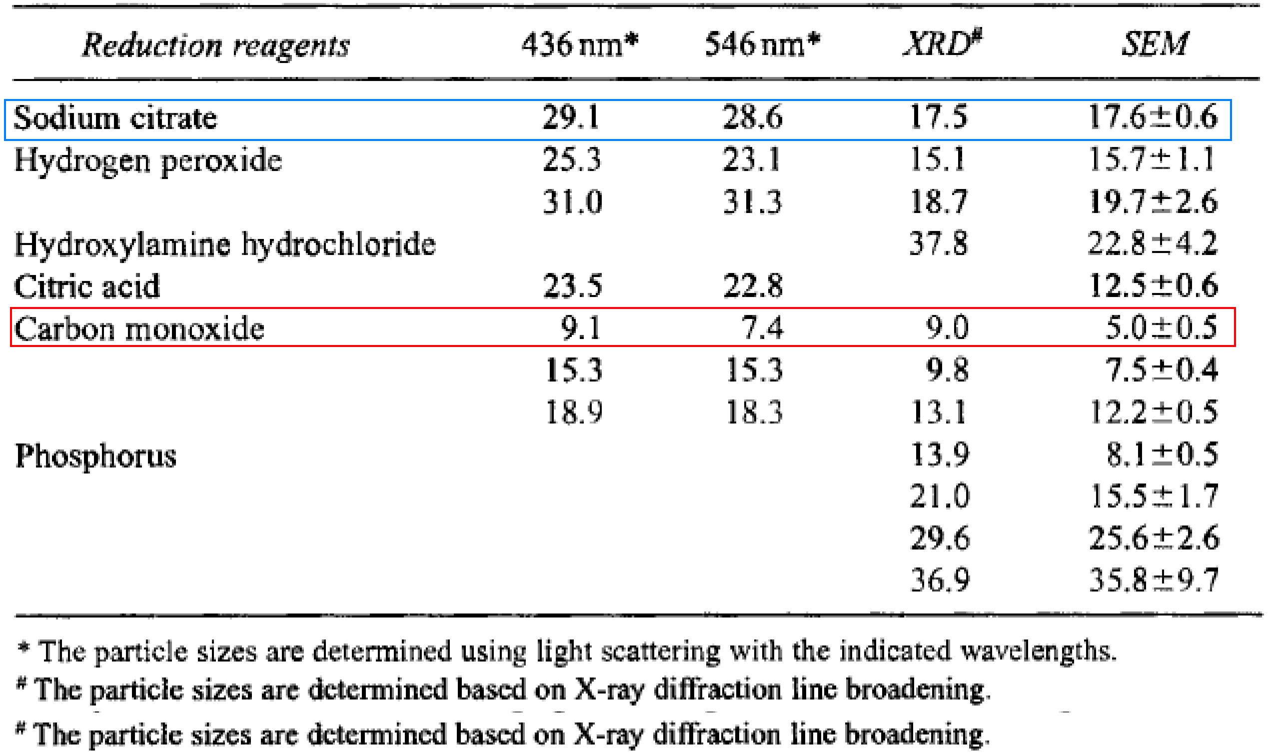


Precursors	*Formula*
Metal anode	Pd, Ni, Co
Palladium chloride	$PdCl_2$
Hydrogen hexachloroplatinate IV	H_2PtCl_6
Potassium tetrachloroplatinate II	K_2PtCl_4
Silver nitrate	$AgNO_3$
Silver tetraoxylchlorate	$AgClO_4$
Chloroauric acid	$HAuCl_4$
Rhodium chloride	$RhCl_3$
Reduction Reagents	
Hydrogen	H_2
Sodium citrate	$Na_3C_6H_5O_7$
Hydroxylamine hydrochloride	$NH_4OH + HCl$
Citric acid	$C_6H_8O_7$
Carbon monoxide	CO
Phosphorus in ether	P
Methanol	CH_3OH
Hydrogen peroxide	H_2O_2
Sodium carbonate	Na_2CO_3
Sodium hydroxide	NaOH
Formaldehyde	HCHO
Sodium tetrahydroborate	$NaBH_4$
Ammonium ions	NH_4^-
Polymer stabilizers	
Poly(vinylpyrrolidone), PVP	
Polyvinylalcohol, PVA	
Polyethyleneimine	
Sodium polyphosphate	
Sodium polyacrylate	
Tetraalkylammonium halogenides	

Influences of reducing reagents

Au nanoparticles

Table 2. Comparison of average sizes of Au nanoparticles synthesized using various reduction [Guozong Chao -*NANOSTRUCTURES AND NANOMATERIALS*, Imperial College Press, 2004]



Reduction reagents	436 nm*	546 nm*	*XRD*#	*SEM*
Sodium citrate	29.1	28.6	17.5	17.6±0.6
Hydrogen peroxide	25.3	23.1	15.1	15.7±1.1
	31.0	31.3	18.7	19.7±2.6
Hydroxylamine hydrochloride			37.8	22.8±4.2
Citric acid	23.5	22.8		12.5±0.6
Carbon monoxide	9.1	7.4	9.0	5.0±0.5
	15.3	15.3	9.8	7.5±0.4
	18.9	18.3	13.1	12.2±0.5
Phosphorus			13.9	8.1±0.5
			21.0	15.5±1.7
			29.6	25.6±2.6
			36.9	35.8±9.7

* The particle sizes are determined using light scattering with the indicated wavelengths.

\# The particle sizes are determined based on X-ray diffraction line broadening.

The particle sizes are determined based on X-ray diffraction line broadening.

Influences of reducing reagents

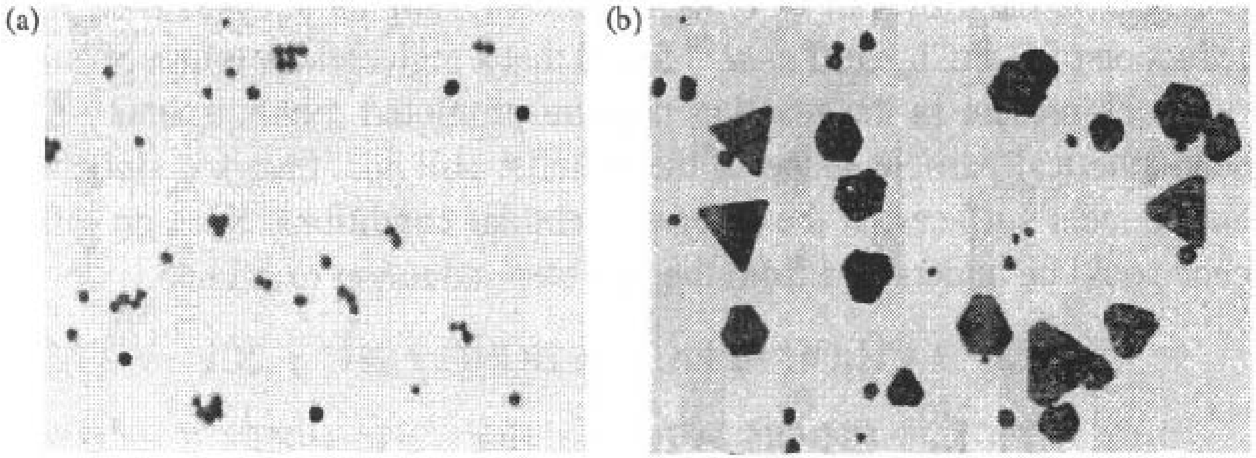


Figure 10. SEM micrographs of gold nanoparticles prepared with sodium citrate (a) and citric acid (b) as reduction reagents, respectively, under otherwise similar synthesis conditions.
[W.O. Miligan and R.H. Morriss, *J.* Am. Chem. SOC. 86, 3461 (1 964).]

Influences of reducing reagents

In the case of Pd → $r_{\text{pivalate}} \sim r_{\text{acetate}} > r_{\text{glycolate}} \gg r_{\text{dichloroacetate}}$

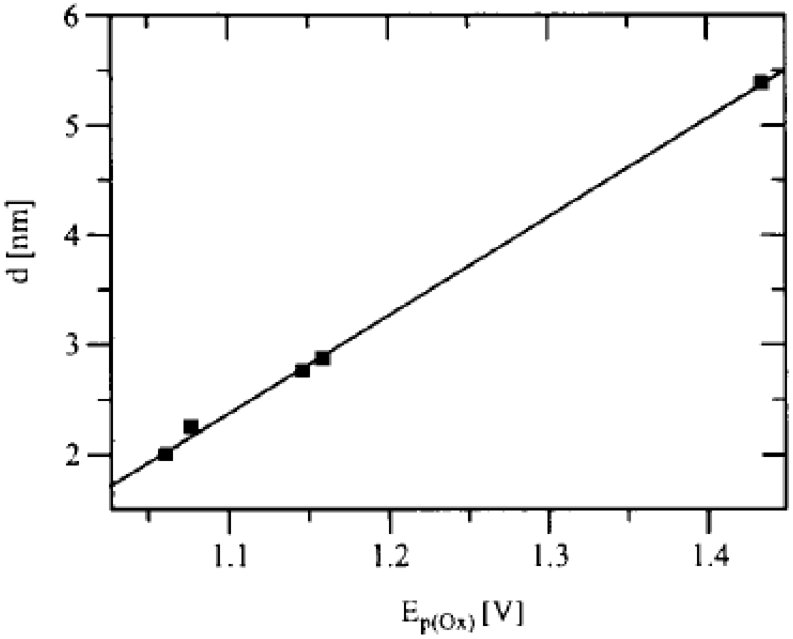


Figure 11. The particle size of Pd colloids as a function of peak potentials of reduction reagent, carboxylates, in which smaller peak potentials mean stronger reduction reagents.
[M.T. Reetz and M. Maase*, Adv. Muter. 11, 773 (1999)]*

Influences of pH

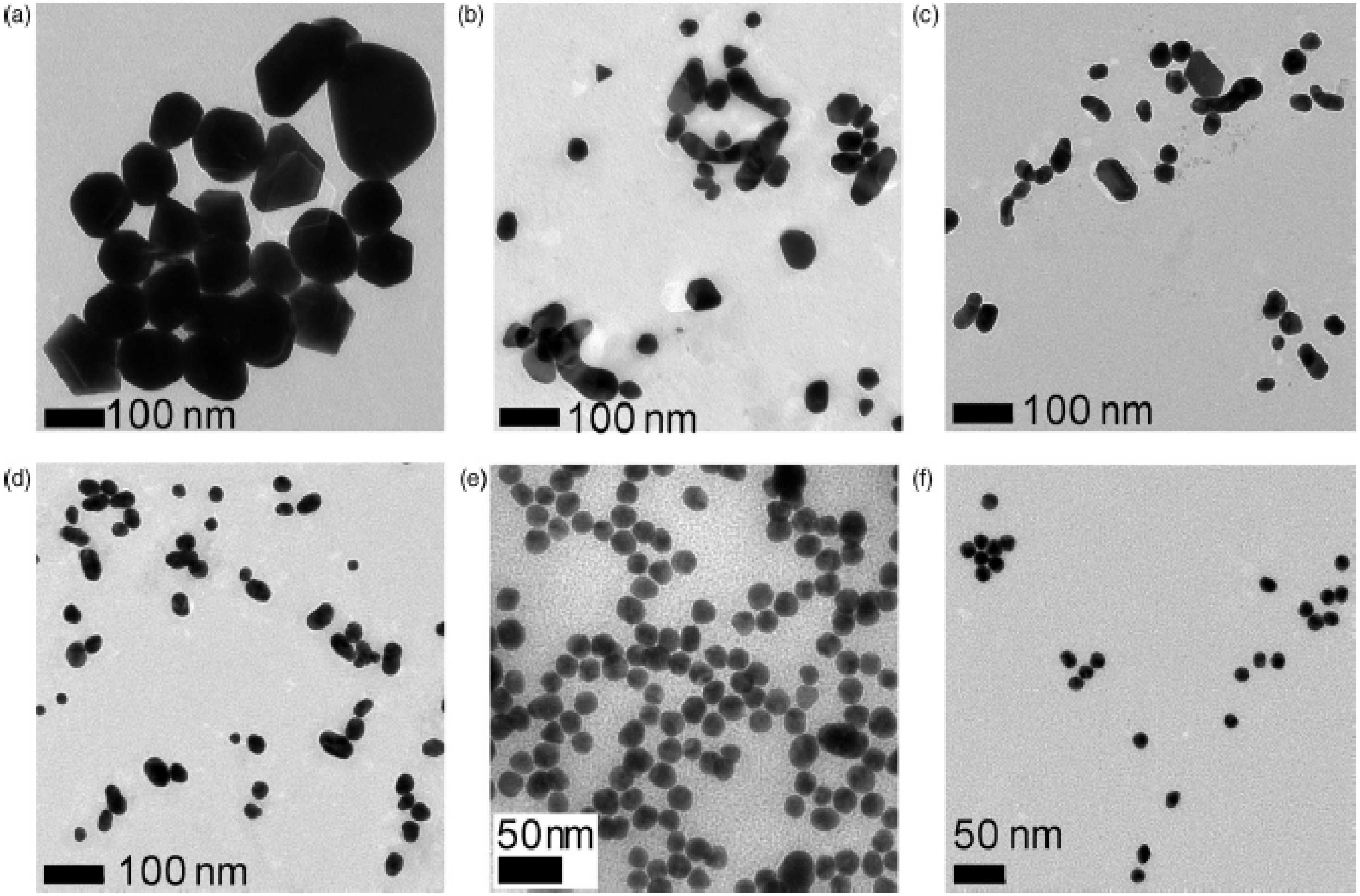
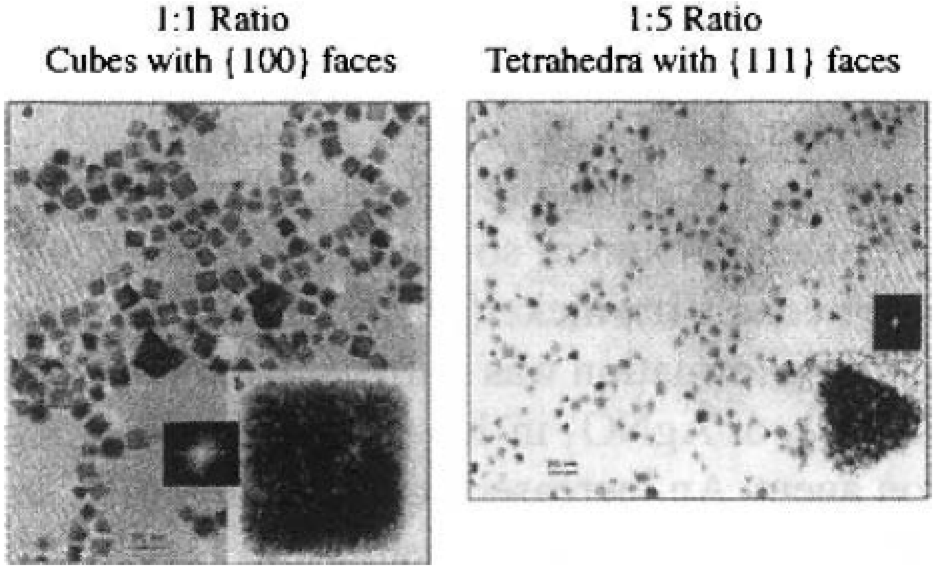


Figure 12. Transmission electron micrographs of gold nanoparticles obtained by citrate reduction at the following pH values: (a) 4.0, (b) 4.5, (c) 5.0, (d) 5.5, (e) 6.0, and (f) 6.5 [W. Patungwasa, J.H. Hodak , Materials Chemistry and Physics 108 (2008)]

Influences of polymer stabilizer

Influence of
sodium
polyacrylate
on the
shape
of Pt NPs



1:1 Ratio
Cubes with {100} faces

1:5 Ratio
Tetrahedra with {111} faces

Figure 13. Pt nanoparticles synthesized in colloidal solution and having different shapes (11 nm cubes on the left and ~7 nm tetrahedrons on the right)
[T.S. Ahmadi, Z.L. Wang, T.C. Green, A. Henglein, M.A. El-Sayed, Science 272, 1924 (1996).]

A.1.1. The alcohol reduction process

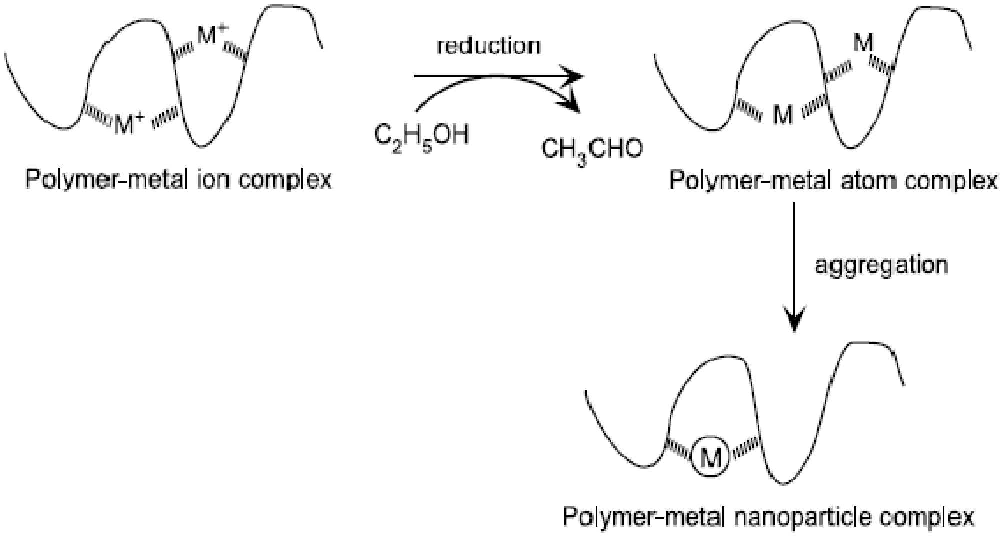


Figure 14. Preparation of polymer-capped metal nanoparticle by alcohol reduction [Marcel Dekker, Dekker Encyclopedia of Nanoscience and Nanotechnology, New York, 2004]

A.2. Microemulsions

- The formation of reverse micelles was confirmed to be an interesting and environmentally friendly alternative to the preparation of metal nanoparticles.

Reverse micelles *Normal micelles*

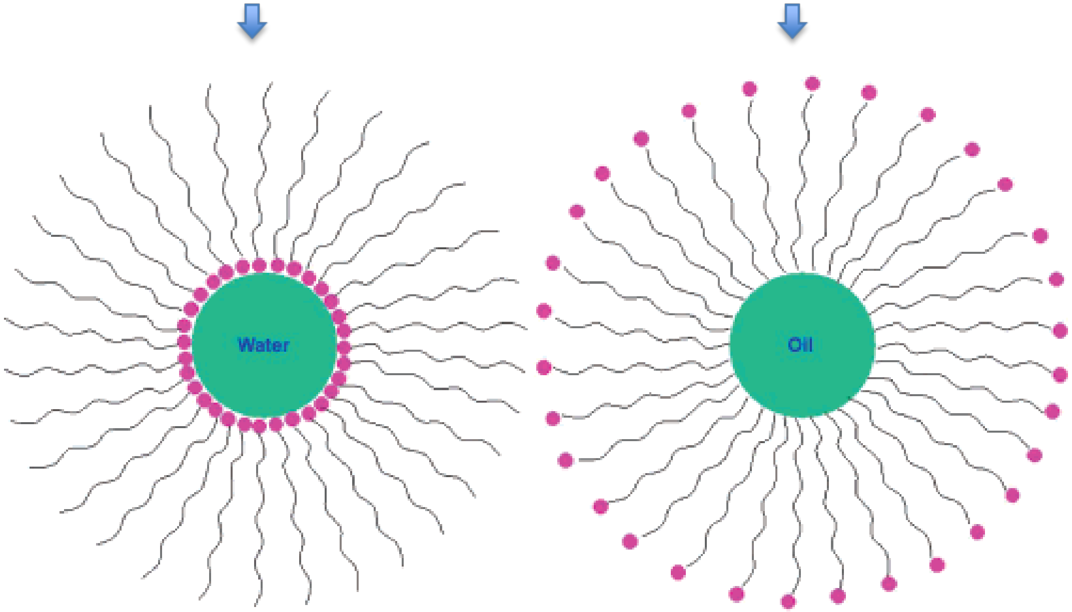


Figure 15. Reverse micelle and normal micelle structures [Burda et al.,Chem.Rev, 2005, 105].

- Also, by turning the reaction parameters, different nanoparticle shapes can be produced

A.2. Microemulsions

- Nanosized Ag particles with a uniform size distribution have been prepared using a reverse micelle process

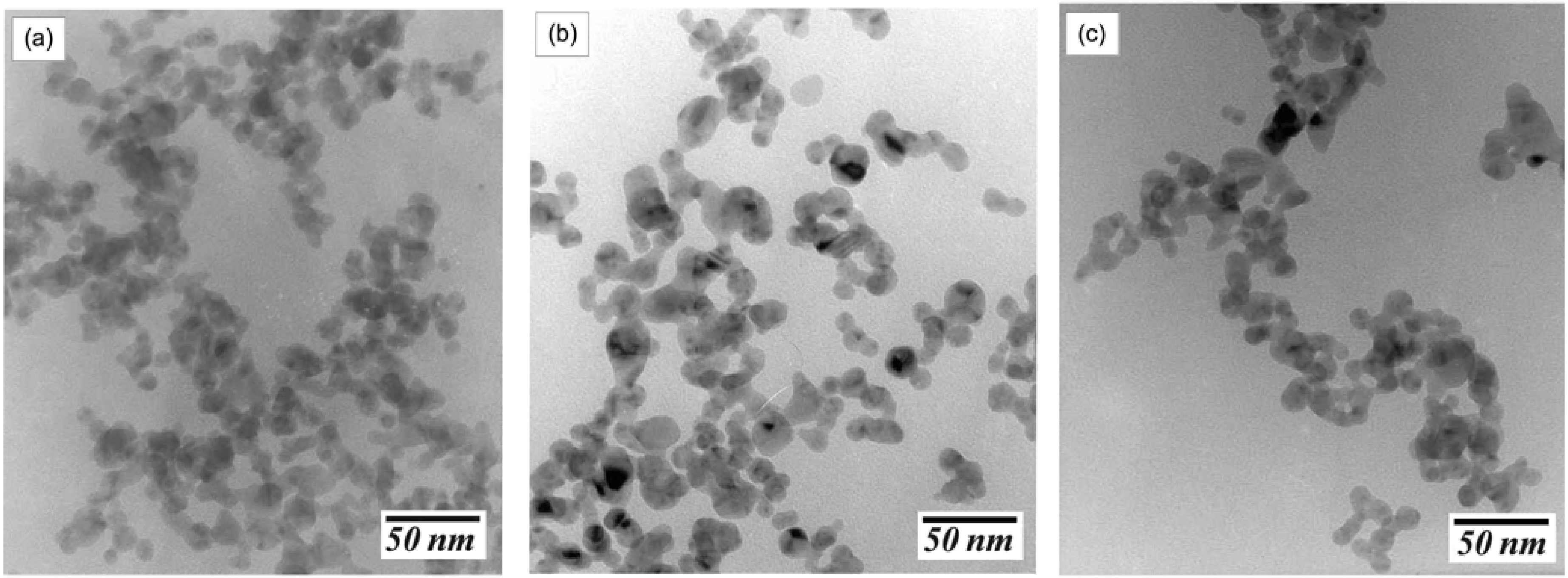


Figure 16. TEM micrographs of the Ag powders synthesized by a reverse micelle process with different water/surfactant ratio: (a) R=4, (b) R=6, and (c) R=8
[Dong-Sik Bae et al., Metals and Materials Int., 11, 4, 2005]

A.3. Thermal decomposition of metal salts

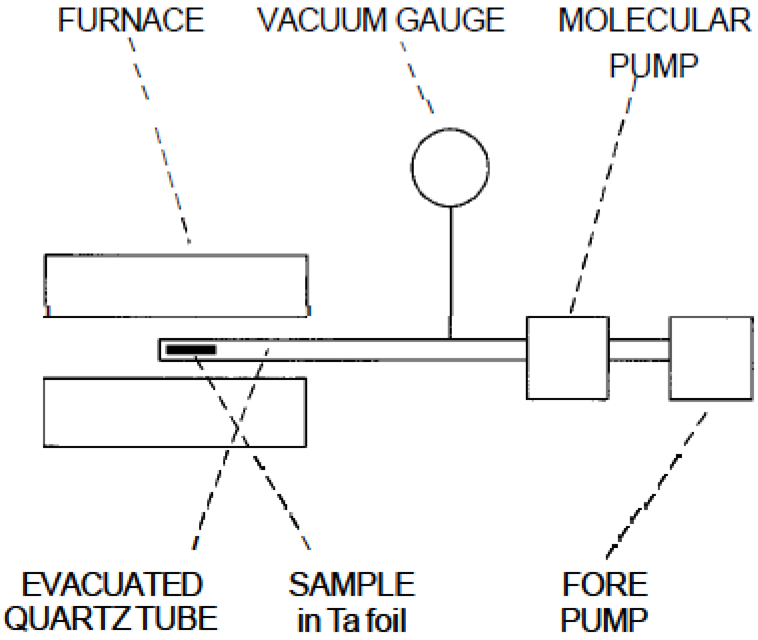


Figure 17. Apparatus used to make metal nanoparticles by thermally decomposing solids consisting of metal cations and molecular anions, or metal organic solids [Charles P. Poole, Jr. Frank J. Owens, *Introduction to nanotechnology*, John Wiley & Sons, Inc., 2003].

A.4. Electrochemical synthesis

The overall process of electrochemical synthesis (equation) can be divided into six elementary steps:

- 1. Oxidative dissolution of the sacrificial M_{bulk} anode.
- 2. Migration of M^{n+} ions to the cathode.
- 3. Reductive formation of zerovalent metal atoms at the cathode.
- 4. Formation of metal particles by nucleation and growth.
- 5. Arrest of the growth process and stabilization of the particles by colloidal protective agents (e.g. tetraalkylammonium ions).
- 6. Precipitation of the nanostructured metal colloids.

$$\begin{array}{lllll}
\text{Anode:} & & M_{bulk} & \rightarrow & M^{n+} + n\,e^{-} \\
\text{Cathode:} & M^{n+} + n\,e^{-} + & \text{stabilizer} & \rightarrow & M_{coll}/\text{stabilizer} \\
\hline
\text{Sum:} & M_{bulk} \; + & \text{stabilizer} & \rightarrow & M_{coll}/\text{stabilizer}
\end{array}$$

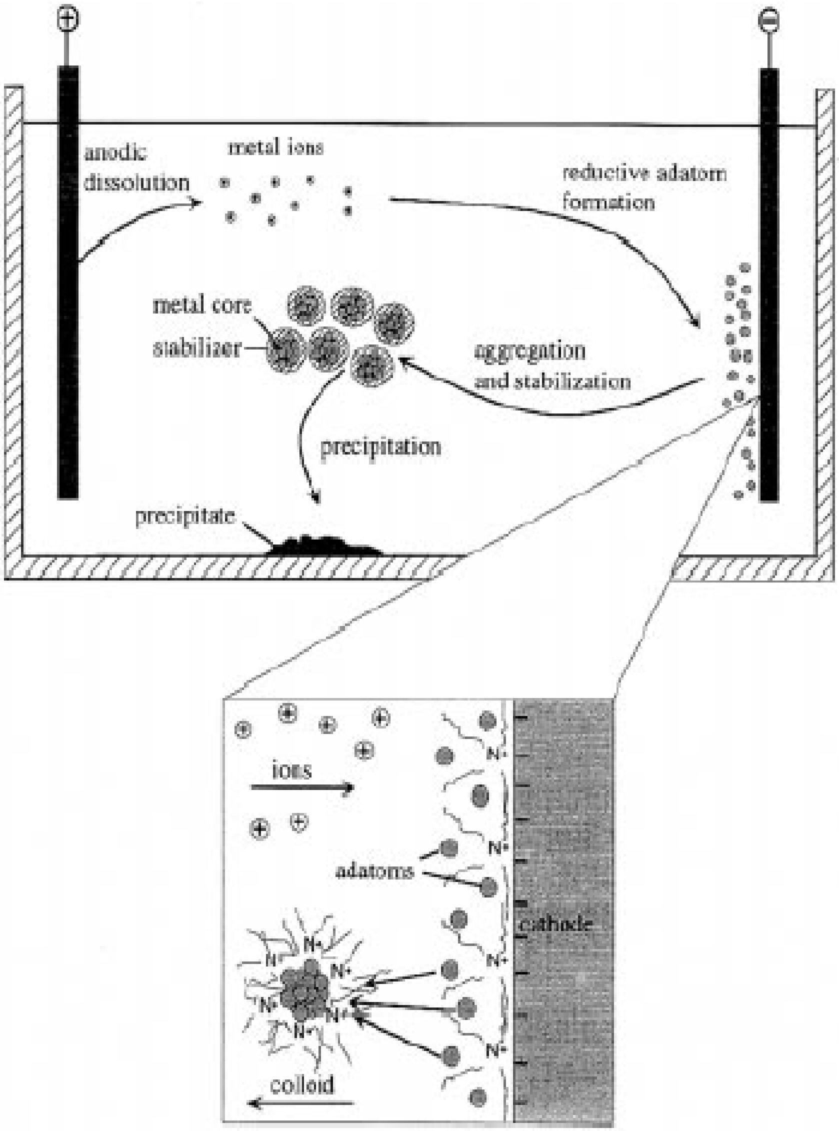


Figure 18. Electrochemical formation of $NR_4^+Cl^-$ stabilized nanometal [Helmut Boennemann – Eur.J.Inorg.Chem.2001]

B. PHYSICAL METHODS

► B.2. Plasma

- A novel plasma reduction method at room temperature has been used to prepare supported metal nanoparticles.
- Legrand et al. employed a dihydrogen microwave plasma to reduce various metal solutions (Au, Pt and Pt-Au) on zeolites.

This technique is a very promising and straightforward way to prepare metal nanoparticles as it is:

- an environmentally friendly,
- fast and
- simple methodology and also a promising alternative to hydrogen reduction at high temperatures.

However, the specialised equipment needed makes difficult its widespread use.

B.5. Pulsed laser ablation

► **The laser approach involves**:

- **the vaporisation of metals employing a pulsed laser (e.g. Nd-YAG) and**

- **subsequent controlled deposition on the surface of the support under well-defined conditions of temperature and pressure or pulsed laser ablation of targets in liquid environment (in solution)**

Advantages of PLA in solution:

➡ a lesser need to add surfactant for capping of colloidal particles so more pure particles can be achieved

➡ nanoparticles can be produced in arbitrary solution – changing the nature of the liquid environment can control the size distribution and stability of metallic NPs

► Some parameters that influence ablation, nucleation, growth and aggregation mechanisms are :

- **Laser wavelength** : the diameter of NPs decreased with an increase of photon energy or laser light
- **Pulse energy :** the diameter of NPs decreased with an increase of pulse number
- **Pulse duration**,
- **Repetition rate**
- **Liquid environment**

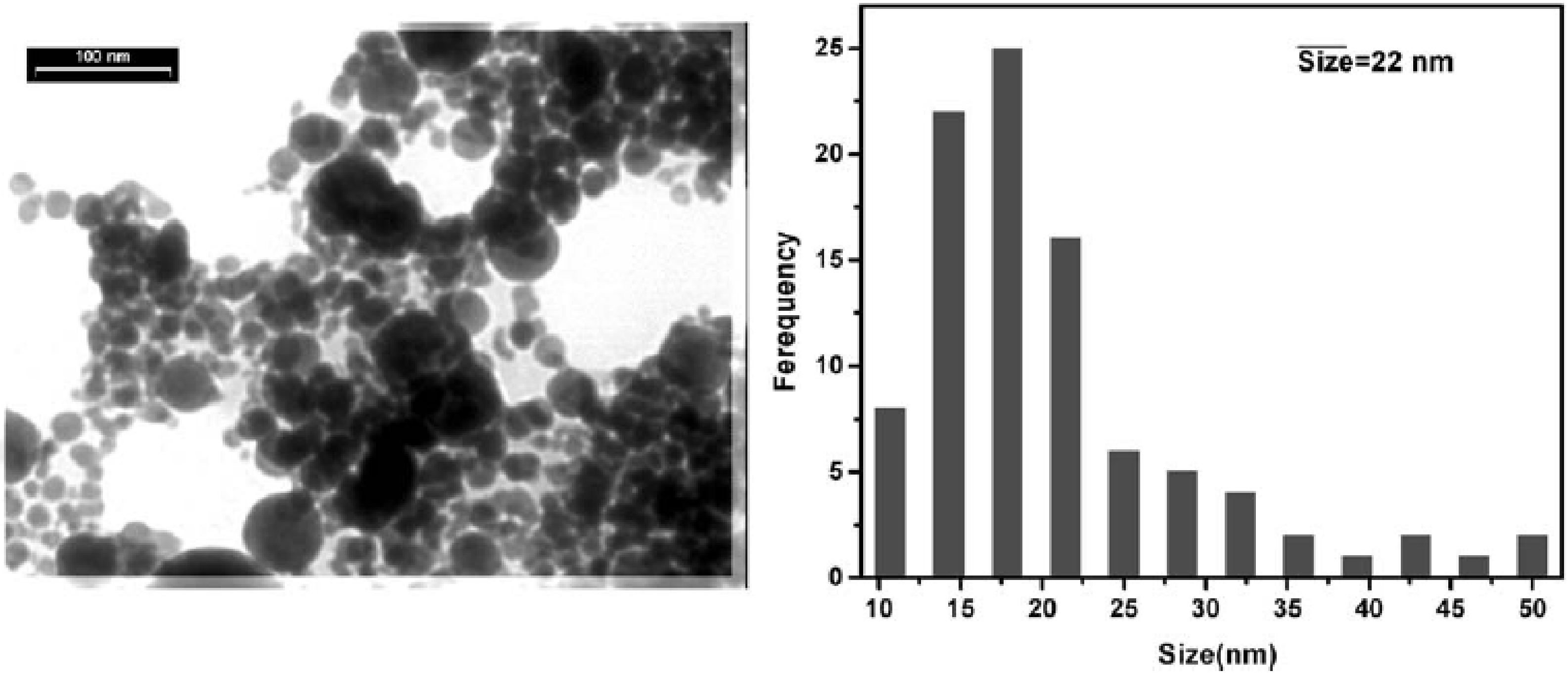


Figure 19. Typical TEM image of silver nanoparticles in ethanol and its size distribution [Tilaki et al. Appl.Phys.A, 84,2006]

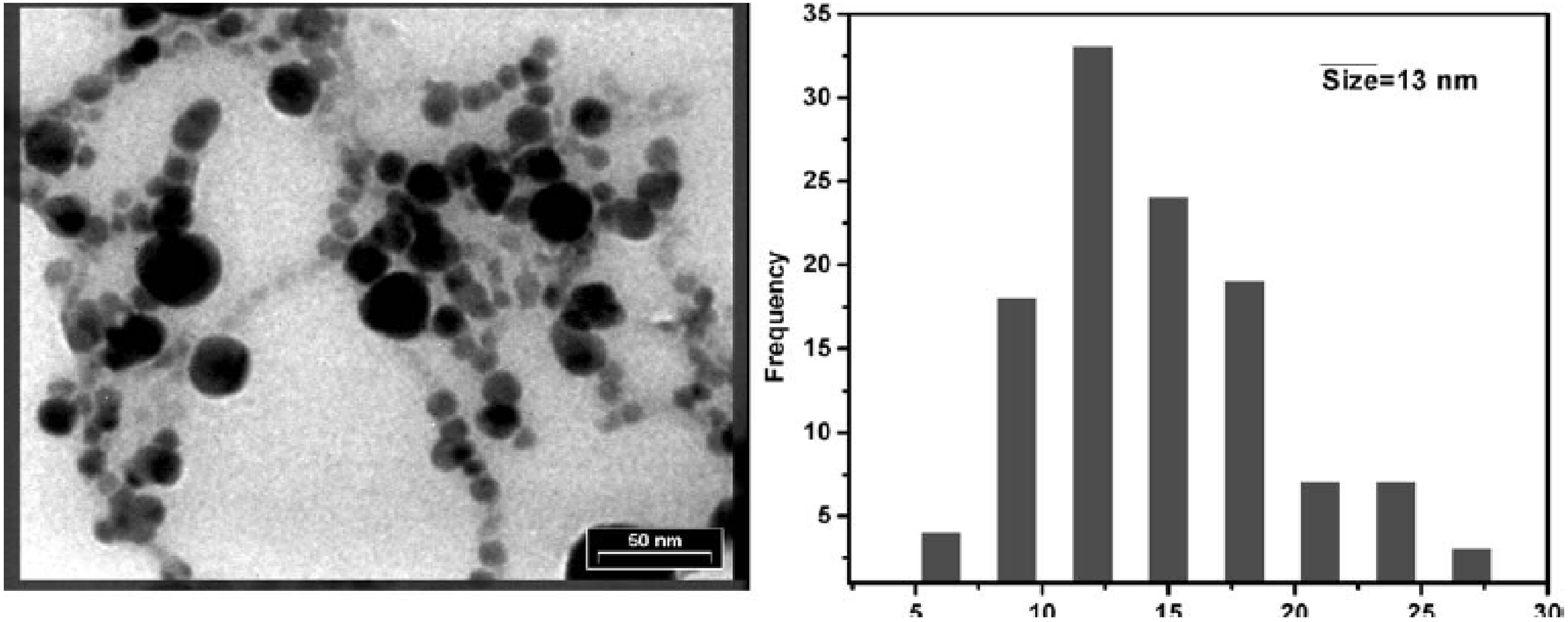


Figure 20. Typical TEM image of silver nanoparticles in water and its size distribution [Tilaki et al. Appl.Phys.A, 84,2006]

Characterization

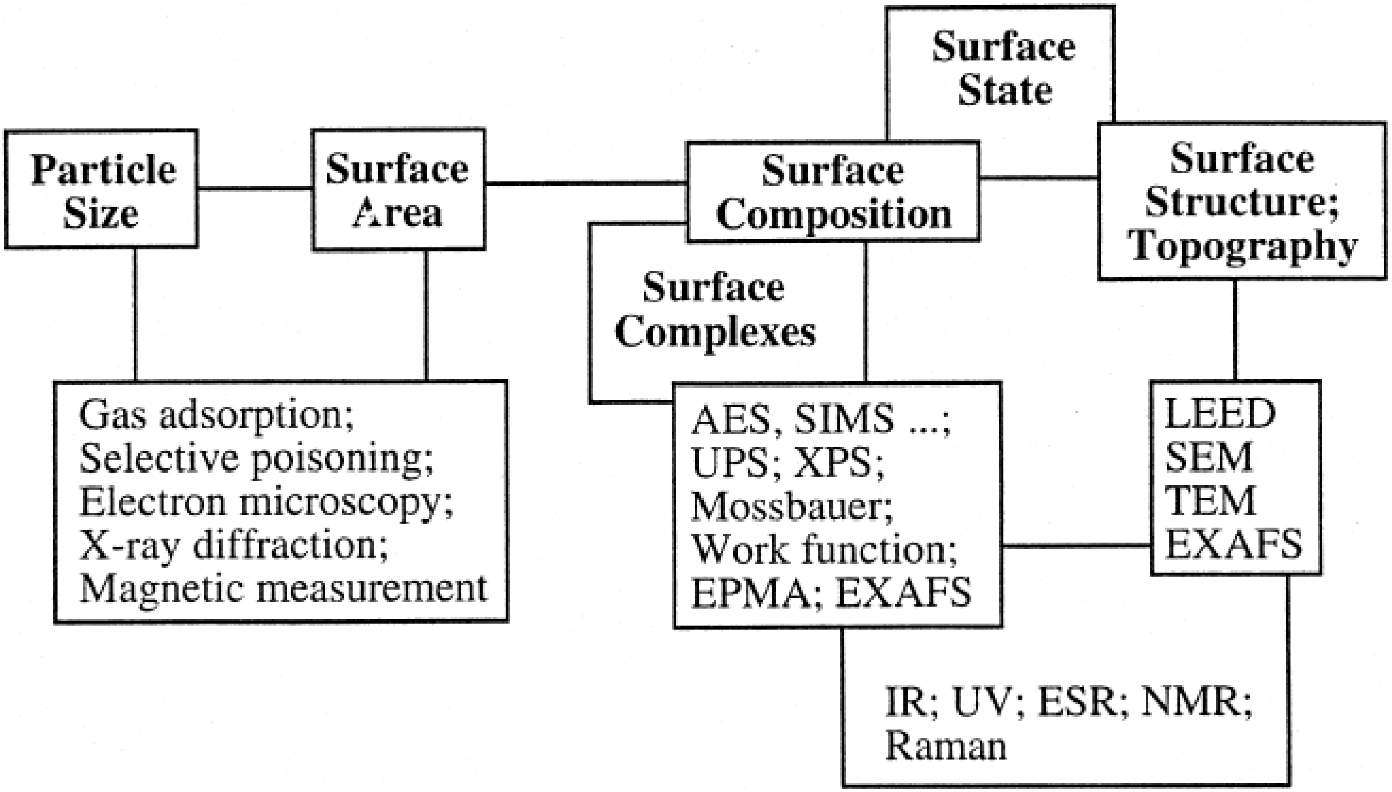


Figure 21. Common methods available for the characterization of matallic NPs [*J.D. Aiken III, Journal of Molecular Catalysis A: Chemical 145 (1999)*]

PROPERTIES

Physical properties

- **Effect of size on melting temperature** ⟶ The melting temperature decreases with the dimensions of metallic NPs

The many surface atoms, being less restricted in their thermal motions, will fluctuate more easily spatially, thereby lowering the melting temperature

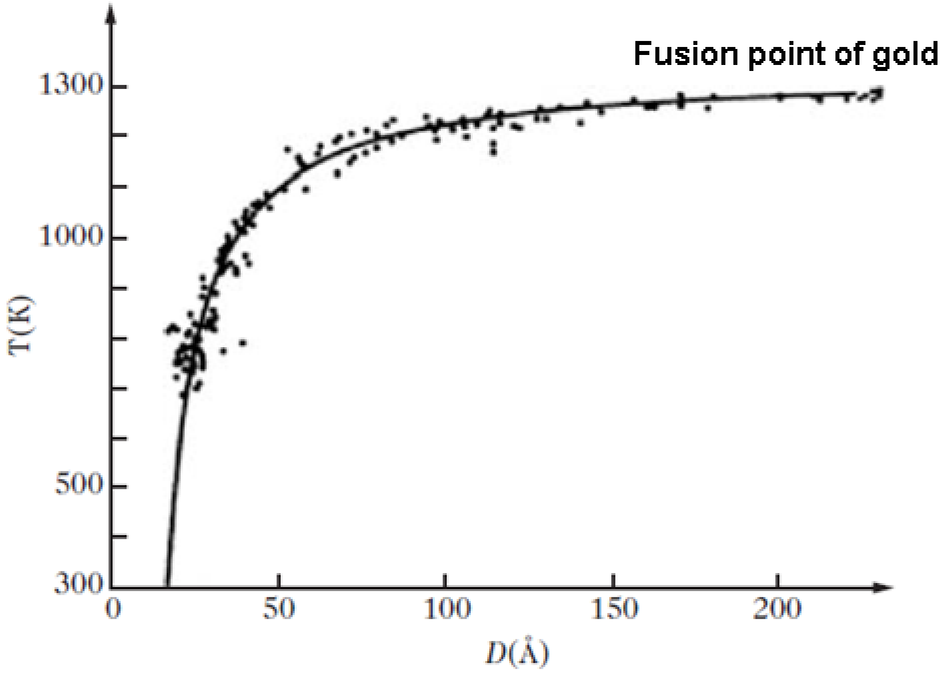


Figure 22. Size dependence of the melting temperature of gold [J.-C. Bertolini, Nanomaterials and Nanochemistry, Springer, Berlin, 2008]

Optical properties

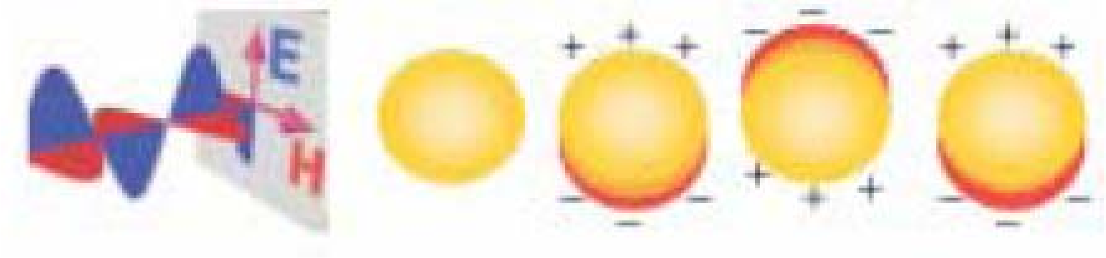


Figure 23. Schematic drawing of the interaction of an electromagnetic radiation with a metal nanosphere. A dipole is induced, which oscillates in phase with the electric field of the incoming light. [Luis M. Liz-Marzán- Nanometals:formation and color, Elsevier, 2004]

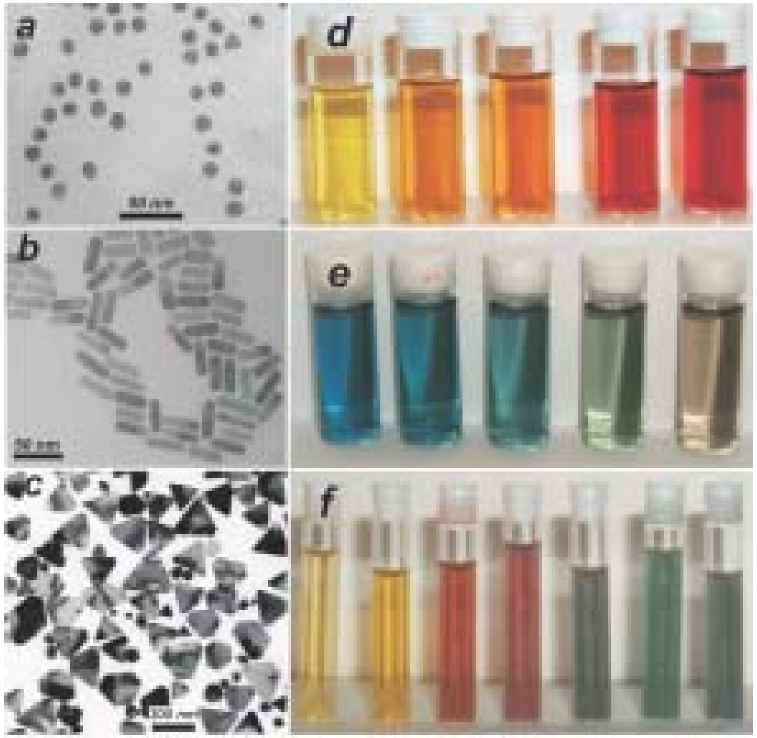


Figure 24*.* Left: Transmission electron micrographs of Au nanospheres and nanorods (a,b) and Ag nanoprisms (c, mostly truncated triangles) formed using citrate reduction, seeded growth, and DMF reduction, respectively.
Right: Photographs of colloidal dispersions of AuAg alloy nanoparticles with increasing Au concentration (d), Au nanorods of increasing aspect ratio (e), and
Ag nanoprisms with increasing lateral size (f)
[Luis M. Liz-Marzán- Nanometals:formation and color, Elsevier, 2004]

Applications

In Catalysis:

Catalysts based on metal NPs are:

- ✓ **Highly active**
- ✓ **Selective**
- ✓ **Exhibit long lifetime for several kind of reactions**

conventional metal catalyst

metal nanoparticles capped by polymers

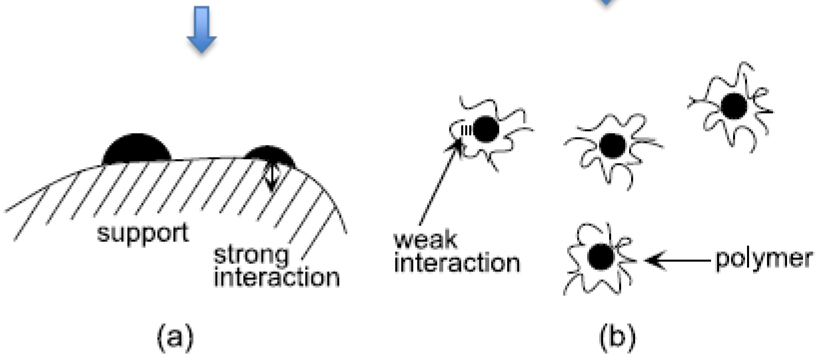


Figure 25. Schematic illustration of the structures of (a) conventional metal catalyst and (b) metal nanoparticles capped by polymers [Marcel Dekker, Dekker Encyclopedia of Nanoscience and Nanotechnology, New York, 2004]

➡ heterogenous catalysts – immobilized on innorganic supports (figure 25 - a)

➡ homogenous catalysts - metal NPs surrounded with stabilizers (figure 25 - b)

Application	Substrate	Support, method, nanoparticle size
Hydrogenations of alkenes, alcohols and aldehydes		Various supports Various methods NP size: variable
Oxidations	alcohols	Metal oxides (e.g. Fe_2O_3, Al_2O_3, TiO_2), carbon Co-precipitation, impregnation/reduction NP size: 2–10 nm
	aldehydes	Al_2O_3, SiO_2, activated carbon Impregnation (from metal sols)/reduction NP size: 2–13 nm
	aromatic amines	Polymers Impregnation NP size: 5–10 nm
	alkenes	Metal oxides (e.g. Al_2O_3, SiO_2), activated carbon, polymers Various methods NP size: variable
	nitroarenes	TiO_2, Fe_2O_3, activated carbon Deposition/precipitation, impregnation NP size: 3–5 nm
Oxidative decomposition of alkylamines and dioxins		Fe_2O_3/La_2O_3 Deposition/precipitation NP size:1–10 nm
Direct epoxidation of propylene		TiO_2 (MCM-48) Deposition/precipitation NP size: 1–10 nm
C–C coupling reactions		Oxides (Ce, Ti, Zr, SiO_2) Deposition/precipitation NP size: 10 nm
Hydroamination of terminal alkynes		Chitosan, chitosan/SiO_2 Impregnation NP size: 2–6 nm
Benzannulation of 2-(phenylethynyl)benzaldehyde and phenylacetylene		CeO_2, TiO_2 and C Impregnation/reduction, precipitation NP size: 3–17 nm
Synthesis of methanol/dimethyl ether from syngas		ZnO, ZnO/Al_2O_3 H-Y zeolite Impregnation
Hydrochlorination of ethyne		Activated carbon Impregnation
Water gas shift reaction		Mesoporous TiO_2, CeO_2

Table 3. Applications of various supported Au metal nanoparticles in catalysis [Juan M. Campelo, ChemSusChem 2009, 2]

- **Applications of homogenous catalysts**:

- Olefin hydrogenation
- Nitrile hydrogenation
- Photoinduced electron transfer

- **Applications of heterogeneous catalysts**:

- Oxidation reactions
- Hydrogenation
- Hydrodechlorination
- Synthesis of H_2O_2
- Water - gas shift

▶ Application in Fuel Cell Catalysts

- The fuell cell technology – allows the direct conversion of chemical energy into electricity

- Hydrogen fuel cell catalysts rely on pure Pt

- Pt alloy electrocatalysts are employed for the conversion of reformer gas into electricity

Examples ⟶ Colloidal Pt/Ru catalysts are used in

- direct methanol fuel cells – DMFCs
- In PEMFCs

▶ Potential Applications in Materials Science

- Planar arrays of uniform metal nanoparticles would alow the design of new ″supercomputers″ having a superior data storage capacity
- Nickel NPs are used as magnetic recording medium, electrical conductive pastes, battery materials, etc.

► Biological Applications

- **Au NPs** 1.4 nm were found to arrange themselves into a linear row when attached to single stranded DNA olinucleotides
- **Magnetic nanoparticles** (with inorganic shells) – have been studied for bilogical application such as:

➡ **For binding BSA**
➡ **For drug delivery**
➡ **For bio-sensing**
➡ **For bio-separations**

▶ Sensors

1. **Electrochemical sensors -** the introduction of metal NPs (mostly supported) on the electrode can:

- decrease the overpotentials of many electrochemical reactions
- turn into reversible some redox reactions that are normally irreversible in conventional unmodified electrodes

Examples: sensitive NO, H_2O_2 and sugar and amino sacid sensors

2. **Biosensors:**

- can enhance the electron transfer between biomolecules
- Ag NPs supported on glass – used as selective biosensors for the biotinstreptavidin system

Silver nanoparticles

is becoming an increasingly important material in many technologies

Ag NPs

exhibits the highest efficiency of plasmon excitation

is the only material whose plasmon resonance can be tuned to any wavelength in the visible spectrum

Ag NPs

SYNTHESIS METHODS

1. Traditional methods → **Aqueous solution reduction**

2. Non-traditional methods

- **Microemulsion techniques**
- **High-temperature reduction in porous solid matrices**
- **Vapor-phase condensation of a metal target onto a solid support**
- **Laser ablation of a metal target into a suspending liquid**
- **Gamma radiation induced methods**
- **Photoreduction of Ag ions**

Ag NPs

Goals and problems regarding the synthesis of Ag NPs

- With the traditional methods, the major problem is often a limited flexibility in the size of particles that can be produced and such methods are usually sold on their ability to make < 10 nm
- the major problems for the non-traditional methods are often a wide size distribution, lack of particle crystallinity, and the cost and scalability of the production
- synthesizing uniform and stable silver nanoparticles with a controllable size is difficult
- **the optimum synthetic method** should address all of the above problems and additionally yield particles with no extraneous chemicals that can potentially alter the particle's optical properties and surface chemistry

Optical properties of Ag NPs

- Ag NPs show remarkable physical and chemical properties zhat are size and shape dependent.

- The main factors that can controle the optical properties of Ag Nps are:

- nanoparticle morphology – size and shape
- the refractive index of the surrounding medium
- adsorption phenomena at the solid-solution interface
- the distance between the particles

Influence of the particle morphology on the SPR of Ag NPS

- in the case of a sphere, a single peak in the optical absorption spectra was found
- for 20 and 100 nm nanospheres, SPR peaks are at about 370 and 600 nm, respectively
- when a nanoparticle becomes truncated, the main resonance is blue shifted
- the resonances vanish as the number of faces increases, or when the symmetry of the nanoparticle is larger

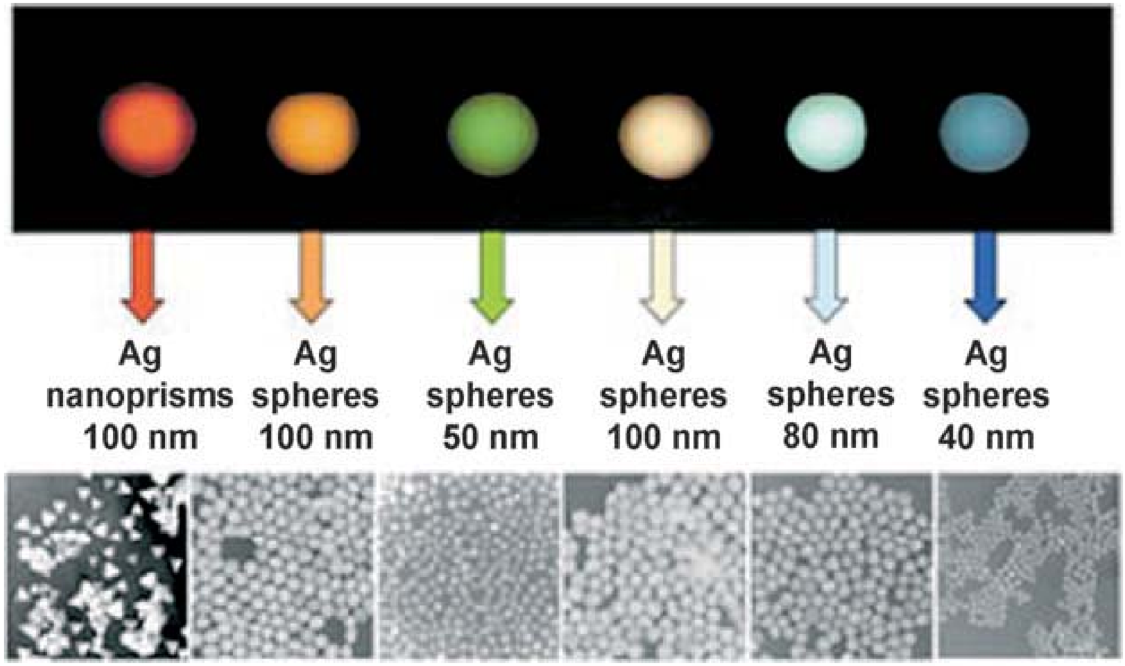


Figure 26. Deviations from spherical geometry strongly affect the optical properties of Ag NPs [Juan M. Campelo – ChemSusChem 2009, 2]

Influence of the surrounding medium

- The location of the surface plasmon resonances is sensitive to the *dielectric environment*, and as the refraction index increases, the SPAB is shifted to longer wavelengths

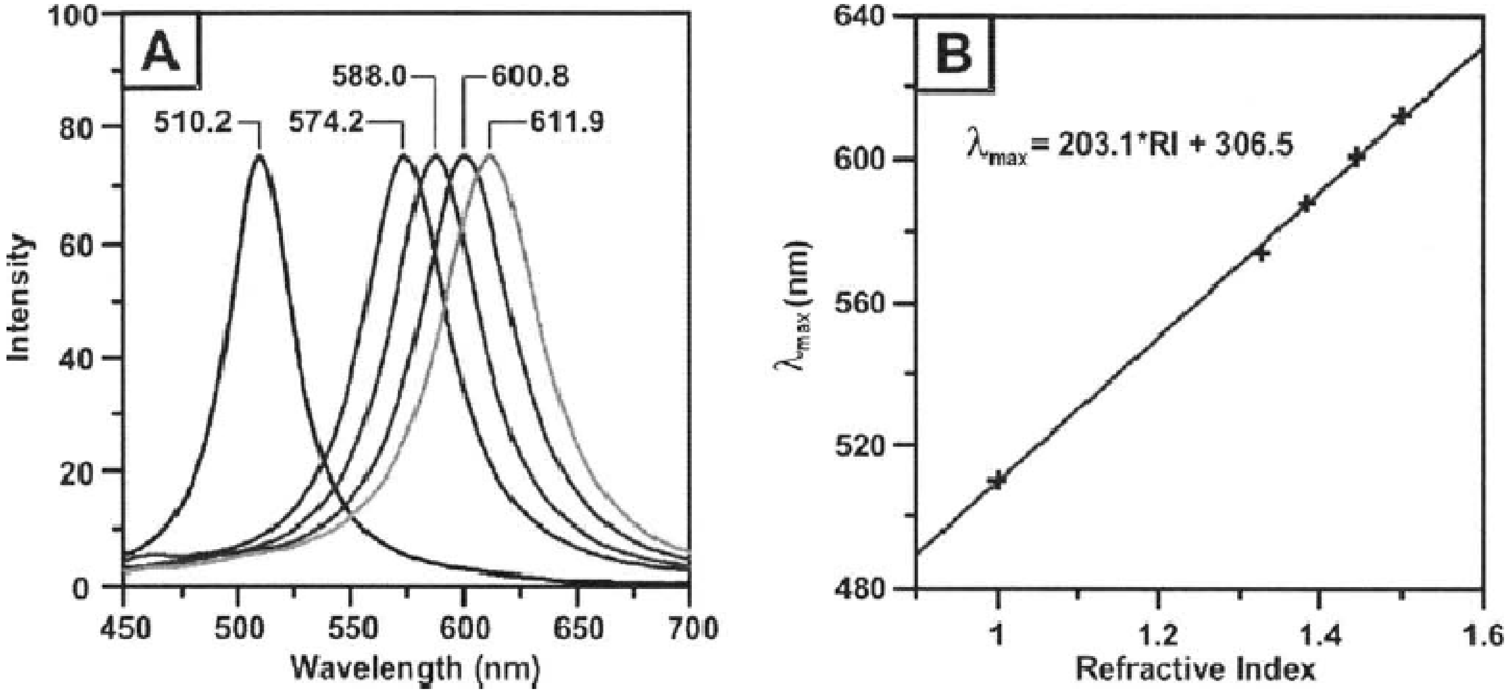


Figure 27. (A) Resonant Rayleigh scattering spectra of an individual Ag NP in various dielectric environments (N_2, methanol, 1-propanol, chloroform, and benzene). (B) A plot depicting the linear relationship between the solvent refactive index and the NP´s λ_{max}.
[Christy L. Haynes, *Nanoparticles with tunable localized SPR*, *Topics in Fluorescence Spectroscopy, Volume 8: Radiative Decay Engineering,* New York, 2005]

Applications of Ag NPs

1. Catalysis

Supported Ag are important in:

- **the *selective oxidation of alcohols, alkanes and alkenes***
- **for the *synthesis of* industrially interesting products including *epoxides* and *aldehydes***

2. Photocatalysis:

- ***water splitting***
- ***degradation of organic pollutants***

3. Biology and Medicine: **Ag is a highly antimicrobial material used in:**

- ***water purification***
- ***wound care***
- ***medical devices***
- ***drog delivery***

4. Optics: ***Optoelectronic devices* – active waveguides in optical devices (amplifiers)**

5. Electronics : ***electronically conductive adhesives* (ECAs)**

CONCLUSIONS

- The 21st century has brought a great interest and expansion of the nanomaterials due to uniques properties that exist at the nanometric scales.
- Recent advances in the design and preparation of metallic NPs have proved that a numerous variety of MNPs can nowadays be synthesised through different preparation routes.
- Synthesis of MNPs is important because of their novel electrical, optical, magnetical and chemical properties.
- Ag NPs are of strong research focus because of their unique functional properties which lead to varied applications.

REFERENCES

1. Robin J. White - Chem. Soc. Rev, 38, 2009,
2. Juan M. Campelo – ChemSusChem, 2, 2009
3. John A. Blackman - Metallic nanoparticles, Elsevier, 2009
4. Gunter Schmid - Clusters and Colloids, VCH, 1994
5. Helmut Boennemann – Eur.J.Inorg.Chem., 2001
6. Guozong Chao -NANOSTRUCTURES AND NANOMATERIALS, Imperial College Press, 2004
7. M.T. Reetz and M. Maase, Adv. Muter. 11, 773, 1999
8. Luis M. Liz-Marzán- Nanometals: formation and color, Elsevier, 2004
9. Burda et al.,Chem.Rev, 2005, 105
10. Tilaki et al. Appl.Phys.A, 84,2006
11. Marcel Dekker, Dekker Encyclopedia of Nanoscience and Nanotechnology, New York, 2004
12. J.D. Aiken III, Journal of Molecular Catalysis A: Chemical 145, 1999
13. G. Chumanov, ChemPhysChem., 6, 2005
14. C.Noguez, J.Phys. Chem. C 2007, 111, 3806
15. M.K. Temgire, Radiation Physics and Chemistry 71, 2004
16. A.L. Gonzalez, Phys.Stat.Sol, 4,11,2007
17. Dapeng Chen, J Mater Sci 44, 2009
18. W.H. Qi, Materials Chemistry and Physics 88, 2004
19. P.A. Chernavskii, Russian Journal of Physical Chemistry B,1,4, 2007
20. Tabrizi, J.Nanopart. Res., Springer, 2009
21. V.N. Pustovit, Eur.Phys.J B 69, 2009
22. W. Wang et al., Journal of Colloid and Interface Science , 323, 2008

THANK YOU FOR YOUR TIME!