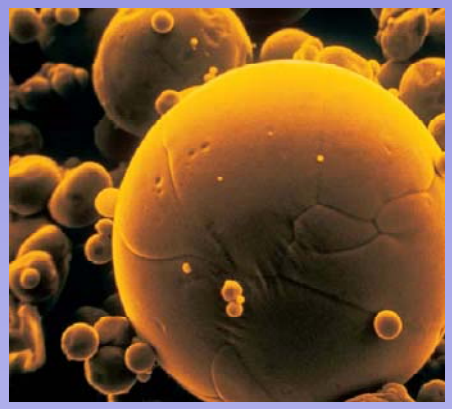
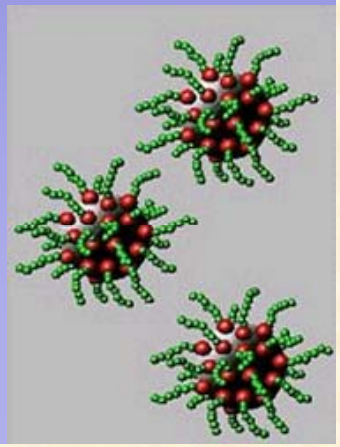
# *Advances in Magnetic Nanoparticles and Metal Clusters*



**José Rivas**

Laboratory of Magnetism and Nanotechnology. Dept. of Applied Physics. University of Santiago de Compostela. E-15782 Santiago de Compostela. Spain



***"Japan-Spain Joint Workshop on Nanoscience and New Materials "  April 20th , 2009.  Tokyo.***

# Laboratory of Magnetism & Nanotechnology (NANOMAG)
# Research Technological Institute, Univ. Santiago de Compostela, SPAIN

**Main Topic: Synthesis and Properties of Nanomaterials**

(founded in 1989)

www.nanomag.org

# The Magnetic Particles

…appear in many materials and are of interest in:

- Metallurgy
- Solid State Physics.
- Catalysis.
- Biology and Biomedicine
- Mineralogy and Geology.
- Environment
- Artistic objects.

Technological interest in:

- Storage media
- Magnetic fluids: Ferrofluids
- Electromagnetic compatibility.
- Granular alloys
- Composites.

… interest in fundamental science.

- Understanding of complex mechanisms.
- Quantum effects: Mesoscopic systems
- Magnetic disorder: Spin Glasses-Clusters

# Main topic in our Lab

***Preparation and properties of nanomaterials***

1. Changing properties by size reduction

2. Changing properties by interactions (functionalization, nanocomposites, self-assembly, templated ordering,...)

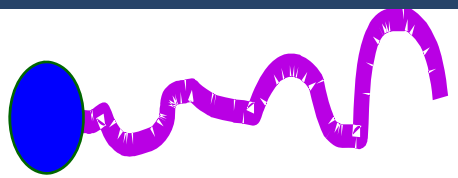
novel properties may appear

# Preparation methods used in our Lab

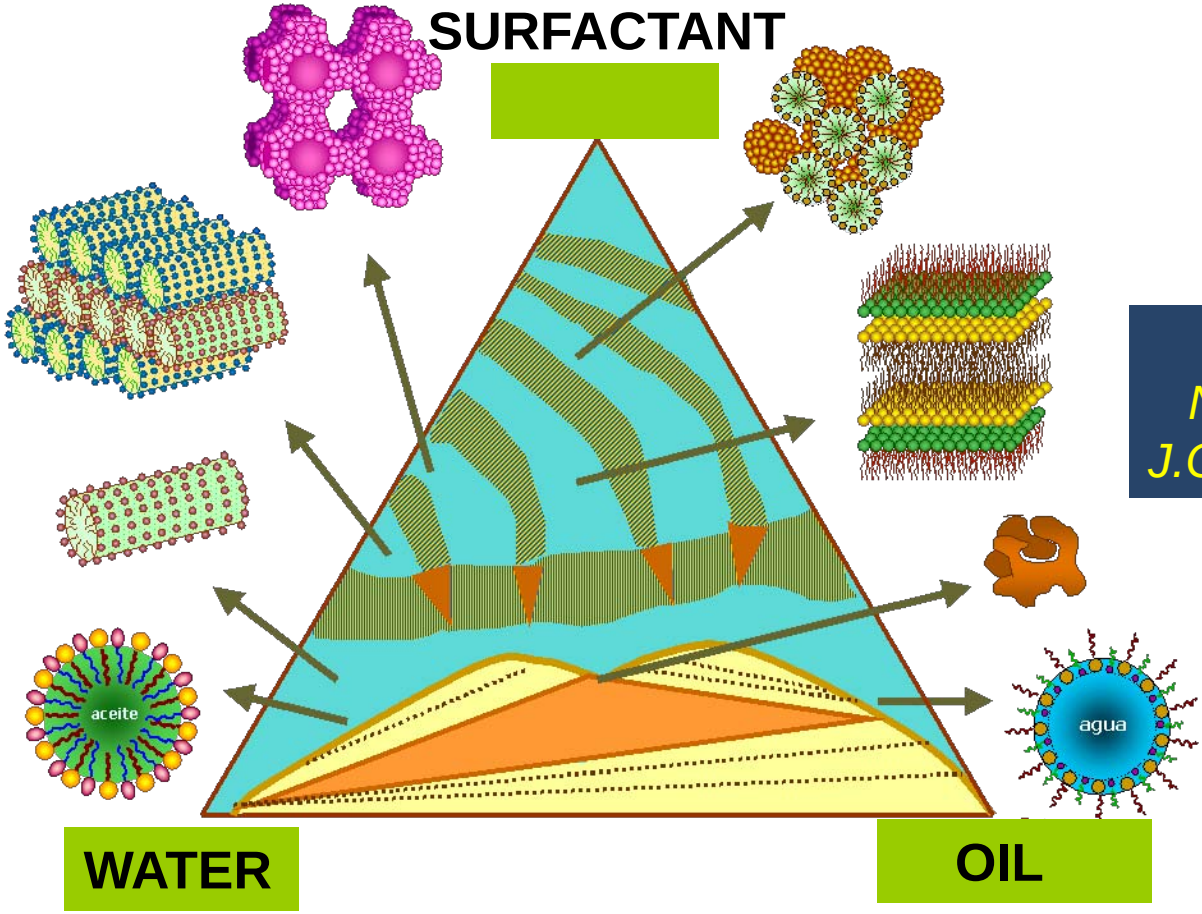
1) Solid state reaction
2) Coprecipitation
3) Sol-gel techniques
    a) Processing of colloids (e.g. urea method)
    b) Processing of metal-organic compounds (e.g. metal alkoxides)
    c) Pechini and citrate gel methods
4) **Microemulsions**
5) Solvothermal synthesis
6) Chemical and electrochemical reduction
7) Thermal decomposition of organic and organometallic reagents
8) Block copolymers

# Microemulsions

**SURFACTANT**



Hydrophilic part  Lypophilic part

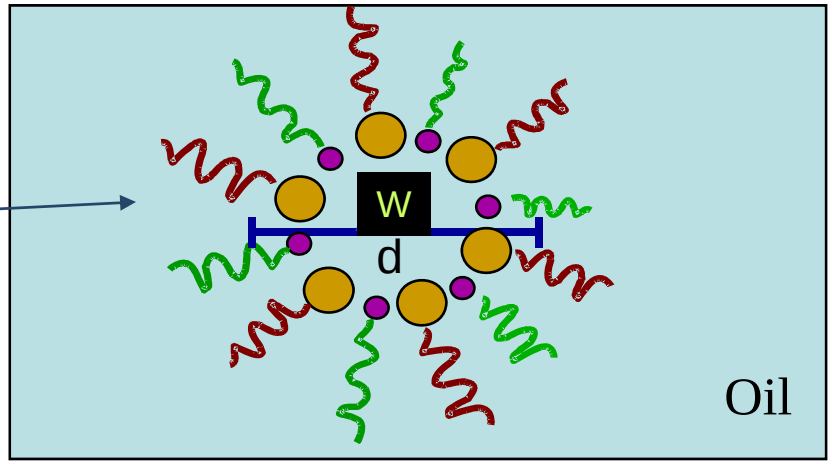



**Schulman**
*Nature*, 1943
*J.Colloid Sci*. 1948

*courtesy of M.C. Buján-Núñez*

- Aerosol OT (AOT): sodium dodecylsulfosuccinate
- Water
- n-Heptane

**W/O Microemulsion**

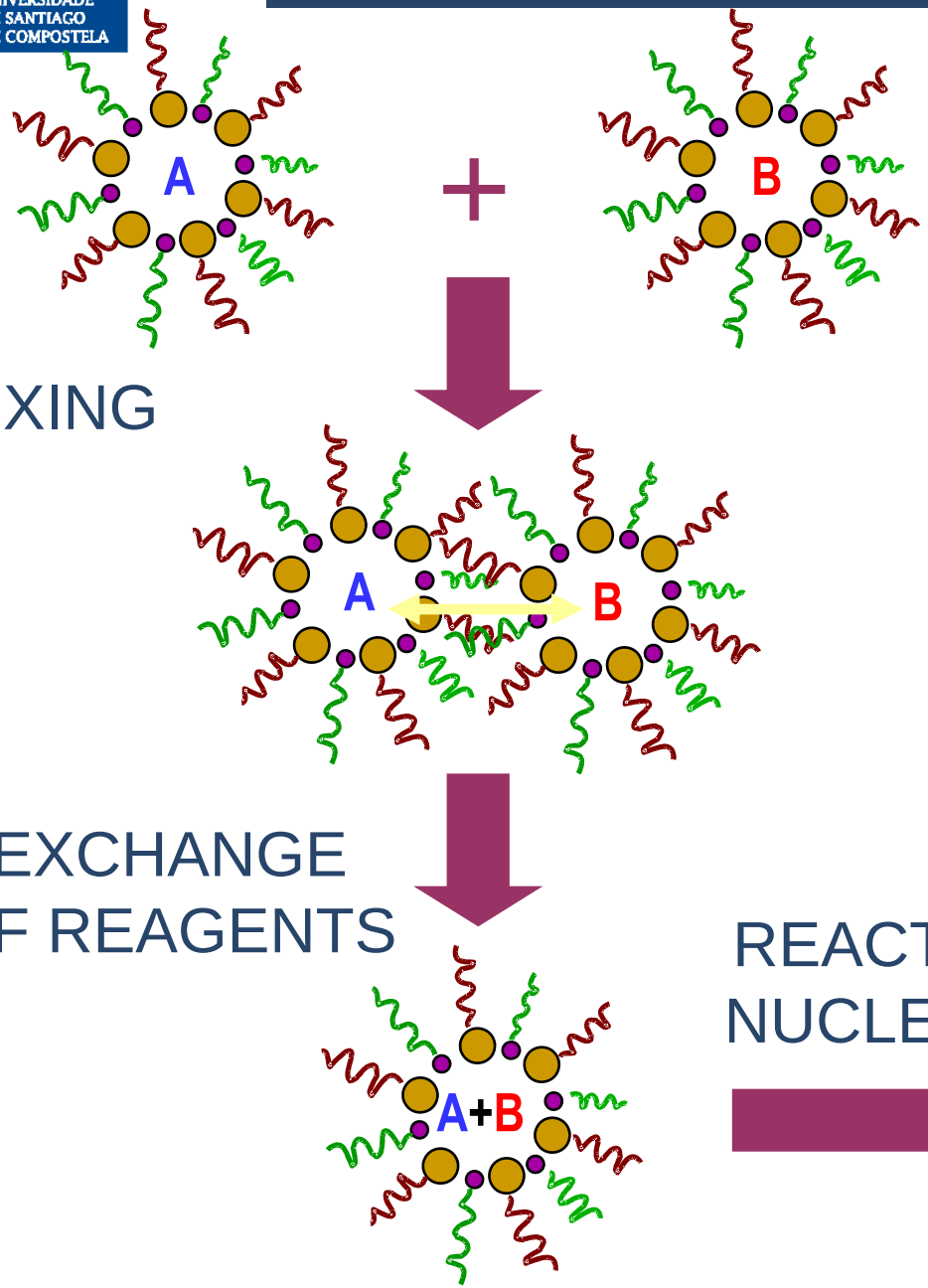



$$r/nm = 1.5 + 0.175\ R$$

| R=[W]/[S] | 1 | 5 | 10 | 20 |
|---|---|---|---|---|
| d=2r (nm) | **3.4** | **4.8** | **6.5** | **10** |
| V (yL*) | 21 | 58 | 140 | 520 |

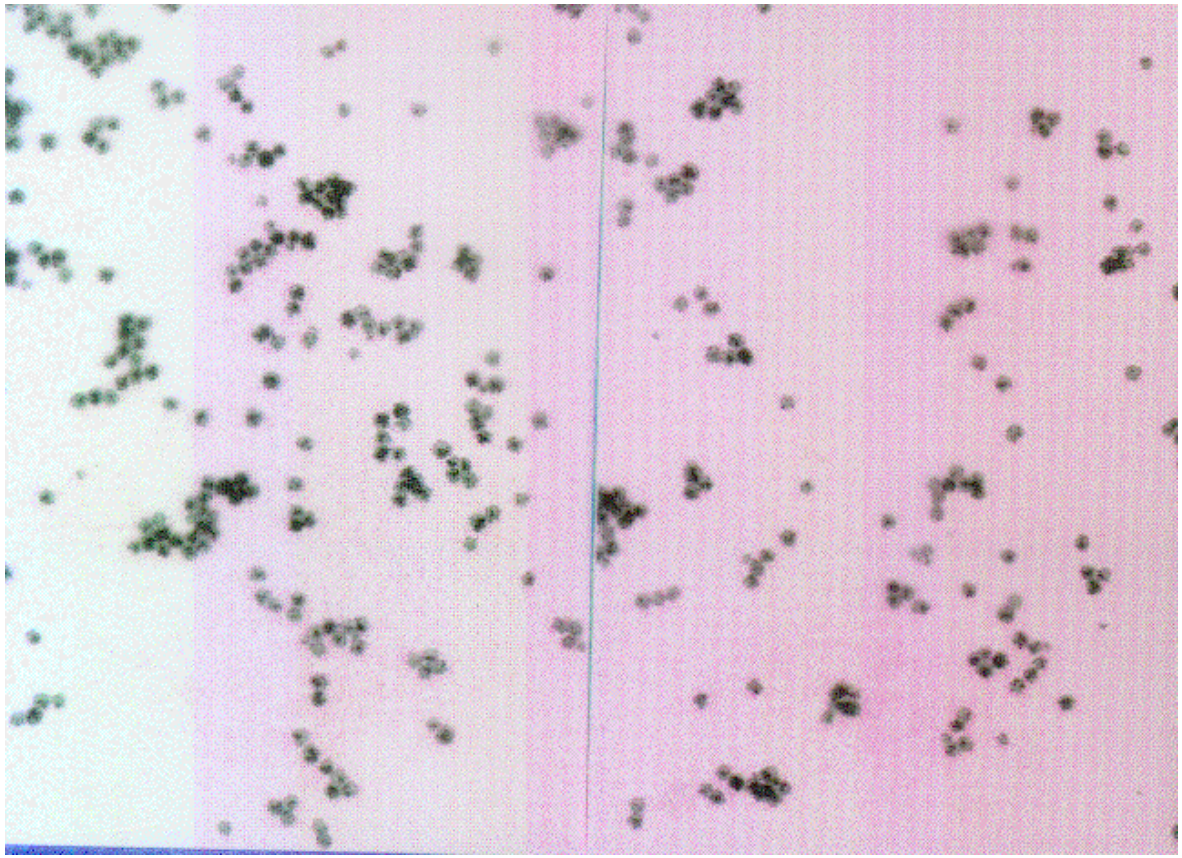
*yL : yocto Liter = $10^{-24}$ L

# Microemulsion Method



# Pt NPs prepared in MEs

**Particle size: 9 nm ≈ droplet size** → **Template**



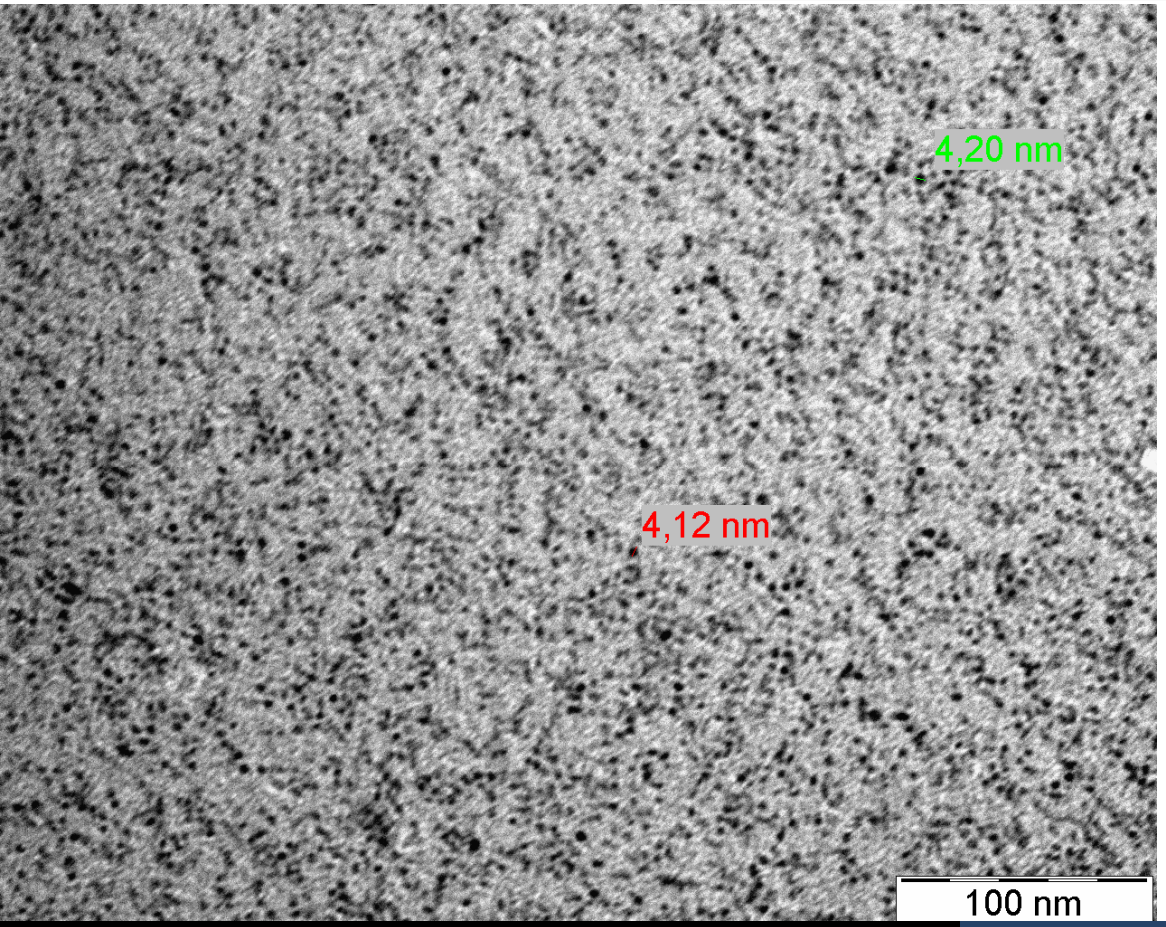
**Very monodisperse!**
**(self-assembly)**

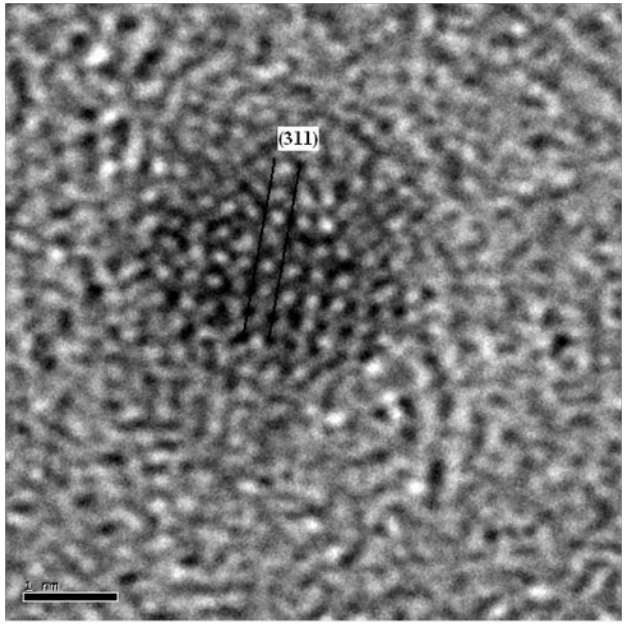
Rivadulla et al. J.Phys.Chem.B, 1997

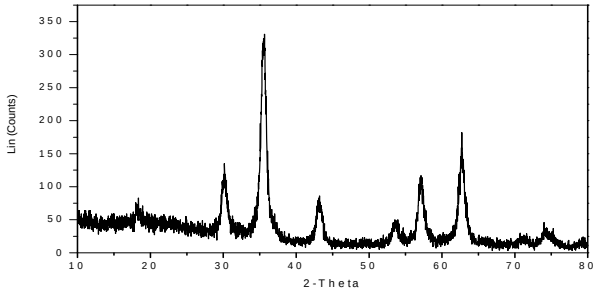
# Magnetite NPs prepared in MEs

-Cristallinity
-Monodispersity
-Stable dispersion

4.1±0.5 nm




Vidal et al. Colloids & Surfaces A, 2006

# Examples of NPs synthesized in our Lab

1) Simple oxides: $\alpha$-$Fe_2O_3$, $Cr_2O_3$, NiO,…

2) Perovskites and perovskite-type oxides:

$YBa_2Cu_3O_{7-x}$

$Ln_{2-x}Ce_xCuO_4$ (Ln= La, Pr, Nd, Sm, Gd,…)

$Ln_{1-x}A_xMO_3$ (Ln= La, Nd, Pr, Gd,…; A= Ca, Sr, Ag,…; M= Mn, Co, Ni, Fe)

3) Spinels: $\gamma$-$Fe_2O_3$, $Fe_3O_4$,

$MFe_{2-x}Cr_xO_3$ ($M= Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}$,…)

4) Garnets: $Y_3Fe_5O_{12}$, $Y_3Al_5O_{12}$

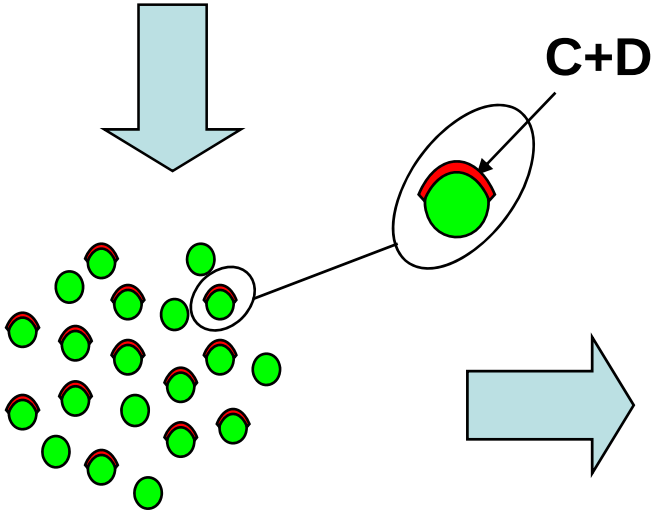
5) Metallic/bimetallic and semiconductor NPs (nanodots): Fe, Co, Ni, Si, Ag, Au, Pt, FePt, $Cu_{1-x}Au_x$,…

6) Core-shell NPs: magnetic core (Fe, Co, FePt, **$Fe_3O_4$**..) @ non-magnetic shell (**Au**, Ag, Cu, $SiO_2$,...)

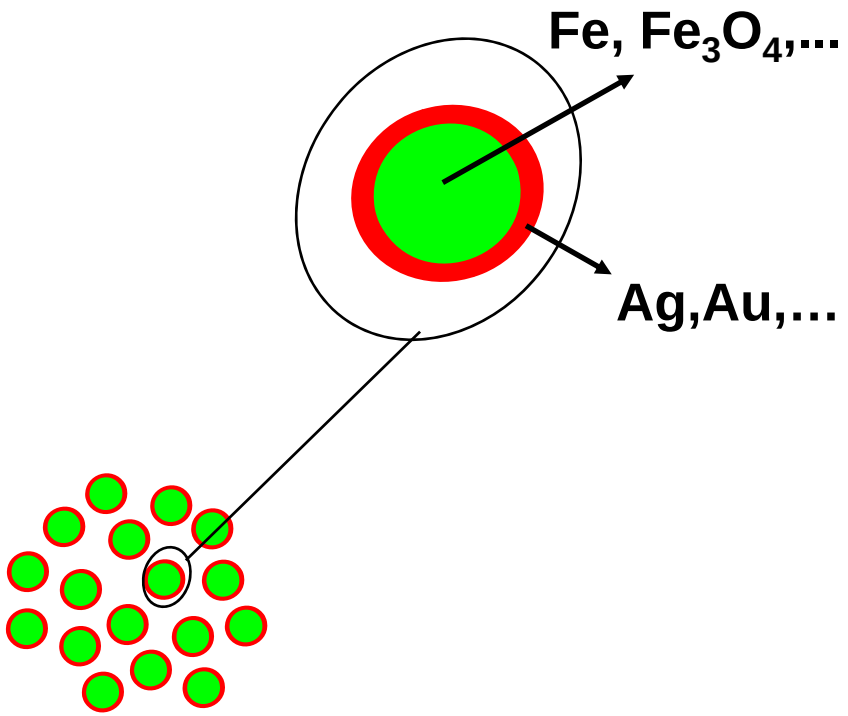
## 2nd step:

***SLOW*** **shell reaction (C+D) in the presence of core nanoparticles**

**(to favor heterogeneous nucleation)**




**Example:**




**Different shell thickness can be obtained by changing the reactant concentrations (C, D)**

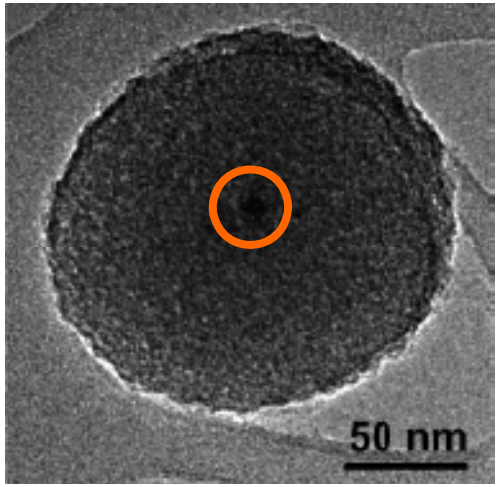
# Core – shell nanoparticles

**$Fe_3O_4$ @ $SiO_2$ @ Au nanoparticles**

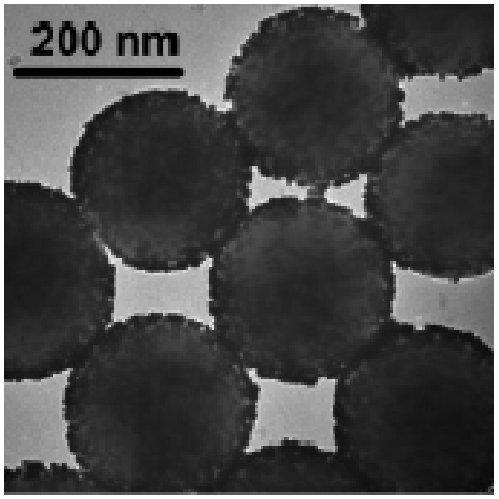
$Fe_3O_4$ → coprecipitation method ($FeCl_3$, $FeSO_4$, $NH_4OH$)

$SiO_2$ inner shell → hydrolysis and condensation reactions (TEOS, $NH_4OH$)

Au outer shell → chemical reduction of $AuCl_4^-$(aq) with sodium citrate



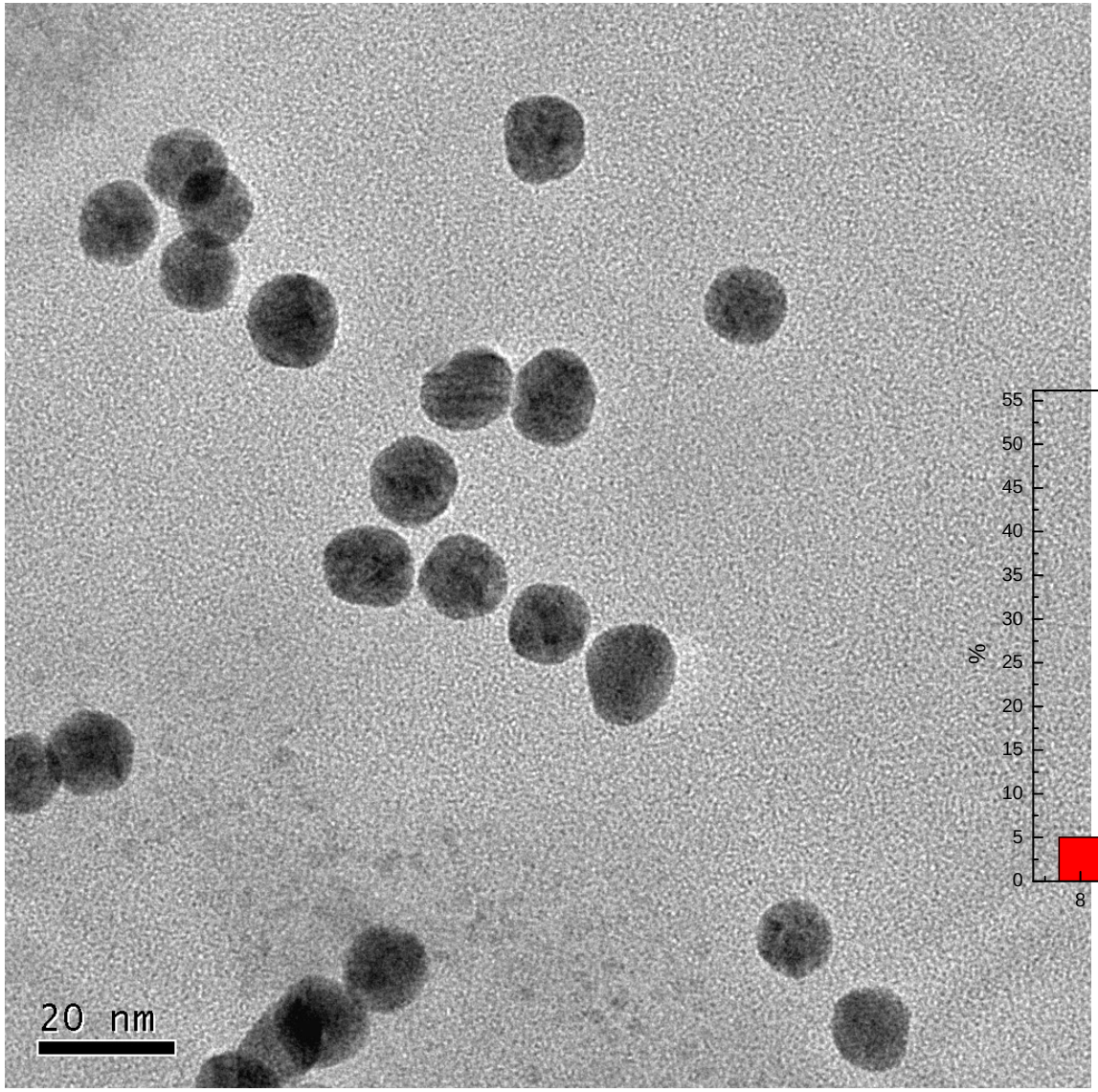

$Fe_3O_4$ @ $SiO_2$ nanoparticles

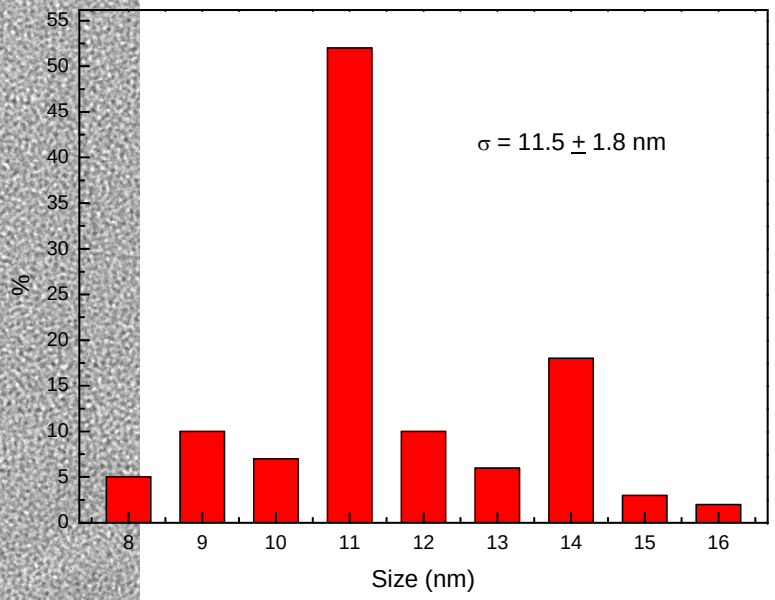



$Fe_3O_4$ @ $SiO_2$ @ Au nanoparticles

V. Salgueiriño-Maceira *et al., Chem. Mater.* **18** (2006) 2701

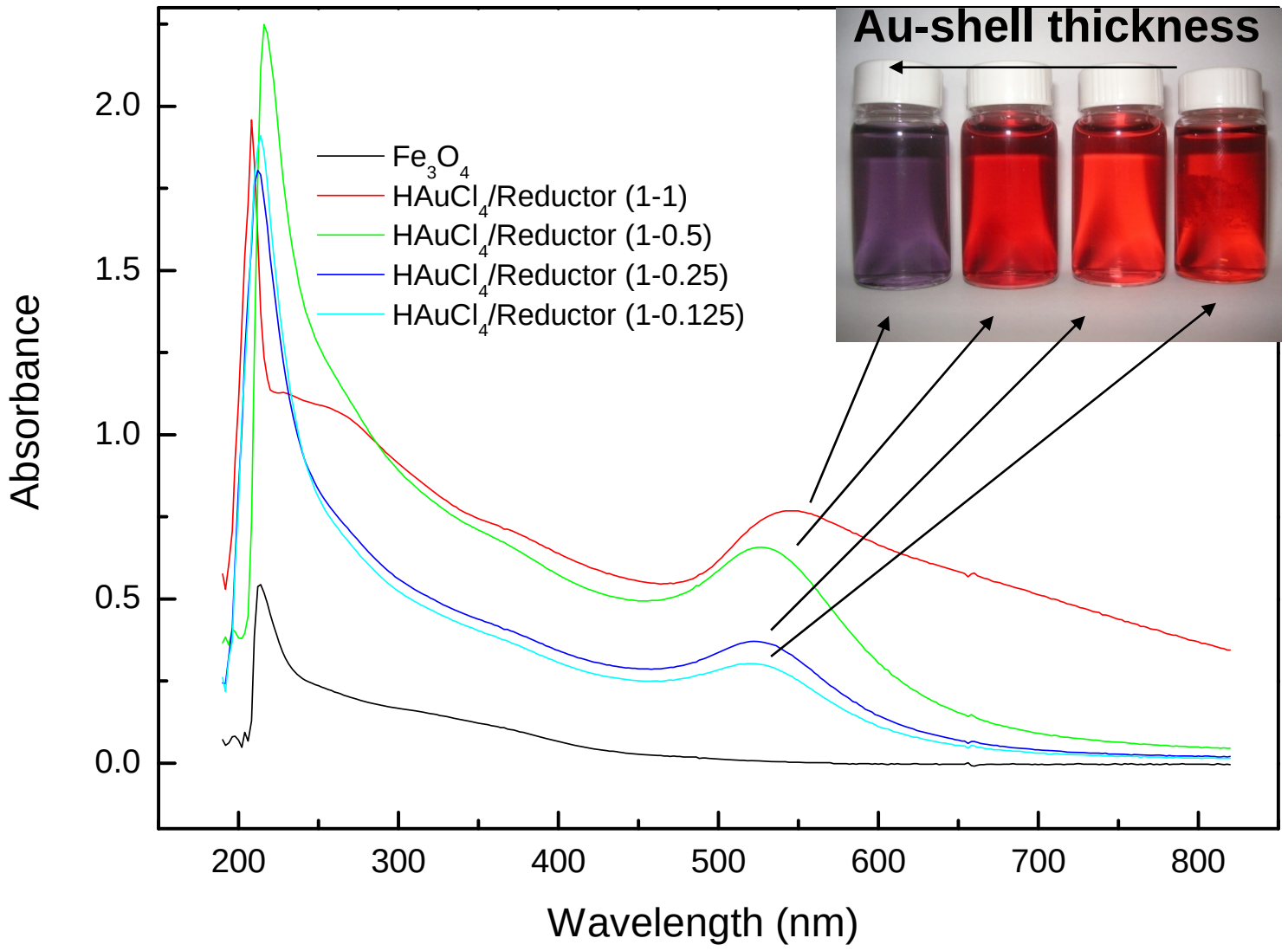
# Theoretical final size: 9+1.8=10.8nm



# Core – shell nanoparticles: $Fe_3O_4$@Au

## UV-Vis

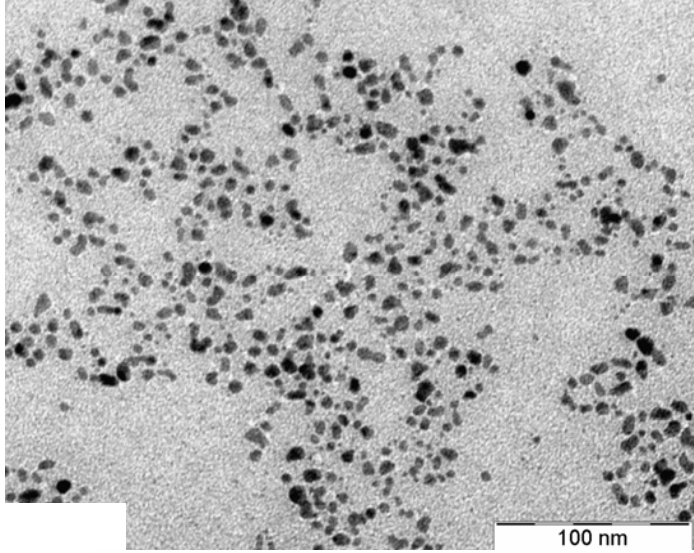



Iglesias-Silva et al. J.Non-Crystalline Solids, 2007

however,
not everything is like it
appears...

# Pt clusters in microemulsions

Size: 4.5 nm, i.e. ≈ $Pt_{2869}$, but...



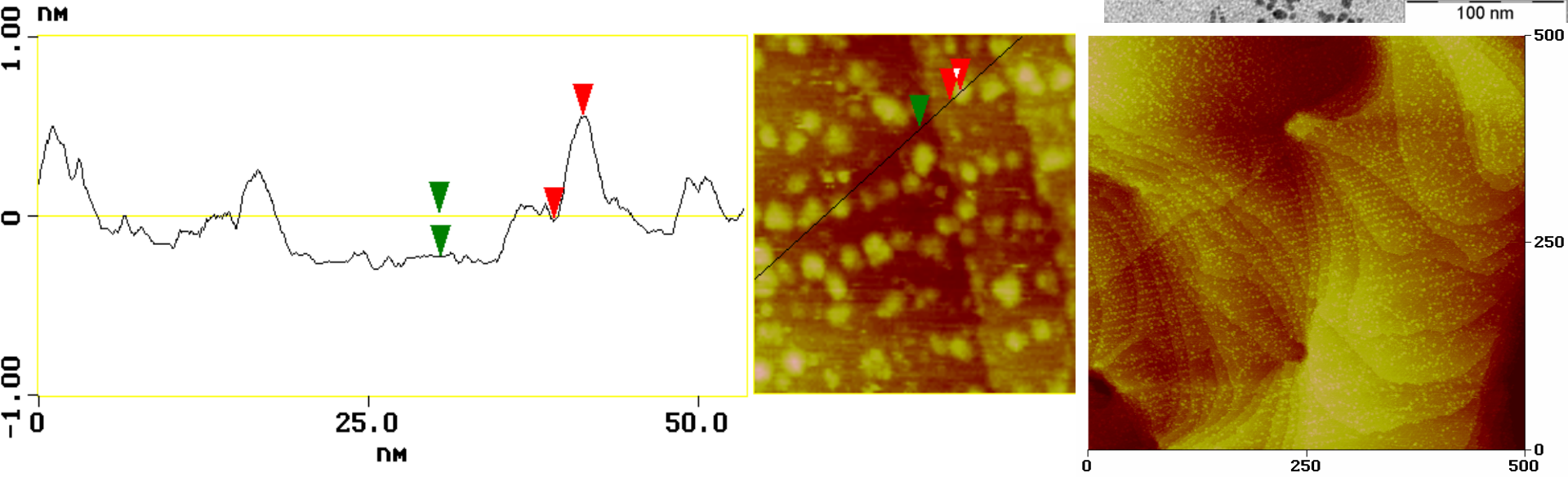



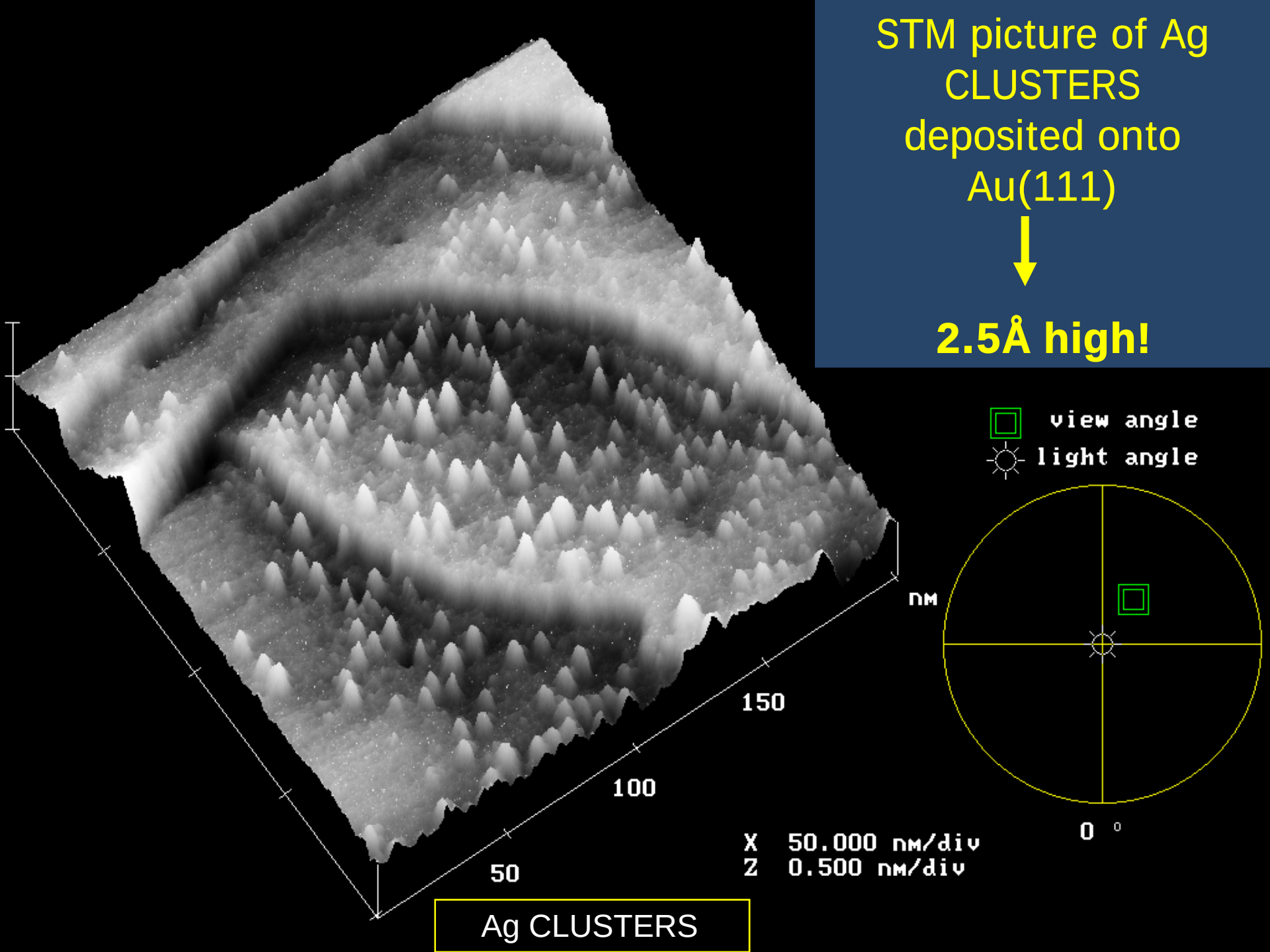

**Figure 2.** Cross section analysis (at left) of the line in 52 x 52 $nm^2$ STM image (right).
Compare the island height (red pointers) with a typical Au(111) monoatomic step (green pointers).

!?

it is only 2 or 3 Pt atoms high! → Pt clusters

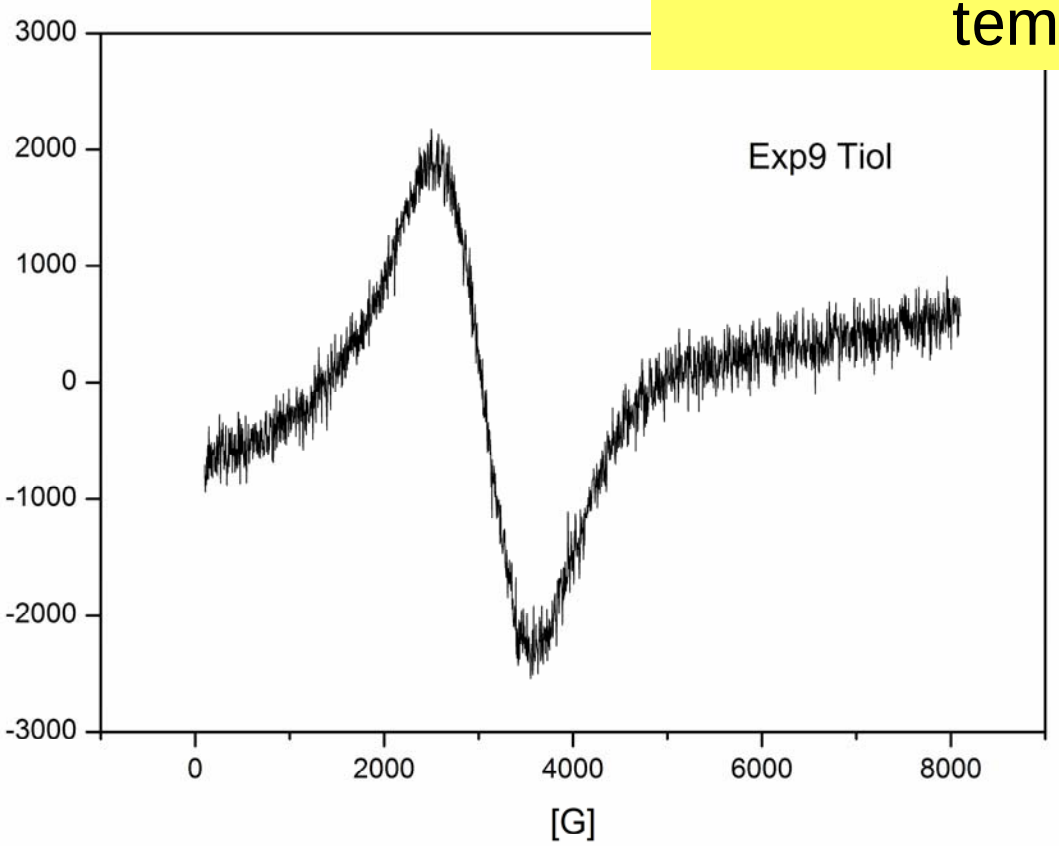
STM picture of Ag CLUSTERS deposited onto Au(111)

**2.5Å high!**




Ag CLUSTERS

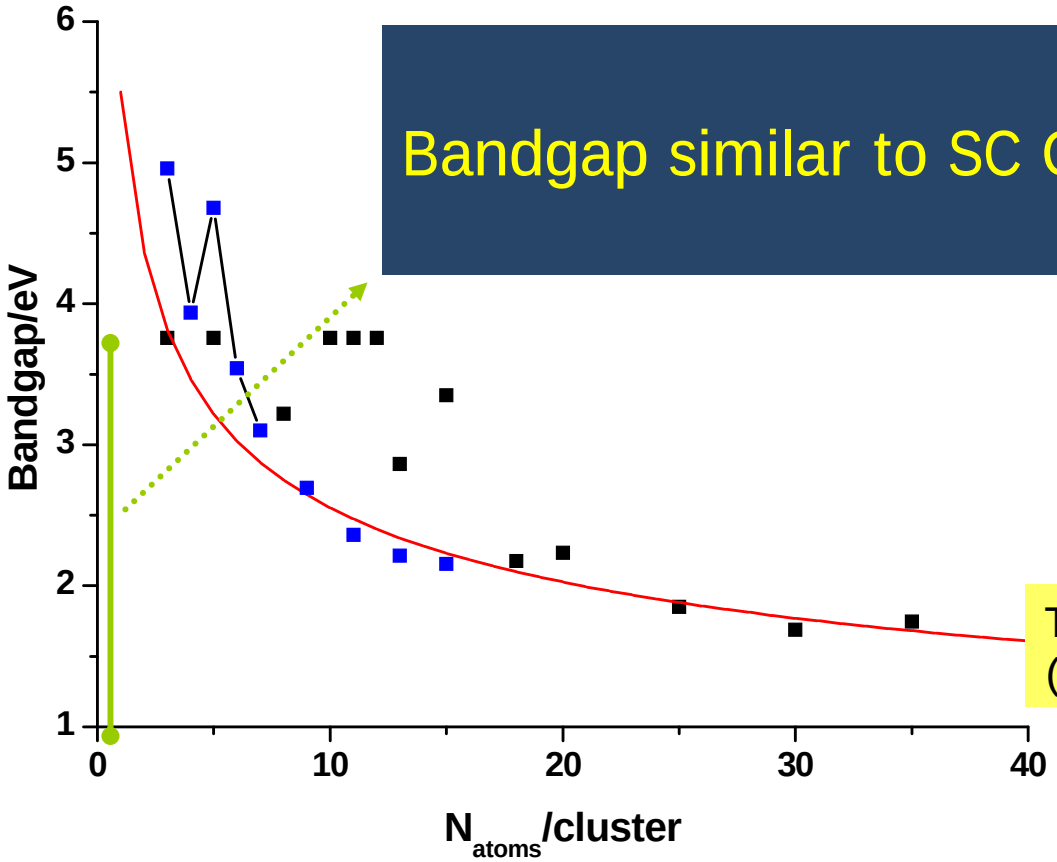
typical paramagnetic response with g = 2.0 at room temperature




**$Ag_5$**

Michalik et al. JACS, 1986

(from mass spectra, UV-Vis spectra and DP voltammetry)



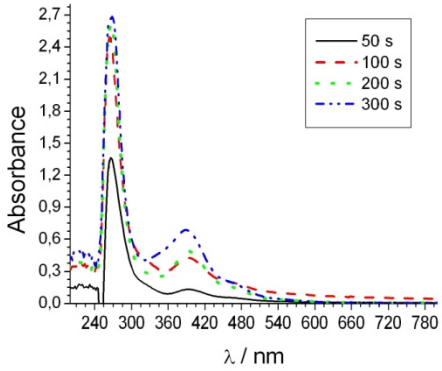

Bandgap similar to SC QDots!

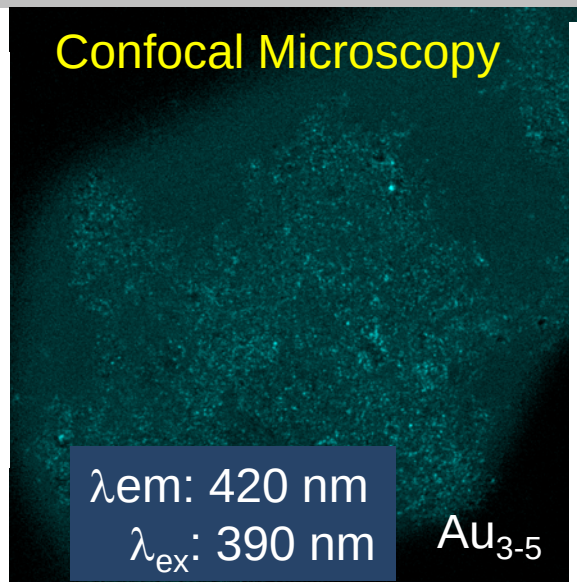
N≈100-200 atoms (1-2nm)

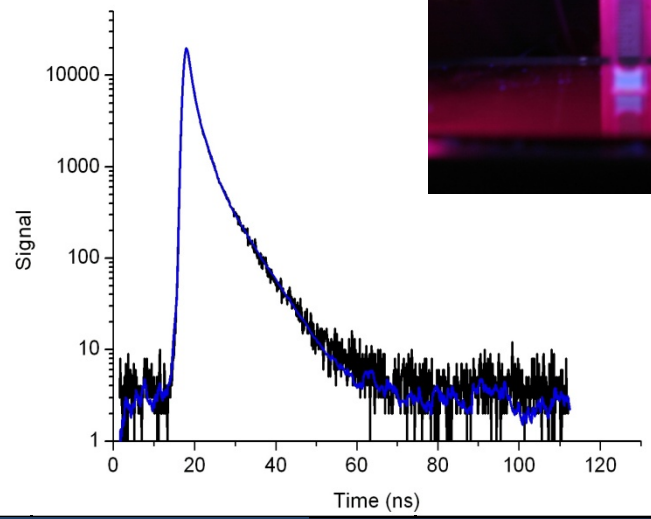
Transition to a metallic behavior (emerging of the plasmon band)

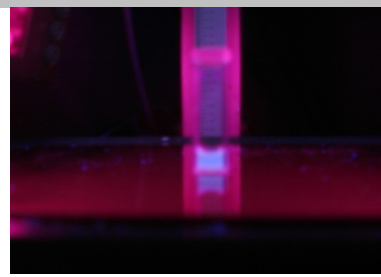
$SnO_2$ $TiO_2$ CdS GaP CdSe CdTe GaAs Si

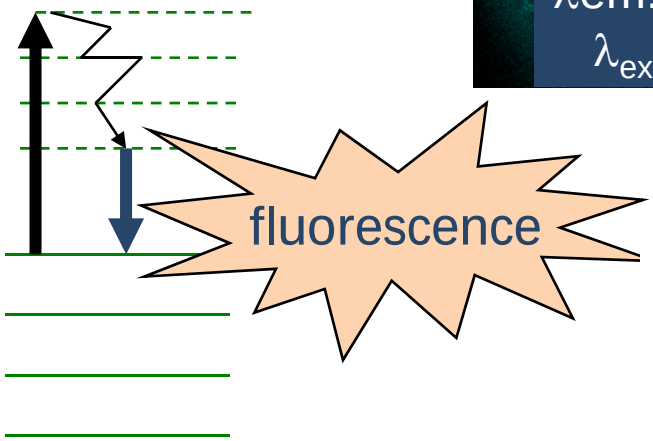
# Au clusters
## fluorescence



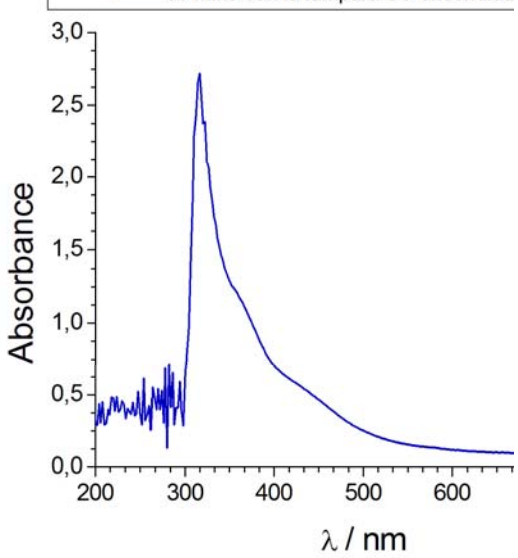



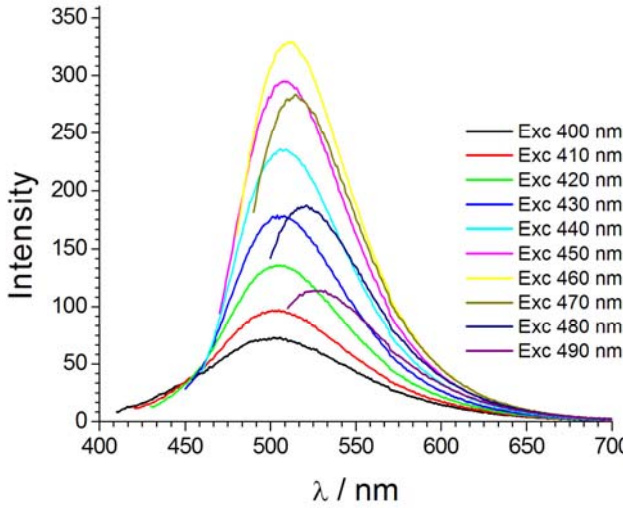






λem: 520 nm
λex: 460 nm
Au13-20




by changing the cluster size, fluorescence wavelength can also be tuned!

Metal Cluster QDots

# Cluster Properties

New fascinating properties seem to emerge in this nanometer/sub-nanometer region:

* M**agnetic properties** (new generation of magnetic storage devices,…) .
***Fluorescent properties** (biosensors, …)
***Catalytic properties** (water and alcohol decomposition: fuel cells,…)
***Surface Enhanced Raman Scattering** (single molecule detection)
***Quirality, Aromaticity**

# Nanogap: a spin-out of the USC

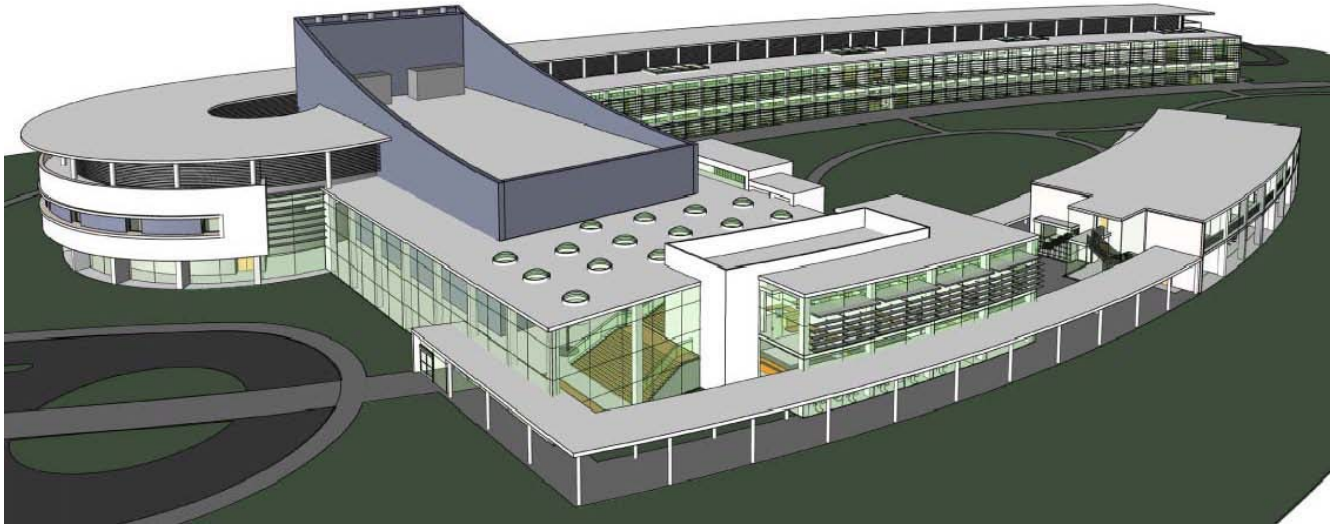
## …a very brief history

- **Nanogap's start up (April 2006)**
- **Nanogap opens its laboratory and production facility (September 2006)**
- Nanogap takes part in the FP6 FLUOROMAG EU Project (November 2006)
- Nanogap is invited to be part of ENTA as member and scientific advisor (January 2007)
- Nanogap becomes member of NanoSpain (March 2007)
- Nanogap is invited as member and expert in AENOR's GET 15 in several ISO/CEN working groups. (March 2007)
- Nanogap is invited to be part of NIA as member (April 2007)
- **Nanogap starts its scaling up process (June 2007)**
- Nanogap is invited to become a member of NanoCentral (October 2007)
- **Nanogap wins Spanish Ministry of Industry's ENISA award (November 2007)**
- **Nanogap will open its first factory (March-June 2008)**

**Laboratory of Magnetism & Nanotechnology (NANOMAG)**
**Research Technological Institute, Univ. Santiago de Compostela, SPAIN**

Financial support:
- MEC (Spain) : MAT2005-07554-C02-01; NAN2006-28515-E; CONSOLIDER-INGENIO 2010
- Xunta de Galicia (Spain): GRC 2006/81
- European Union (FR6 Framework Program): FLUOROMAG

# International Iberian Nanotechnology Laboratory as an Example of International Cooperation



José Rivas
INL
Director General
farivas@iinl.org

# The Idea

**The decision to create the INL**

**8 November 2003:** Scientific and Technological Co-operation Agreement between the Portuguese Republic and the Kingdom of Spain

**19 November 2005:** creation and the joint management of a Portuguese and Spanish Institute of R&D (Portuguese and Spanish International Research Laboratory) .

**23 November 2006:** Approval of the legal statutes, conferring an international character to the Institute

**19 March 2007:** Creation of a Commission to prepare the installation of the INL .

**18 January, 2008**: the President of the Government of Spain and the Prime Minister of Portugal inaugurated the INL with a symbolic “foundation stone”

# The Idea

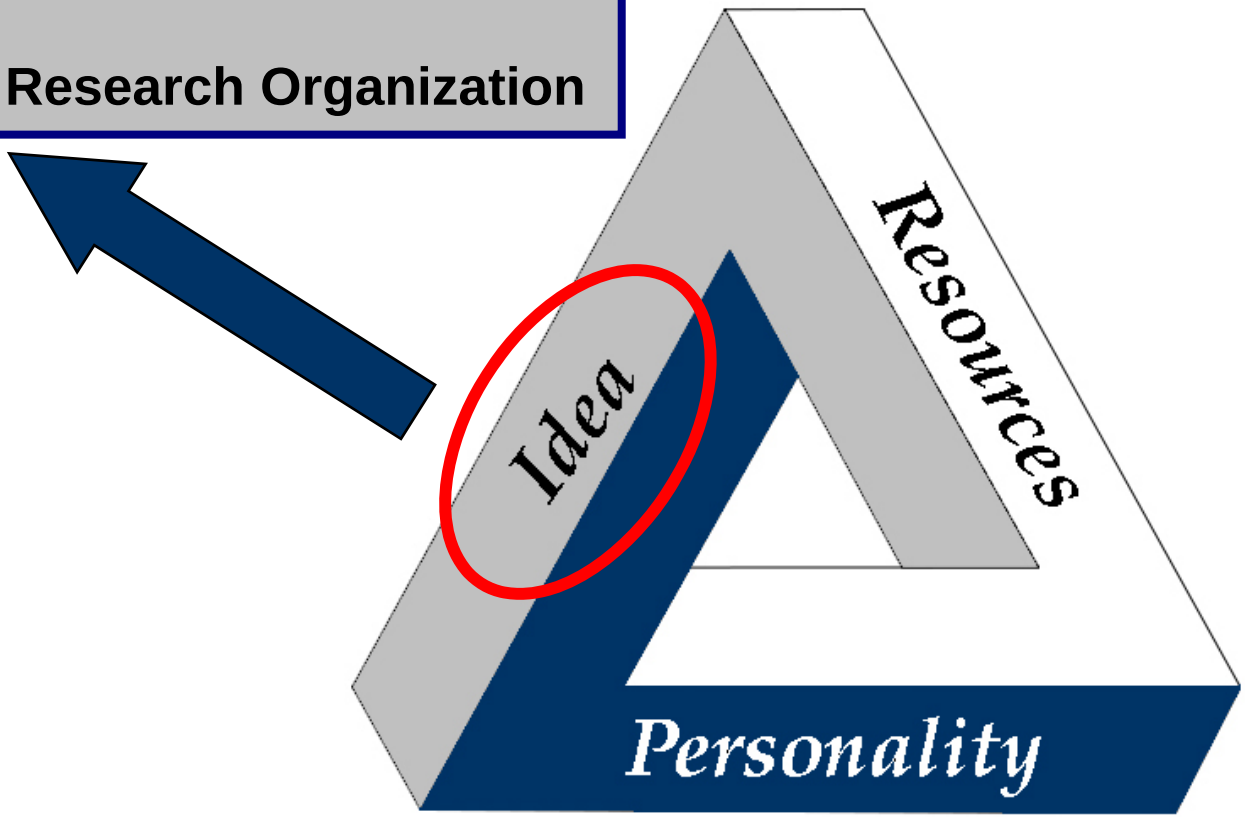
Subject: **Nanotecnology& Nanoscience**

Researchers: **~ 200**

Total Staff: **~ 400 people**

Location: **Braga**

Status: **International Research Organization**

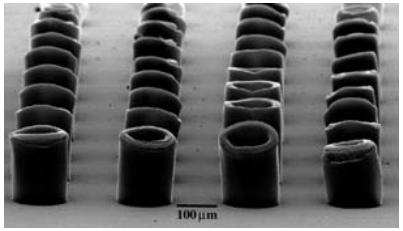


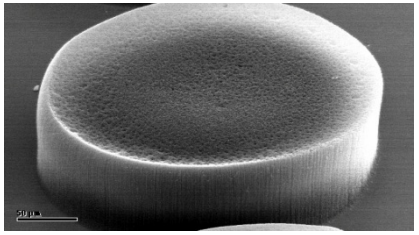
# The Idea

INL have International legal framework

INL is located in Braga, Portugal.

# The Idea





**1)NANOMEDICINE:**
Drug Delivery systems, molecular diagnosis systems, cell therapy and tissue engineering

**2) ENVIRONMENTAL AND FOOD CONTROL:**
Nanotechnology applied to Food industry, food safety and environmental control

**3) NANOELECTRONICS:**
Nanofluidics, CNTs, Molecular electronics, Spintronics, Nanophotonics, NEMS and other Nanotechnologies to support the previous research areas

**4) NANOMANIPULATION:**
Molecular devices using biomolecules as building blocks for nanodevices.

# Personality, Infrastructures 2008

Infrastructures

**The future INL Campus**

- 47,000 $m^2$ of ground.
- Total Building area of 26,000 $m^2$
- Main Scientific Building of 22,700 $m^2$
- Social Building (3,300 $m^2$)

**MAIN ACTIONS YEAR 2008**

- **Project Design from Z+W Zander**
- **Ground Leveling Tasks**
- **First Tender**
- **25% of Construction activities completed**
- **Expected date for initiate operations fall semester 2009**

# Personality -Networking

International Networking

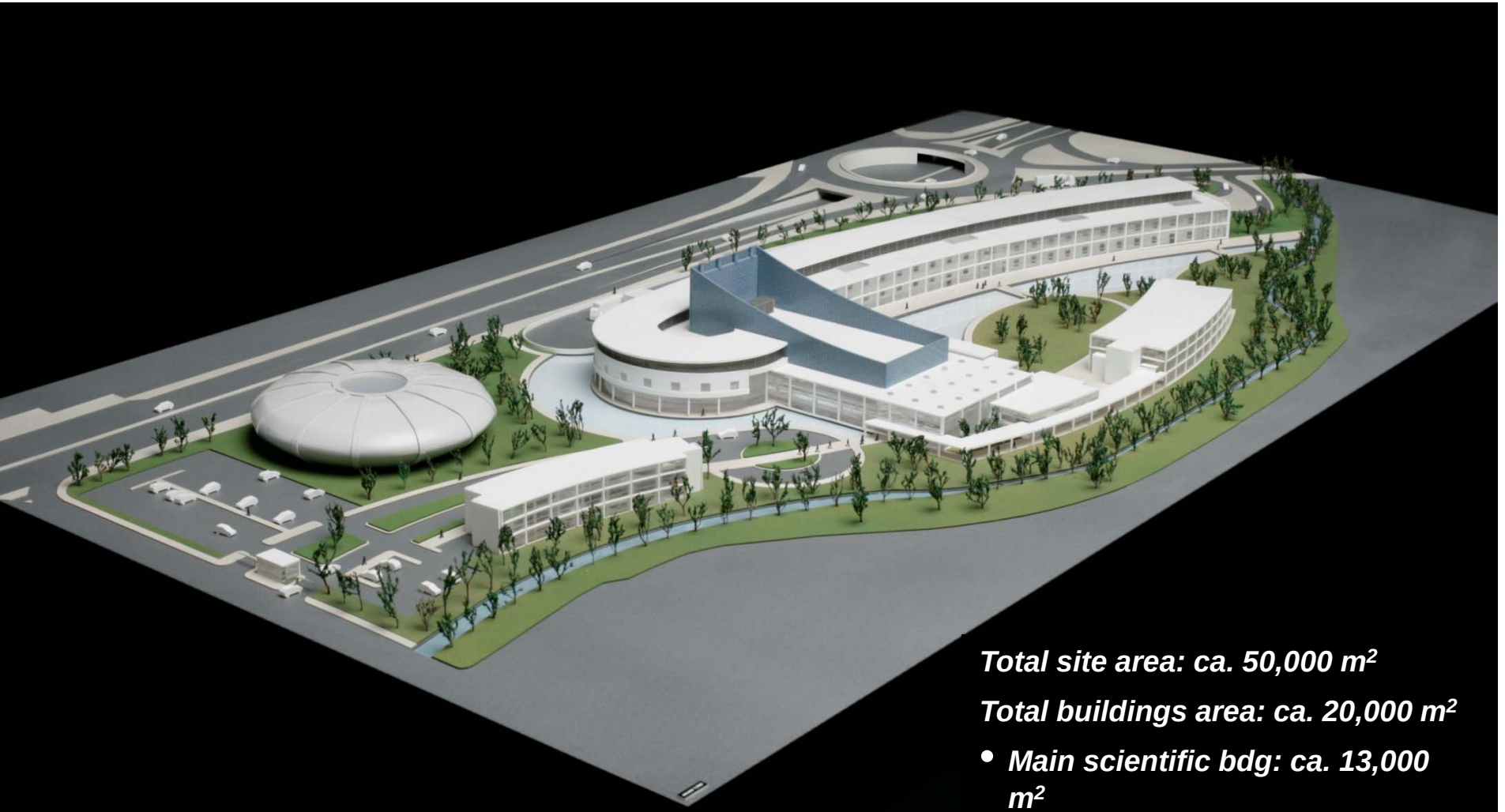
**8 Collaboration Agreements signed**

**MPI for Biochemistry (Munich) and MPI of Microstructure Physics (Halle) negotiations have not finished yet.**

**Negotiations with MIT are also in progress.**

****Negotiations with the Max Planck Society, in relation with a more ambitious MOU, were also maintained.**

# Personality –Future Plan 2008



*Total site area: ca. 50,000 m²*

*Total buildings area: ca. 20,000 m²*

- *Main scientific bdg: ca. 13,000 m²*
- *Hostel*
- *Science Alive building*
- *Incubator*