Electronic and structural investigation on gold monometallic and bimetallic nanoparticles using XAS spectroscopy: a short review.

Antonella Balerna

INFN-LNF DAΦNE-Light

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Outline

- **Nanoparticles – NP**
- **Properties of Au metal, monometallic and bimetallic NPs**
- **Information on some preparation methods**
- **Information on some catalytic applications**
- **XAS spectroscopy and electronic and structural information achieved**

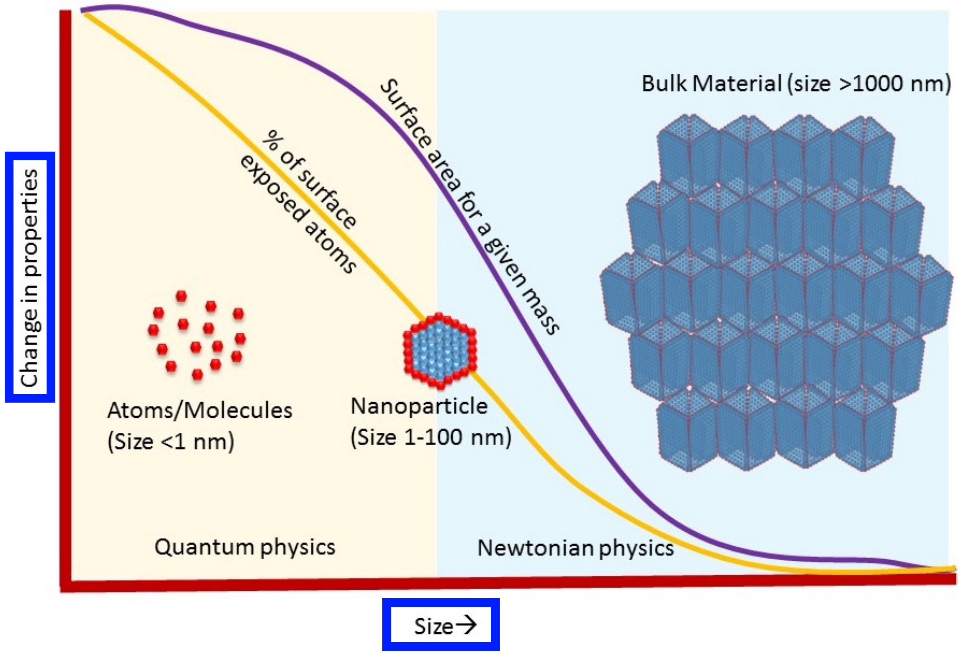
Nanoparticles

Nanoparticles are aggregates of a small and finite number of atoms characterized by at **least one dimension in the nanometer** (1 nm = 10^{-9} m) **range.**

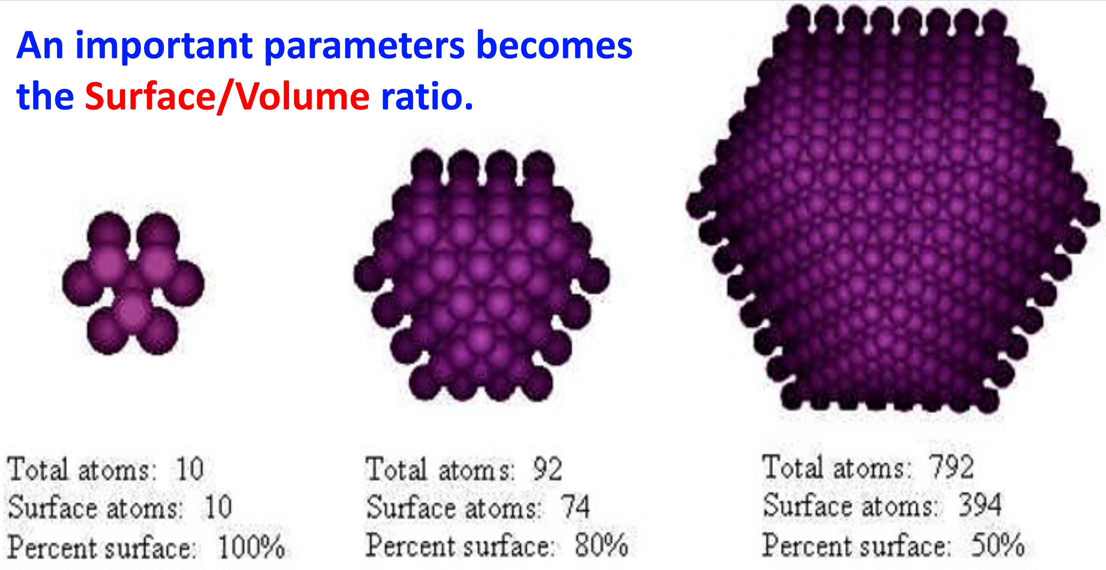
Nanoparticles bridge the gap between the isolated atom and the infinite solid.

The **physical and chemical properties of nanoparticles are different** from the **bulk also having the same chemical composition**.

Due to their **small sizes**, the **surface or the outermost layer of atoms**, determines their specific properties.



An important parameters becomes the Surface/Volume ratio.

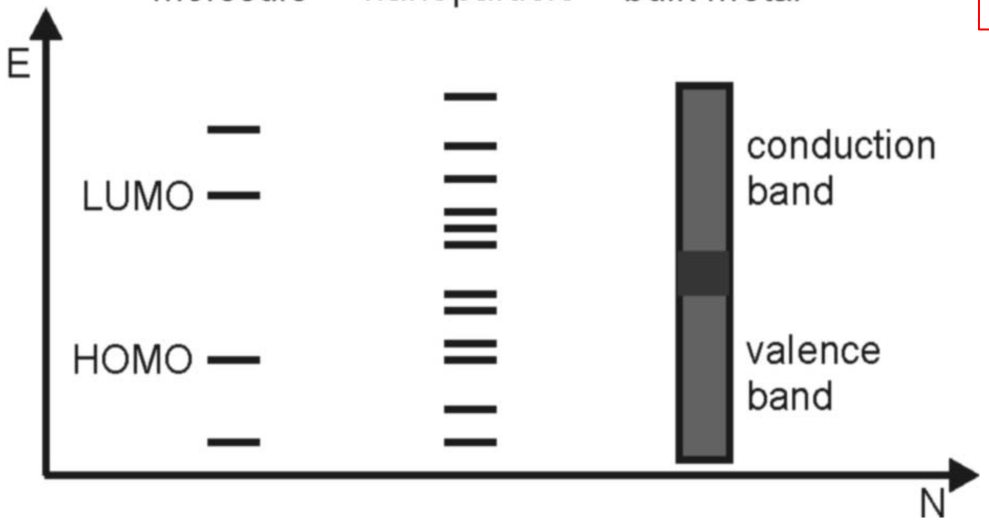


Nanoparticles and quantum confinement

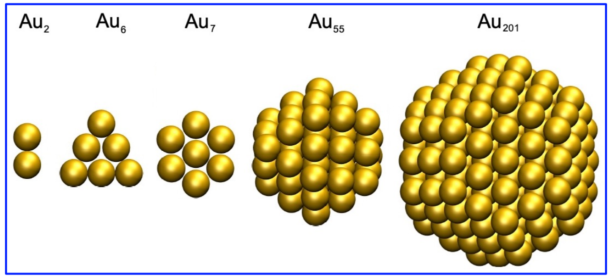
A **high percentage of surface atoms** introduces many **size-dependent phenomena**.

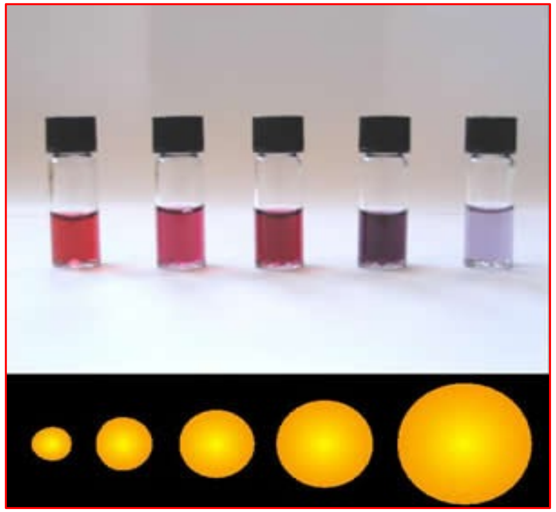
The **finite size of the particles** (small number of atoms) **confines the spatial distribution of the electrons, leading to quantized energy levels** due to size effects: **quantum-size effects (QSE)**.

Energy levels vs. size



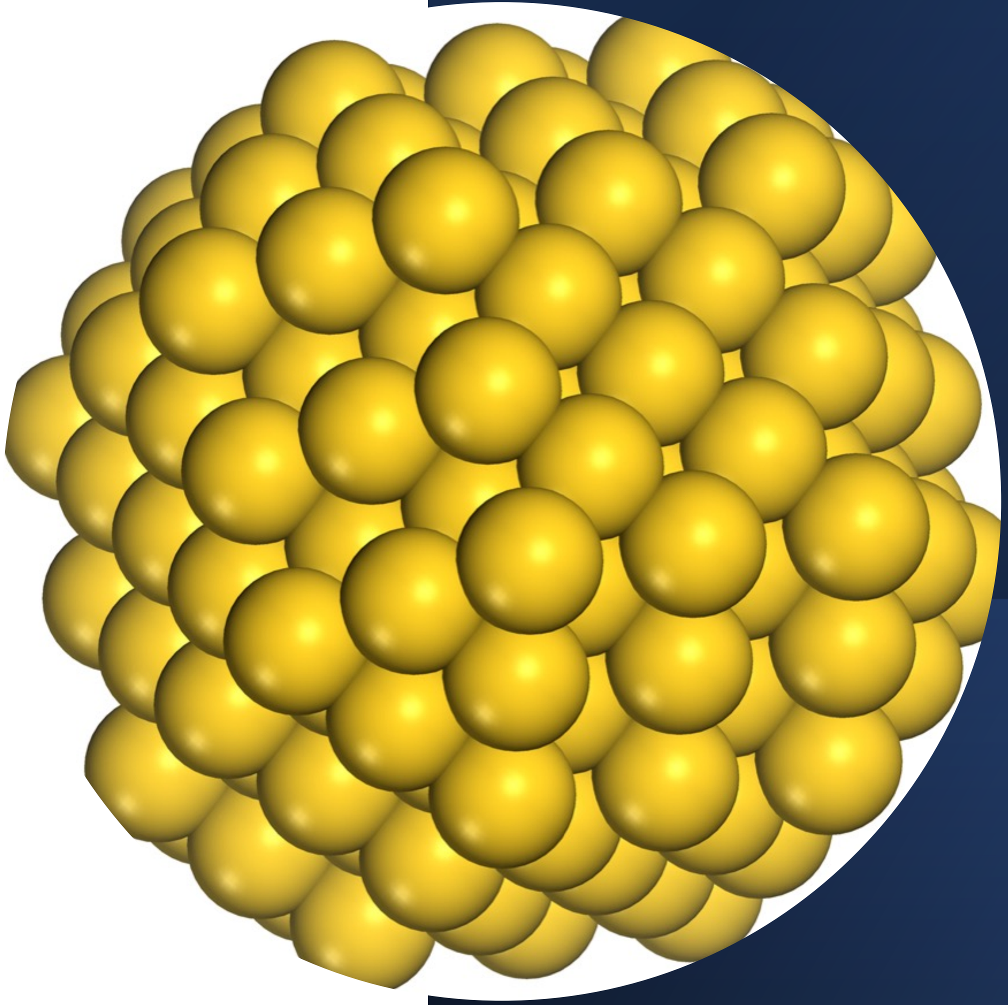
Size-dependent changes give relevant effects in the **structural**, **electric**, **magnetic** and **optical properties**, **chemical reactivity** and **catalytic activity**.





In the gold nanoparticles, electrons oscillate collectively - These **oscillations affect how light interacts with the nanoparticles** - The **specific oscillations depend on the size and shape of particles, so nanoparticles of different sizes have different colors** (Surface Plasmon Resonance)

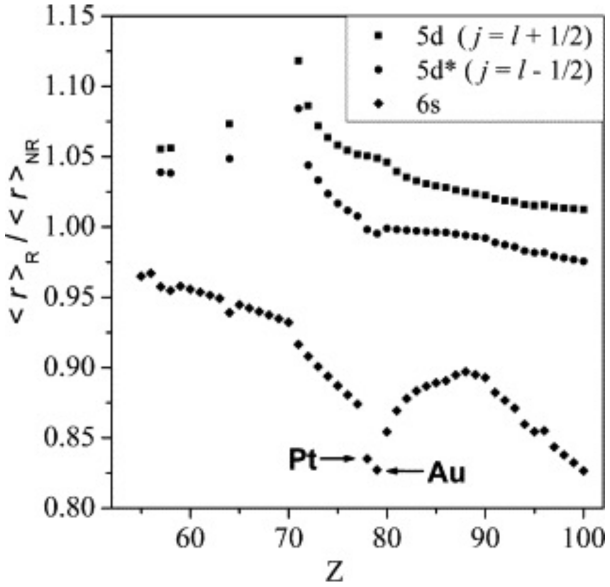
Au metal and Au nanoparticles



Au metal

Gold is a very interesting metal and its inertness is well known.

In **atoms of high atomic numbers** (**Z**), the **s electrons** of an atom become **more bound** and **their orbitals smaller (contraction)**. Simultaneously, the **d** (and **f**) electrons **are less bound** (relativistic effect scales roughly as Z^2). This accounts for **gold being more resistant to oxidation than silver**.



Radial contraction $\langle r\rangle_R/\langle r\rangle_{NR}$ for gold 6s orbital.

Au $4f^{14}\,5d^{10}\,6s^1$

		Z=79 Au	Z=47 Ag
Ionization potentials (eV)	1st:	9.225	7.576
	2nd:	20.5	21.49
Electron affinity (eV)		2.039	1.202
Heats of atomization (kjoules mol^{-1})		368	285
Melting point (°C)		1063	961
A-A distance in f.c.c. cells (Å), 25°C :		2.8840	2.8894

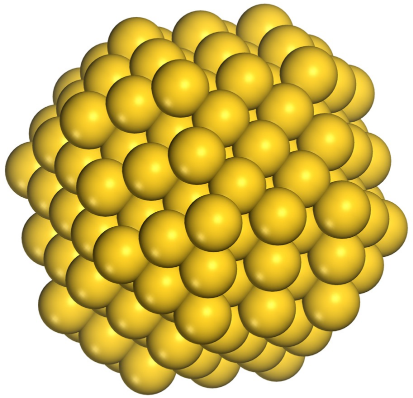
1) **P. Pyykko**, Annu. Rev. Phys. Chem. 63 (**2012**) 45–64, DOI: 10.1146/annurev-physchem-032511-143755
2) **M. Jansen**, Solid State Sciences 7 (**2005**) 1464–1474
3) **N. Bartlett,** Gold Bulletin 31 (**1998**) 1

Also if Gold metal is inert, at a nm scale, it has outstanding properties and is used in very important applications.

Applications of Au monometallic nanoparticles

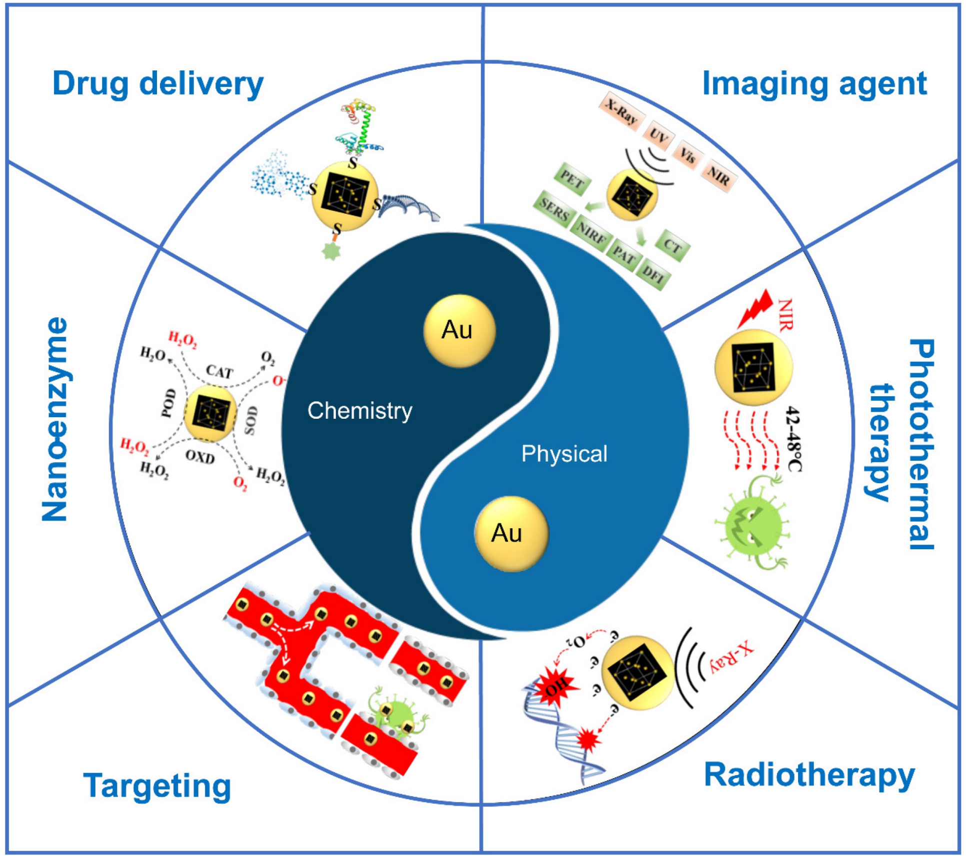
Catalysis

Nonlinear optics



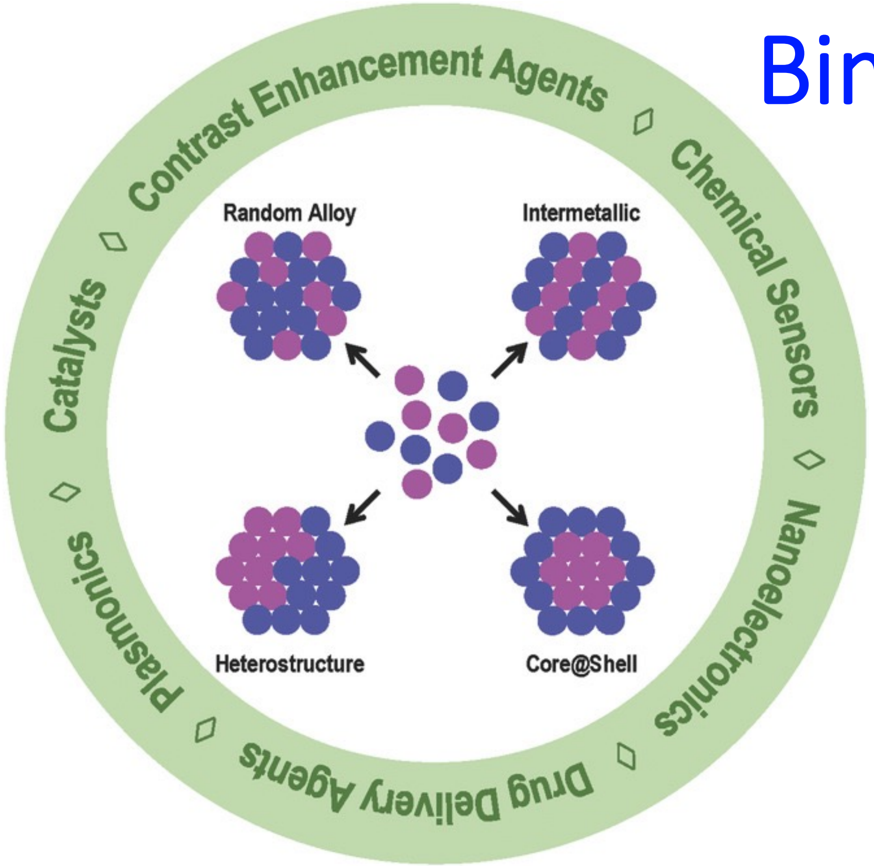
Biomedical Applications

Nanoelectronics



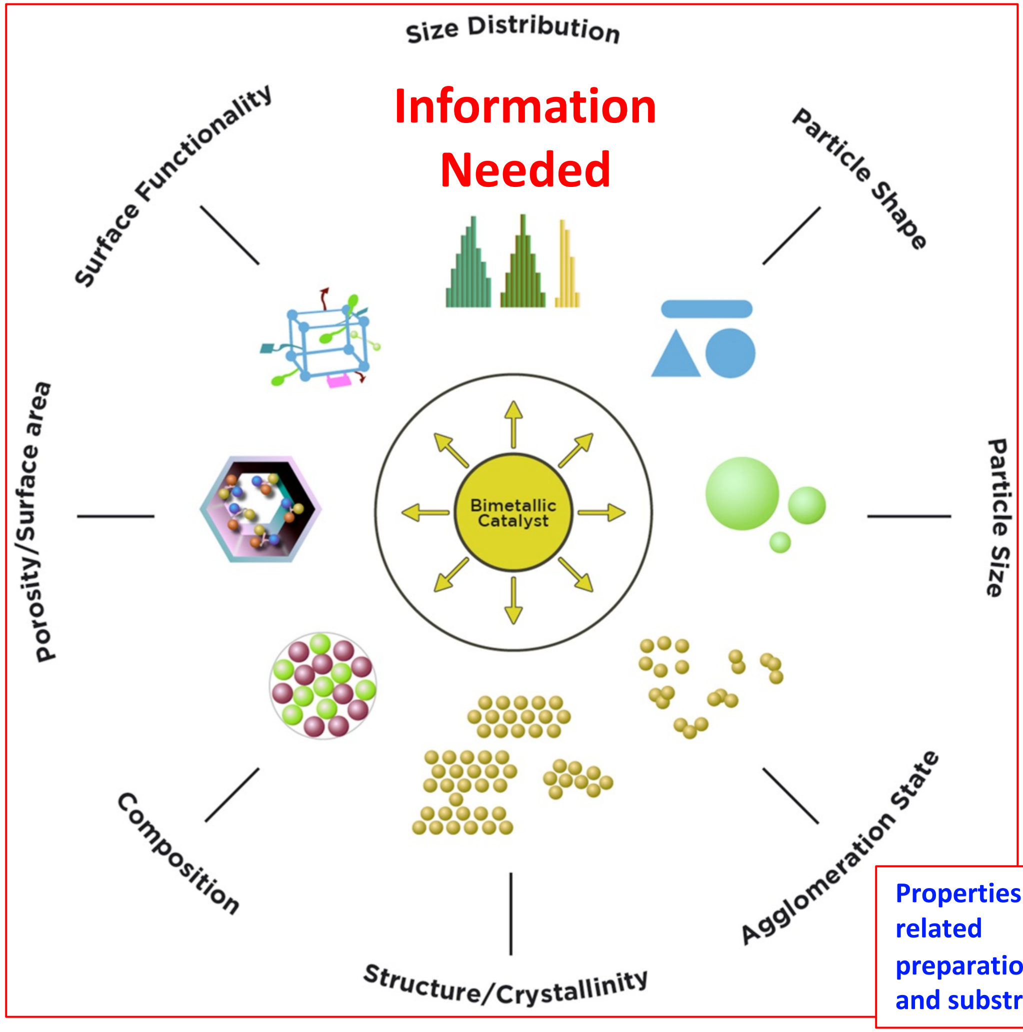
X. Bai et al. *The Basic Properties of Gold Nanoparticles and their Application in Tumour Diagnosis and Treatment.* **Int. J. Mol. Sci. 2020, 21, 2480**
DOI: 10.3390/ijms21072480

Bimetallic nanoparticles including Au



S. E. Skrabalak et al, *Beyond the Gold Standard: Bimetallic Nanomaterials Bring New Properties and Functions*, **Part. Part. Syst. Charact**. 35 (**2018**) 1800111
DOI: 10.1002/ppsc.201800111

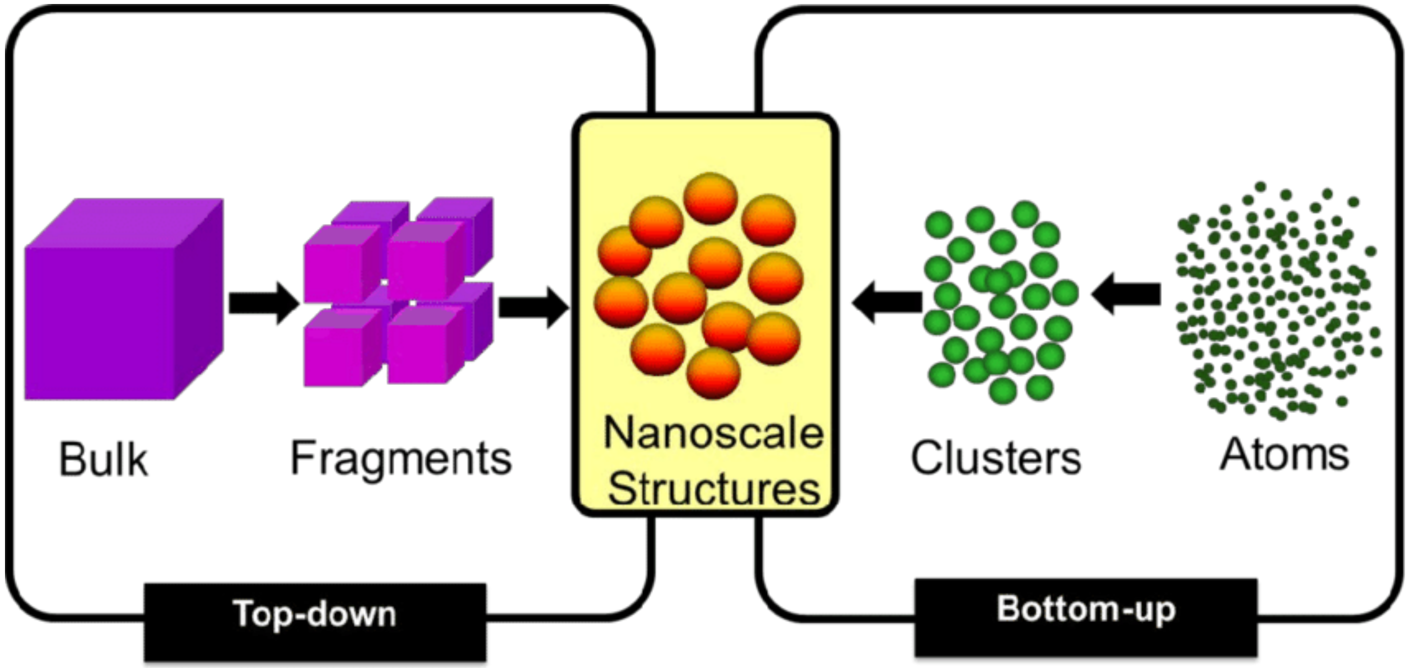
Bimetallic nanomaterials are of interest because in this case the **unique nanoscale properties of each metal** are **integrated** into **one nanoparticle** to achieve **multifunctionality**.
In addition, completely **new properties can emerge** mixing two metals at the nanoscale. Technological advances enable the growth of different types of bimetallic nanoparticles, including **alloys**, **intermetallic**, **heterostructures**, and even **core@shell** structures, where **properties and functionalities are directly related to the differences in bimetallic distributions**.



Properties are also related to the preparation method and substrate used.

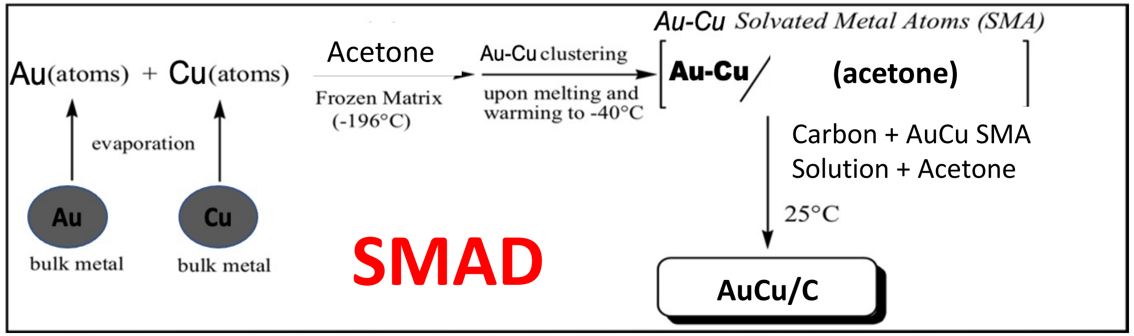
A. Alshammari et al. *Bimetallic Catalysts Containing Gold and Palladium for Environmentally Important Reactions*, **Catalysts** 6 (**2016**) 97
doi:10.3390/catal6070097

Au Nanoparticles and preparation methods



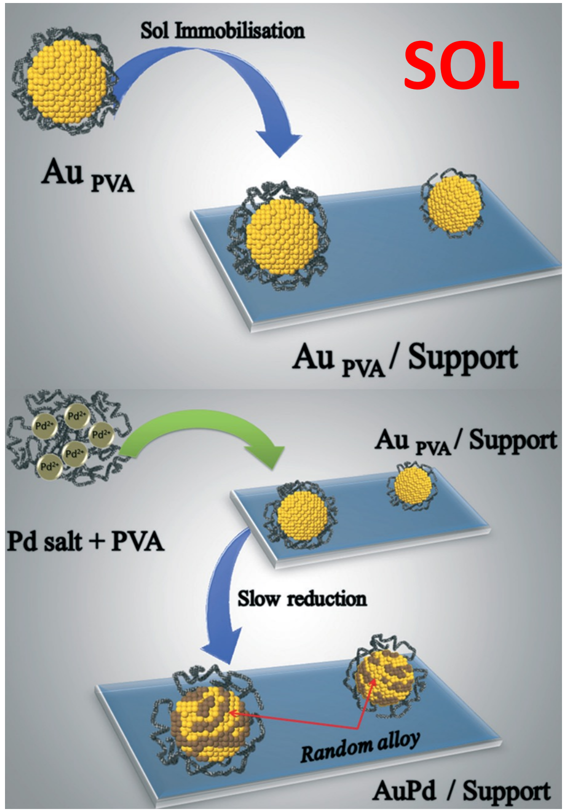
R. S. Rawat, *Dense Plasma Focus -From Alternative Fusion Source to Versatile High Energy Density Plasma Source for Plasma Nanotechnology*. **J. Phys.: Conf. Ser.** 591 (**2015**) 012021 DOI:10.1088/1742-6596/591/1/012021

Nanoparticles and some preparation methods



SMAD preparation method starts from Au and Cu vapors co-condensed at LNT with vapours of acetone. The acetone-solvated Au/Cu atom solution is then siphoned at −40 °C. AuCu NPs are then deposited onto carbon by adding the NP solution to a suspension of the support in acetone at 25 °C.

M. Marelli et al., *Hybrid Au/CuO Nanoparticles: Effect of Structural Features for Selective Benzyl Alcohol Oxidation*. **J. Phys. Chem. C** 123 (**2019**) 2864, DOI: 10.1021/acs.jpcc.8b09449



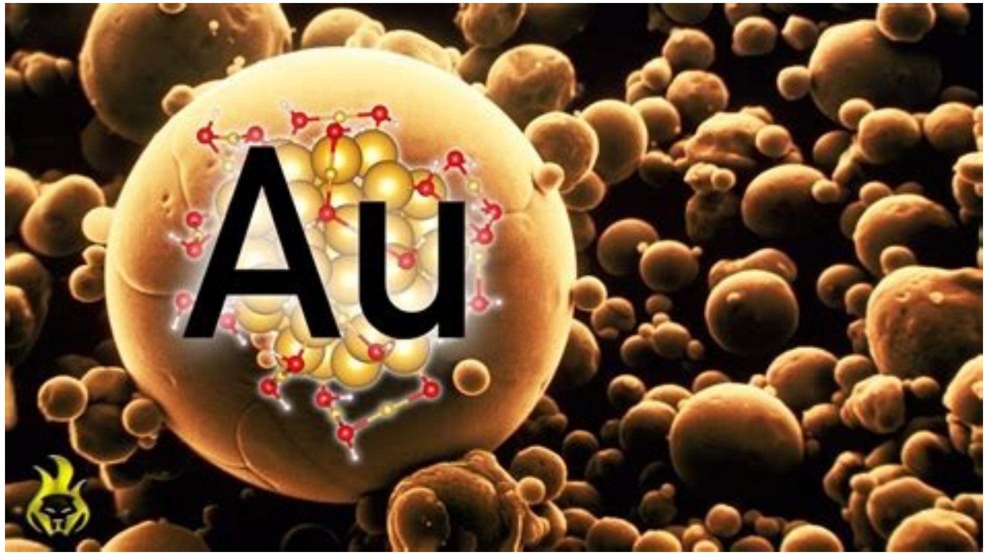
Resistive evaporation method is a physical vapor deposition technique were vaporized molecules then travel from the source to the substrate where they nucleate together, forming a thin-film coating.

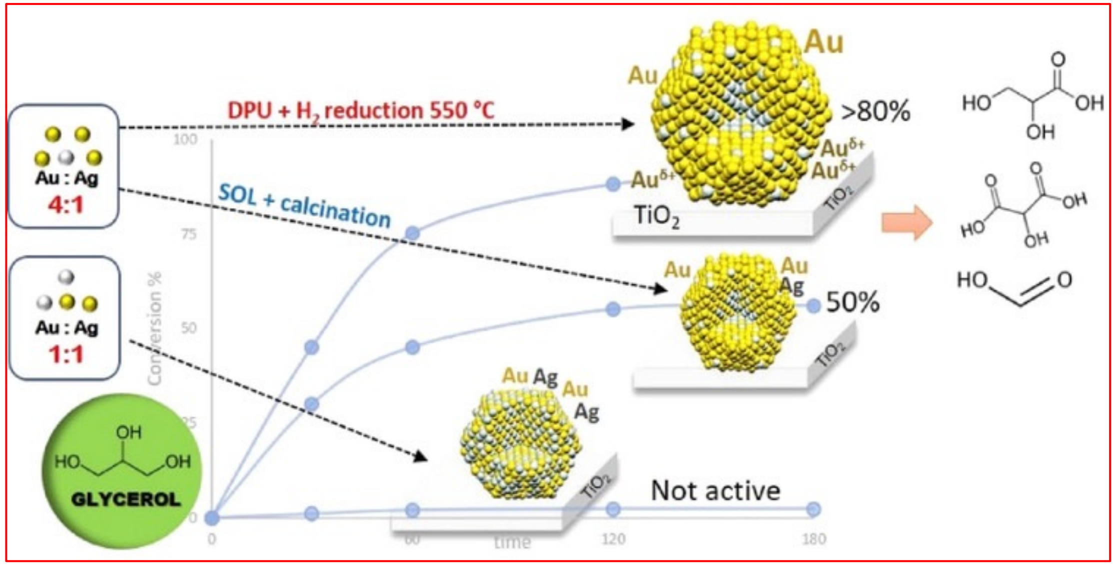
https://angstromengineering.com/resistive-thermal-evaporation-pvd-system/

A. Villa et al. *New challenges in gold catalysis: bimetallic systems* **Catal. Sci. Technol.** 5 (**2015**) 55. DOI: 10.1039/c4cy00976b

SOL preparation of mono-bimetallic systems using reduction, co-reduction or consecutive reduction of metal precursors in the presence of a stabilizing agent (polyvinyl alcohol -PVA) , which passivates the nanoparticles' surface and prevents them from aggregation, and their subsequent immobilization on a support

Bimetallic Au NPs and some applications in catalysis related to this short review





AuAg

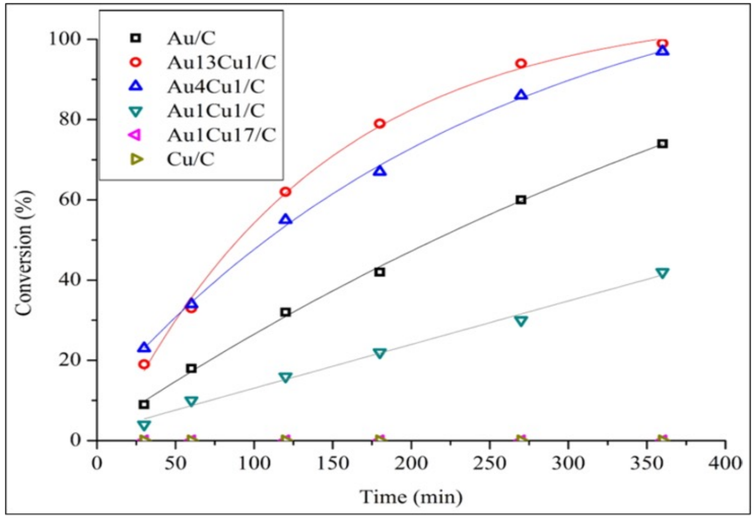
Gold-silver catalysts: Effects of catalyst structure on the selectivity of glycerol oxidation.

The catalytic oxidation of glycerol at mild conditions for the formation of valuable oxygenated compounds is used in the chemical and pharmaceutical industry.

M. Stucchi et al. *Gold-Silver Catalysts: Ruling Factors for Establishing Synergism*, **ChemCatChem** 11 (**2019**) 4043

AuCu

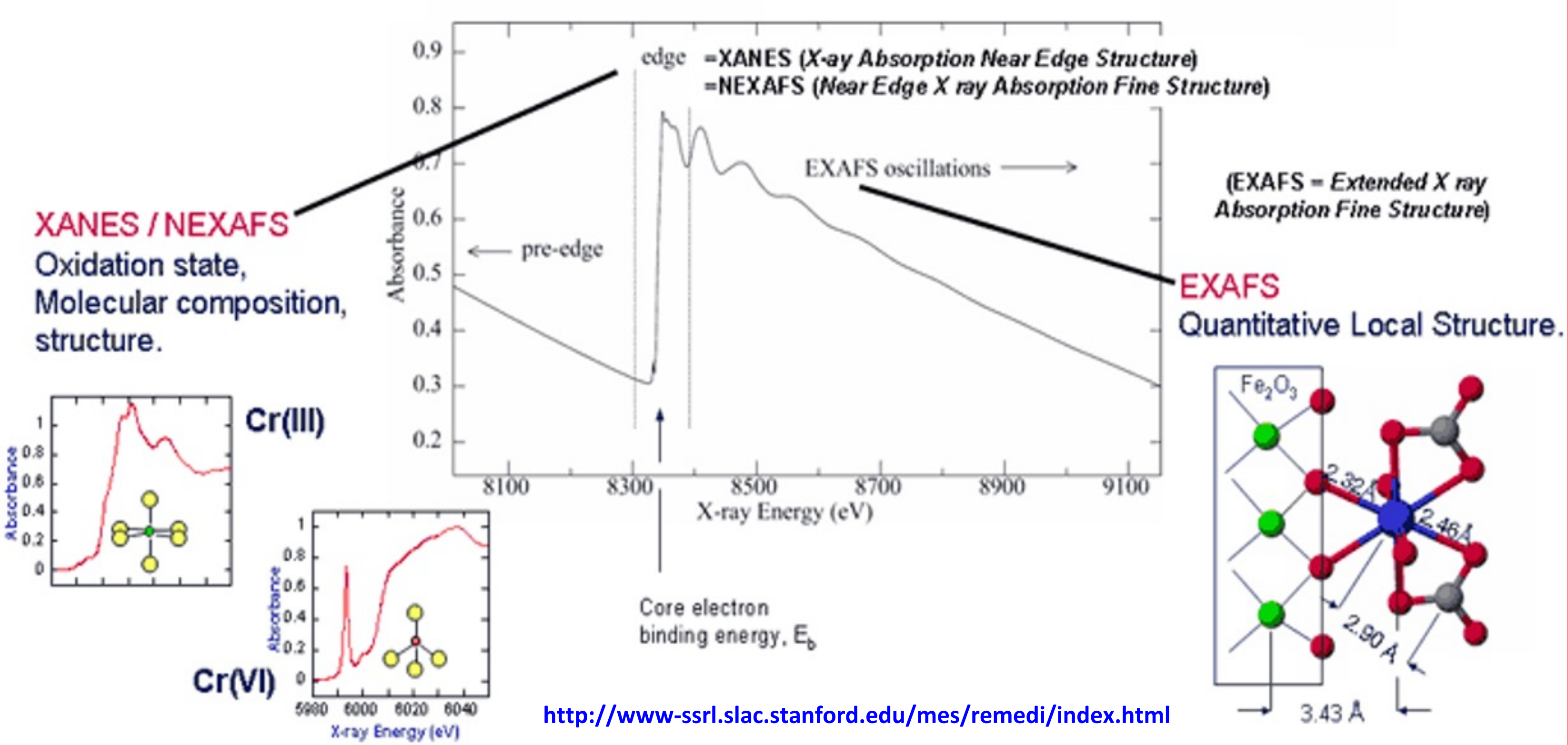
Selective liquid-phase oxidation of benzyl alcohol to benzaldehyde has both academic and industrial interest because of the applications in perfumery and agro-chemical industries.



M. Marelli et al., *Hybrid Au/CuO Nanoparticles: Effect of Structural Features for Selective Benzyl Alcohol Oxidation*. **J. Phys. Chem. C** 123 (**2019**) 2864, DOI: 10.1021/acs.jpcc.8b09449

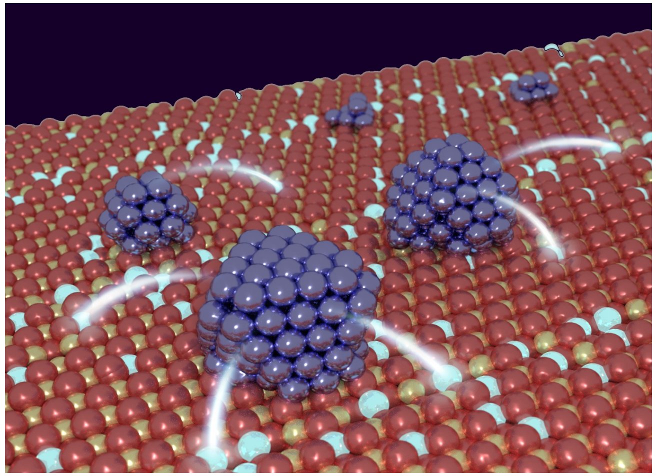
XAS: electronic and structural information

XAS and mono- and bimetallic nanoparticles



It is clearly really **important to correlate atomic structure of nanoparticles (NPs)** with their **properties**.

XAS or **X**-ray **A**bsorption **S**pectroscopy is an **experimental techniques able to provide structural information** on NPs.

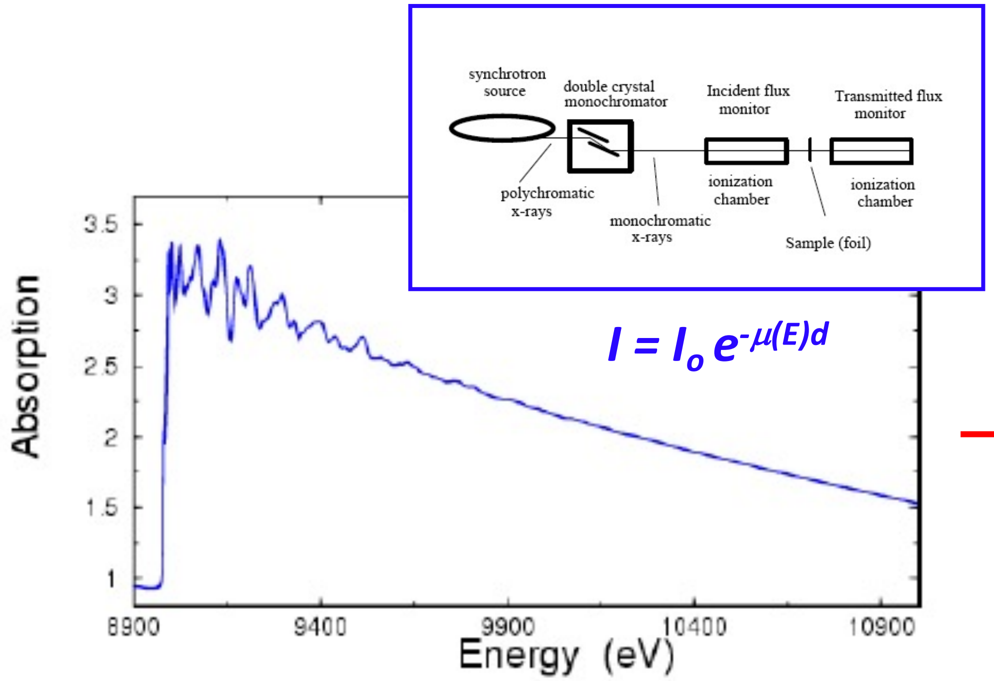


XAS = XANES + EXAFS

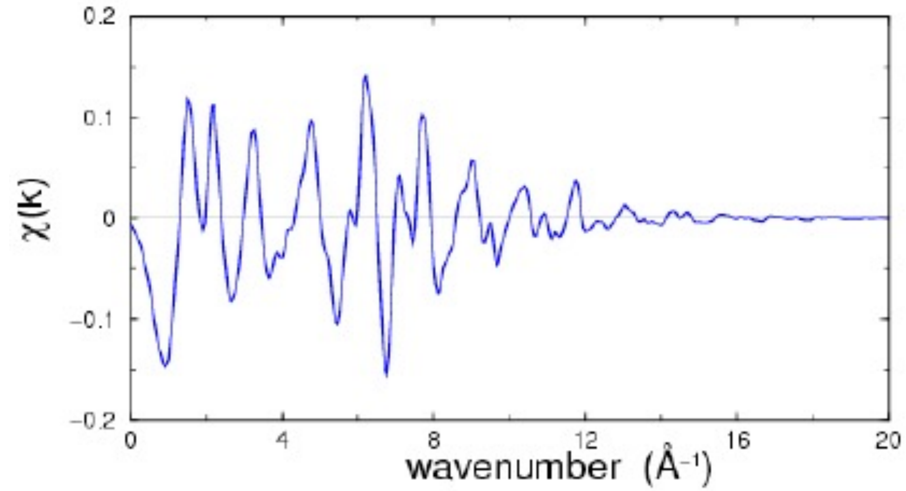
N. B. XAS measurements on low Z elements can be performed also the INFN- LNF DAΦNE-Light DXR1 soft X-ray beamline

***In situ* measurements** can be performed during **chemical reactions measuring time-resolved XAS spectra**.

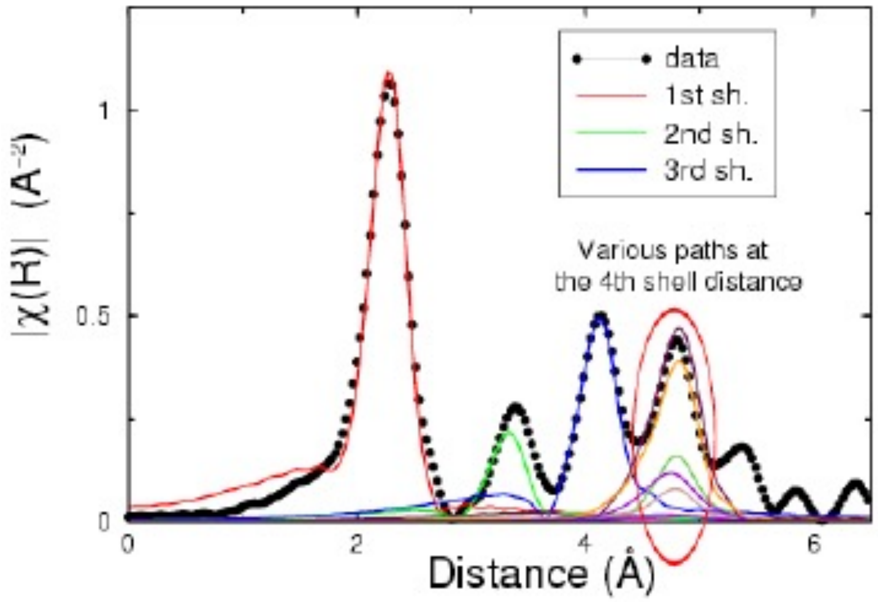
EXAFS Structural Information

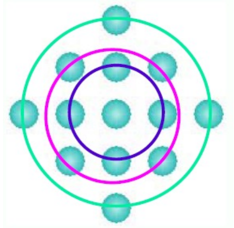


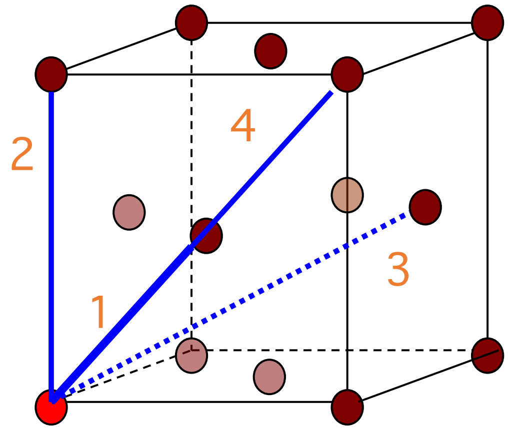
$$I = I_o e^{-\mu(E)d}$$



$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^{\,2}} \sin[2kR_j + \delta_j(k)]$$

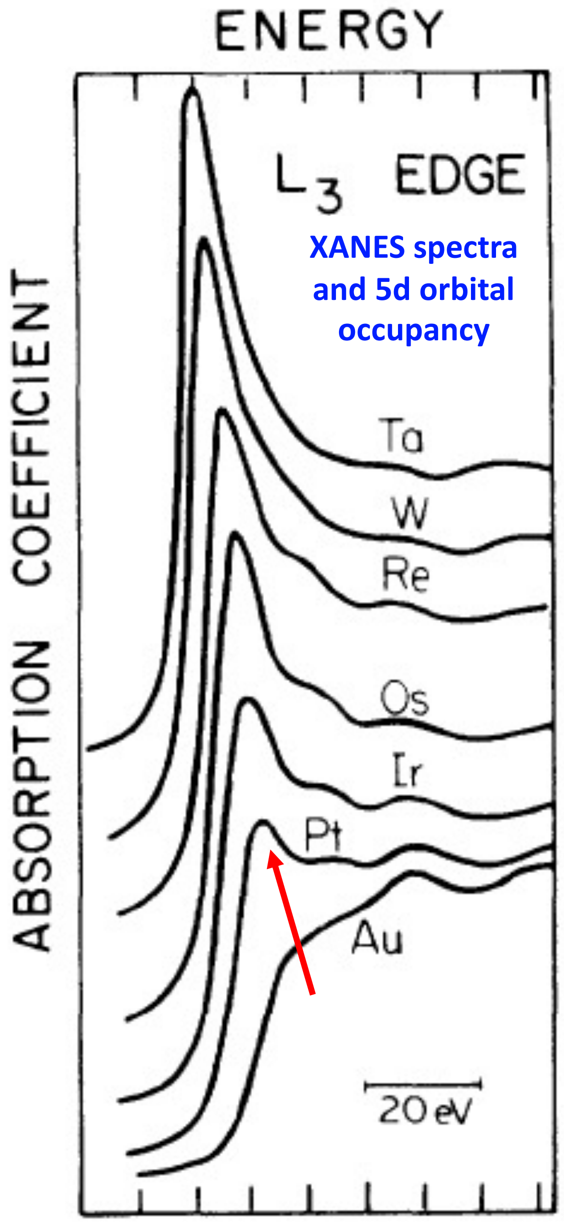




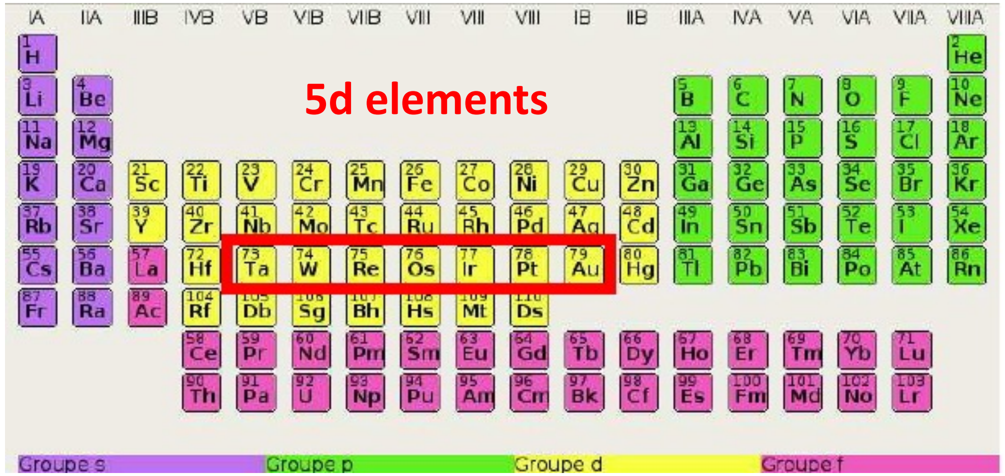


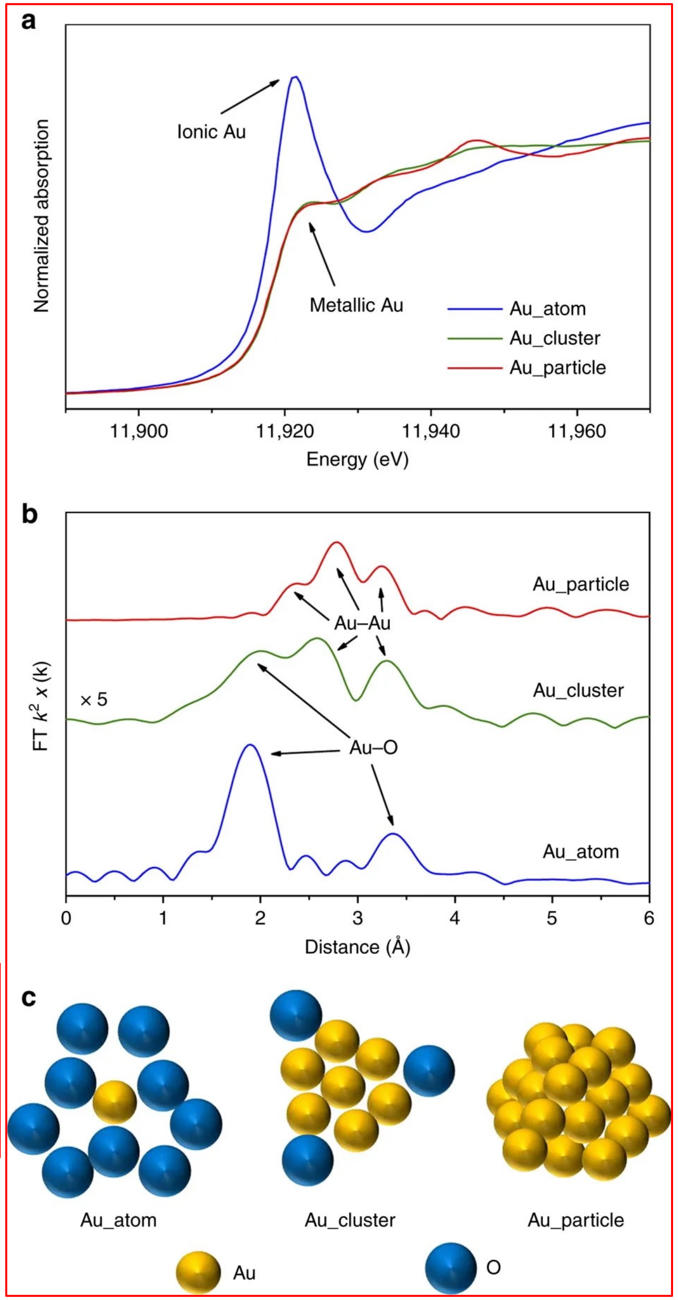
XAS studies on mono and bimetallic Au NPs: a Short Review

XAS and L_3 edges



XANES spectra and 5d orbital occupancy





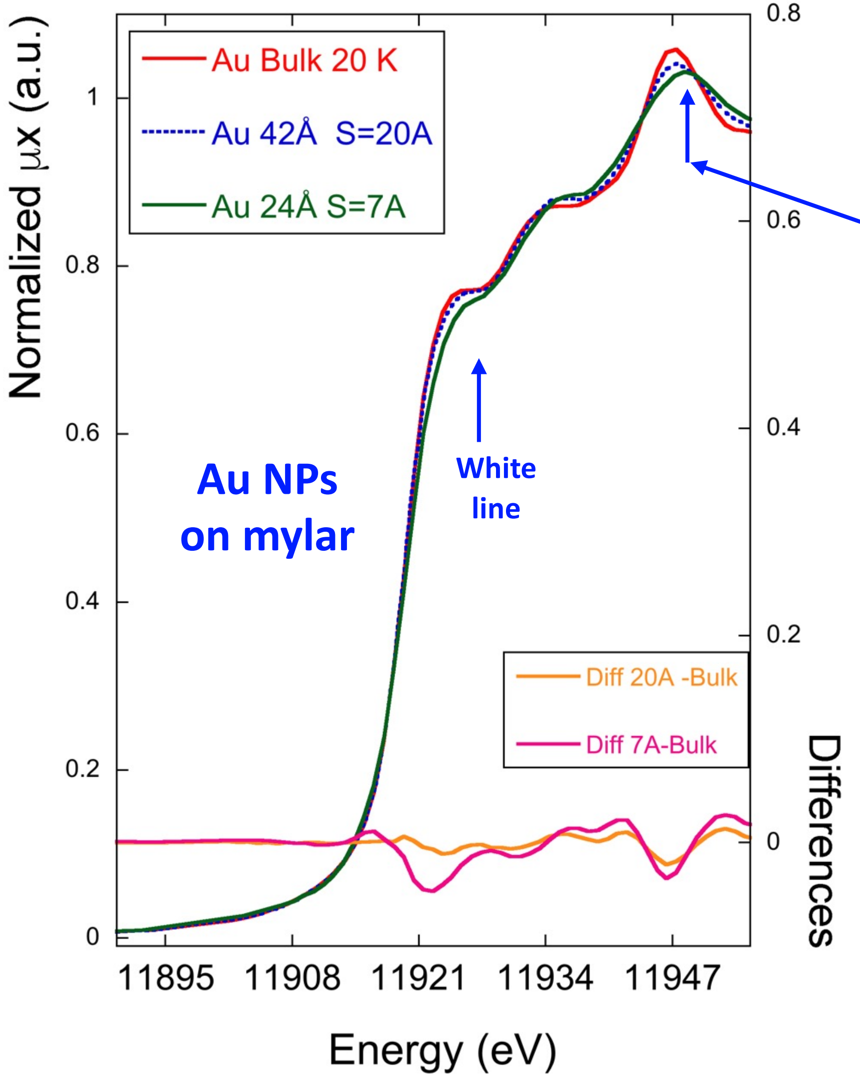
Contributions of distinct gold species to catalytic reactivity for carbon monoxide oxidation

B. Qi et al. *L_2 and L_3 measurements of transition-metal 5d orbital occupancy, spin-orbit effects and chemical bonding.* **Phys. Rev. B** 36 (**1987**) 2972

Li-Wen Guo et al. **Nature Comm. 2016**
DOI: 10.1038/ncomms13481

Monometallic Au nanoparticles

XANES and EXAFS of Au/mylar



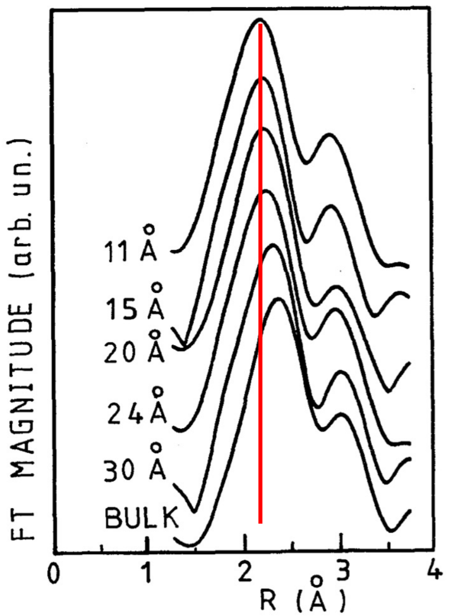


FIG. 6. Fourier transforms of the films and bulk EXAFS spectra. The transformations are now in the range 3—11 $Å^{-1}$ with k^1 weight and a Gaussian window function.

The XANES peak shift is related to the interatomic distance contraction of the NPs compared to Au bulk found by EXAFS data analysis.

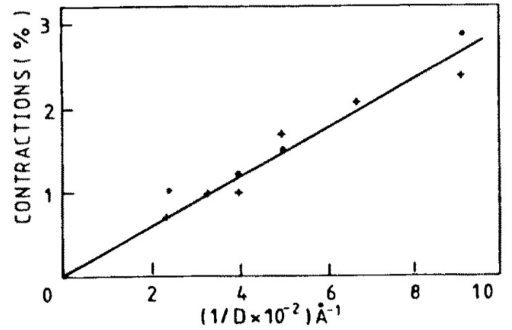


Fig. 5. Plot of the first (+) and second (●) neighbour distances contraction percentage versus the inverse of cluster mean diameter. The straight line drawn is a mean square linear fit of the data.

EXAFS data analysis

$$\Delta R = -\tfrac{4}{3} K R_b f \frac{1}{D}$$

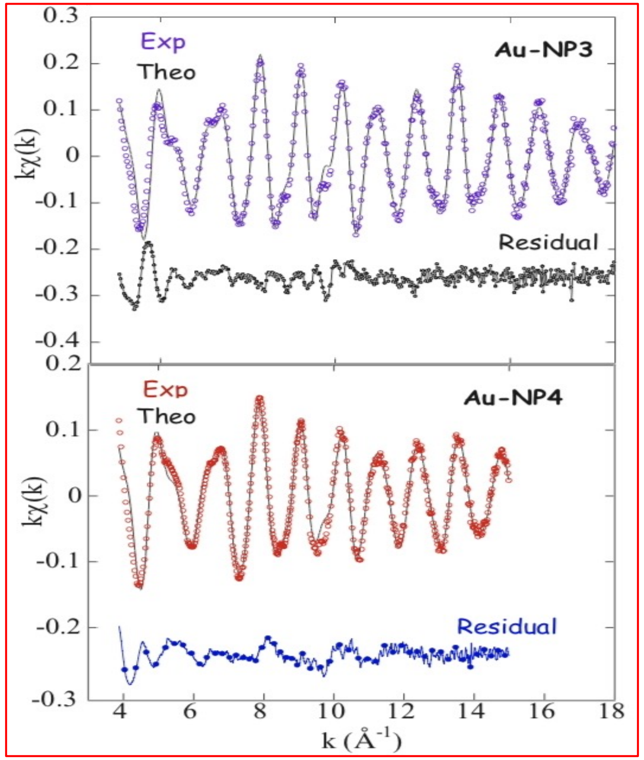
Contractions explained with a macroscopic liquid drop model

ΔR = contraction *f* = surface stress R_b= bulk NN distance
D = nanoparticle diameter.

In gold bulk, the presence of this white line is ascribed to the ***s-p-d* atomic level hybridization** that gives a **partial depletion of the filled $5d^{10}$ orbitals**. In the small **Au NPs this hybridization is reduced**, leading to an **increase of the 5d occupancy** and therefore **a reduction of the intensity of white-line**.

A. Balerna et al. *EXAFS and NES on evaporated small clusters of Au*. **Phys. Rev. B** 31 (**1985**) 5058

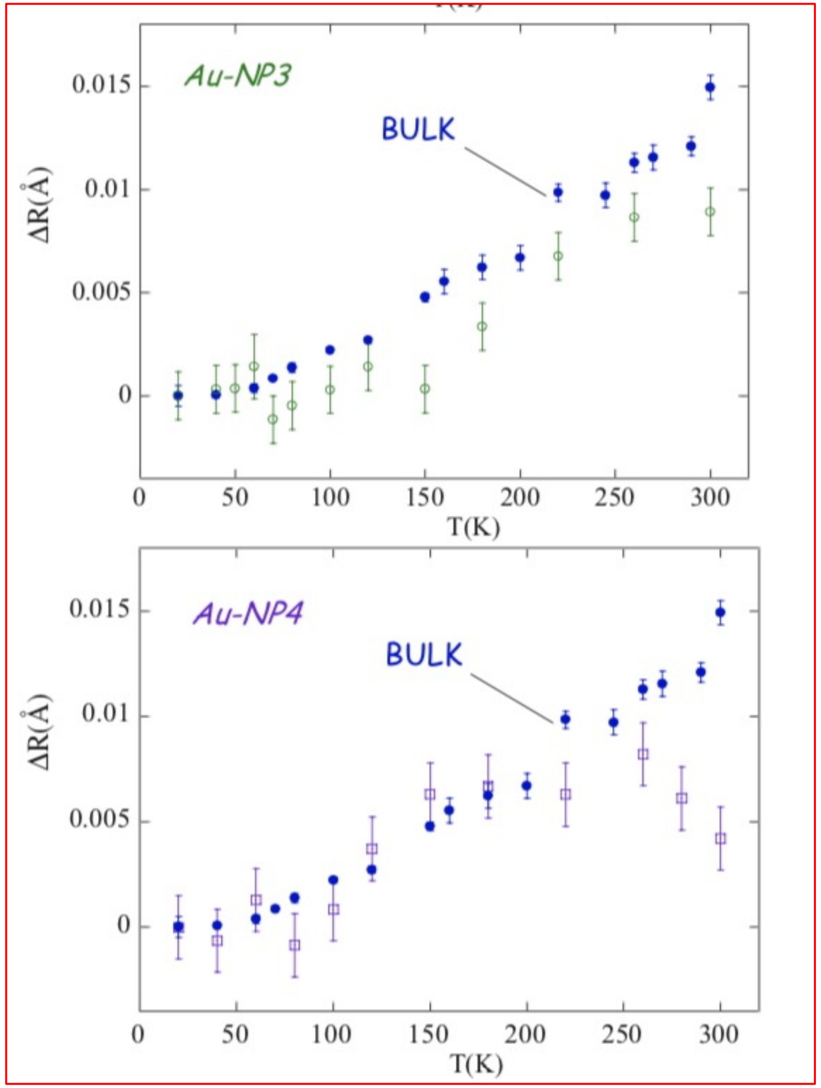
EXAFS of Au/mylar



LISA CRG Beamline - ESRF

Changes in the thermal behaviour of small nanoparticles is size dependent

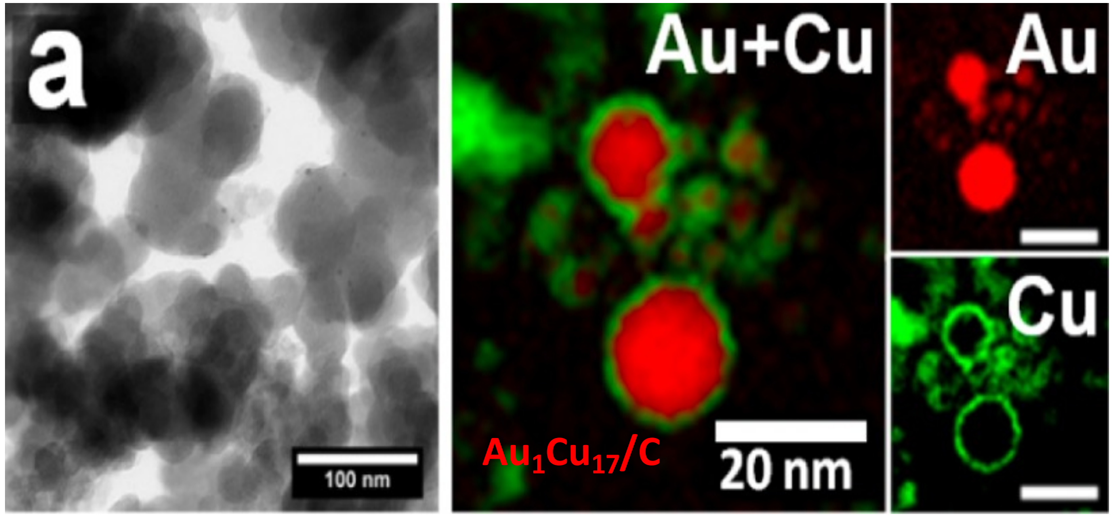
Crossover from an initial thermal expansion to a thermal contraction for the smaller nanoparticles.



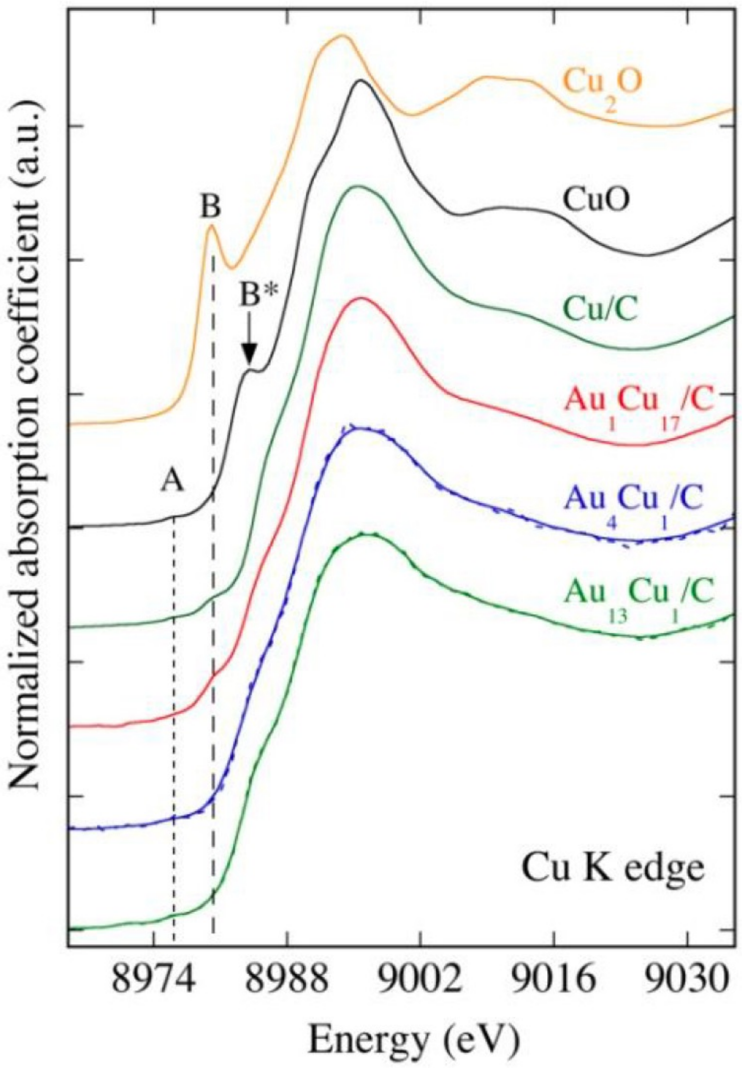
T. Comaschi et al. *Temperature dependence of the structural parameters of gold nanoparticles investigated with EXAFS*. **Phys. Rev. B** 77 **(2008)** 075432. DOI: 10.1103/PhysRevB.77.075432

Bimetallic AuCu, AuPd, AuAg nanoparticles

AuCu/C nanoparticles (Au)core@(Cu)shell



TEM micrograph (left side) and STEM energy filtered maps for Au and Cu
Au@2239.0–2477.0 eV–Cu@953.0–1202.0 eV

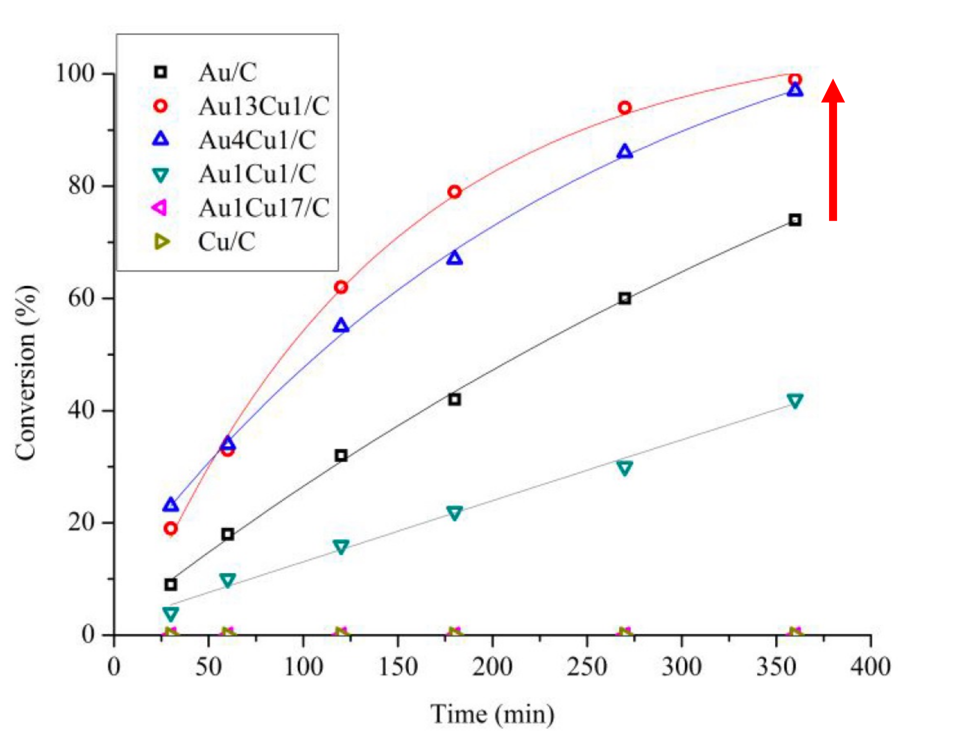


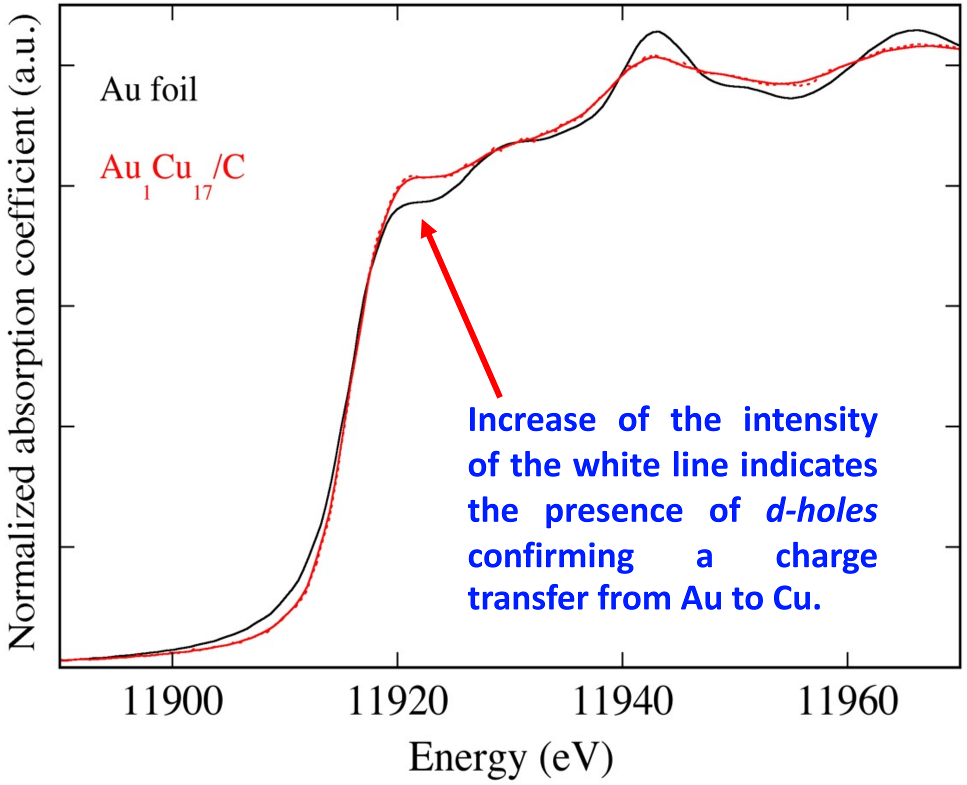
XAS measurements of bimetallic NPs with **different Au/Cu molar ratios showed the presence of a Au/CuO core@shell** structure.

M. Marelli et al., *Hybrid Au/CuO Nanoparticles: Effect of Structural Features for Selective Benzyl Alcohol Oxidation*. **J. Phys. Chem. C** 123 (**2019**) 2864, DOI: 10.1021/acs.jpcc.8b09449

AuCu/C nanoparticles (Au)core@(Cu)shell

Highest catalytic activity was observed when the **CuO shell only partially covered the Au NP surface** while at **high Cu loadings the CuO shell wraps the Au core completely, inhibiting the catalytic activity**.

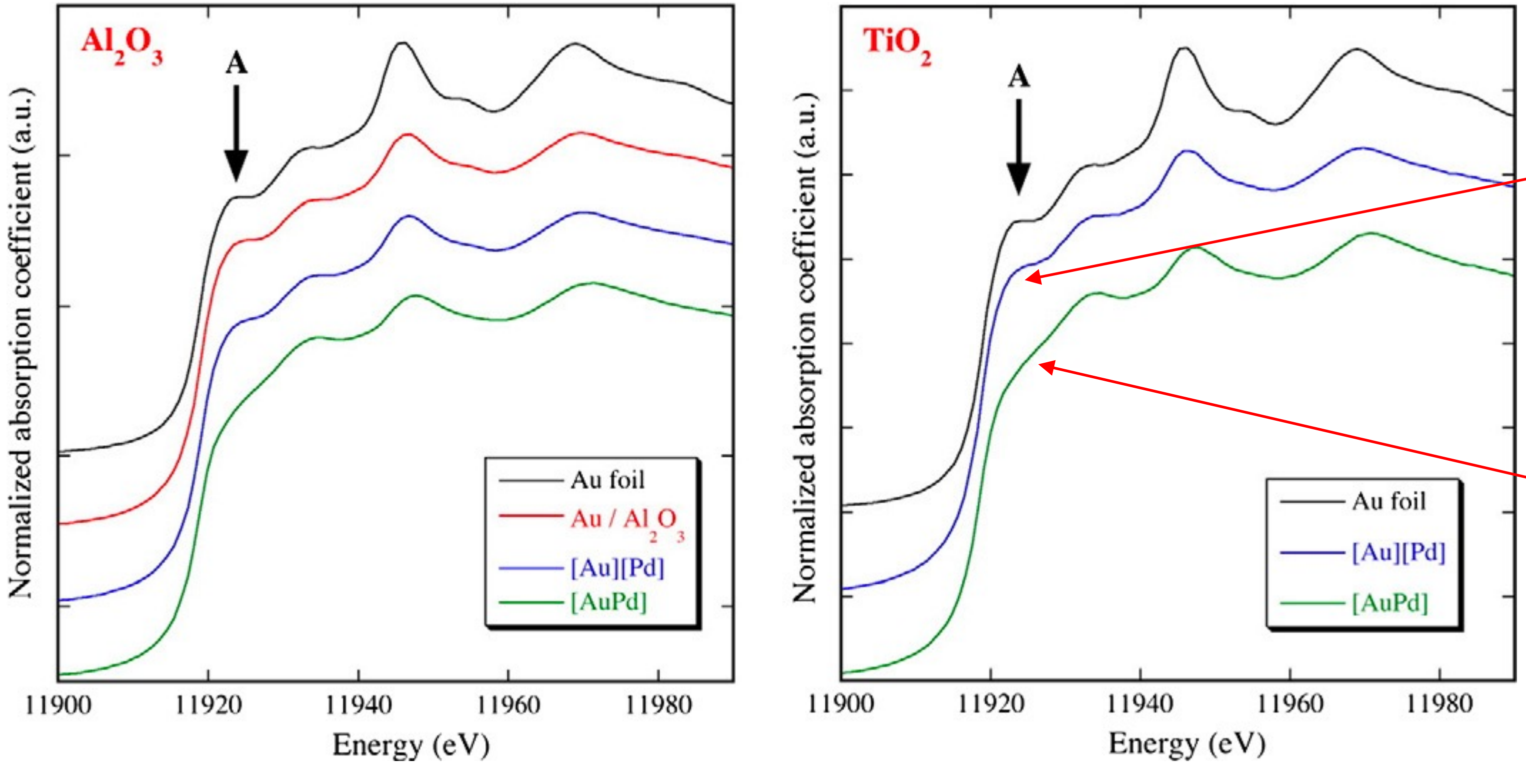




M. Marelli et al., *Hybrid Au/CuO Nanoparticles: Effect of Structural Features for Selective Benzyl Alcohol Oxidation*. **J. Phys. Chem. C** 123 (**2019**) 2864, DOI: 10.1021/acs.jpcc.8b09449

AuPd

XANES and EXAFS of $AuPd/Al_2O_3$ and $AuPd/TiO_2$ NPs



[Au][Pd] A feature decrease due to NPs small dimensions

[AuPd] A feature further decrease due to charge transfer from Pd to Au

In the nanoparticles, the **reduced number of Au–Au bonds reduces the hybridization as well resulting in an increase in the 5d level occupancy and hence in a decrease in the intensity of the feature A**; in the [AuPd] NPs, a **further reduction in the intensity of the white line (feature A) can be due to a charge transfer from Pd to Au.**

C. Evangelisti et al. *Bimetallic Gold–Palladium vapour derived catalysts: The role of structural features on their catalytic activity*. **Journal of Catalysis** 286 (**2012**) 224–236

XANES and EXAFS of $AuPd/Al_2O_3$ and $AuPd/TiO_2$ NPs

Al_2O_3

Table 1
Distances (R), coordination numbers (N), distances and Debye Waller factors (σ^2) achieved for the Au bulk sample, for the Au monometallic catalyst and for the bimetallic samples on γ-Al_2O_3 at the Au L_3 edge.

Sample	Shell number	N	R (Å)	σ^2 (Å^2)
Au bulk	1	12(fixed)	2.875(5)	0.0020(5)
R-factor = 0.002	2	6(fixed)	4.067(7)	0.0026(7)
	3	24(fixed)	4.986(7)	0.0031(7)
	4	12(fixed)	5.758(7)	0.0032(7)
Au/γ-Al_2O_3	1	10.9(4)	2.867(5)	0.0031(8)
Au (1%)	2	5.1(2)	4.061(7)	0.0043(9)
R-factor = 0.006	3	20.3(8)	4.976(7)	0.0046(9)
	4	10.5(4)	5.749(7)	0.0050(9)
[Au][Pd]	Au–Au	10.2(9)	2.854(7)	0.0062(9)
R-factor = 0.006	Au–Pd	0.9(2)	2.793(7)	0.0063(9)
[AuPd]	Au–Au	5.5(5)	2.815(8)	0.0087(9)
R-factor = 0.005	Au–Pd	3.6(5)	2.794(8)	0.0071(9)

TiO_2

Table 2
Results achieved on the bimetallic samples on TiO_2 at the Au L_3 edge.

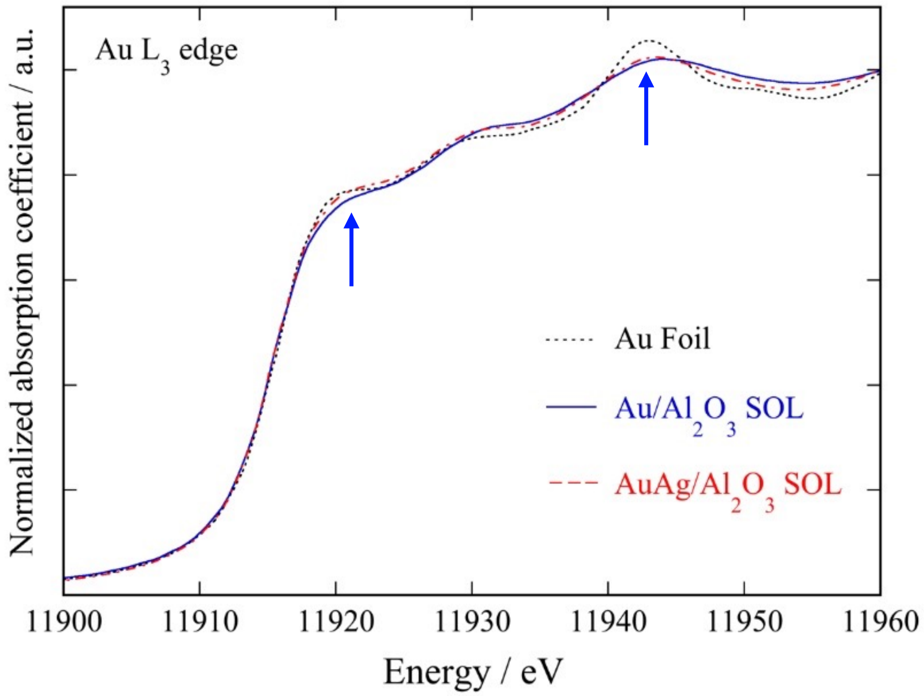
Sample	Shell	N	R (Å)	σ^2 (Å^2)
[Au][Pd]	Au–Au	9.5(9)	2.850(7)	0.0068(9)
R-factor = 0.006	Au–Pd	0.9(2)	2.794(7)	0.0075(9)
[AuPd]	Au–Au	5.0(5)	2.814(8)	0.0045(9)
R-factor = 0.003	Au–Pd	3.4(5)	2.793(8)	0.0031(9)

The bimetallic **[AuPd] co-condensed systems**, tested in the selective oxidation of benzyl alcohol with molecular oxygen both in toluene solvent and in solvent-free conditions, **showed higher catalytic activity and selectivity than the corresponding monometallic systems** as well as of the **analogous systems obtained by separate evaporation [Au][Pd] of the two metals.**

C. Evangelisti et al. *Bimetallic Gold–Palladium vapour derived catalysts: The role of structural features on their catalytic activity.* **Journal of Catalysis** 286 (**2012**) 224–236

AuAg

XANES and EXAFS of AuAg/Al_2O_3 NPs

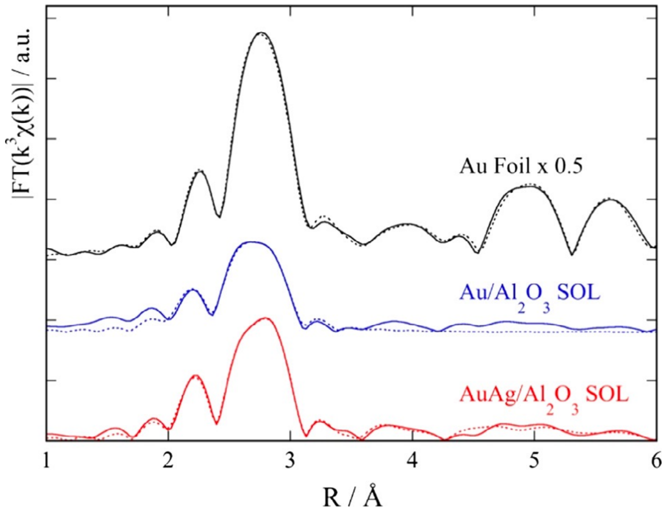


Sol Immobilization (SOL)

In the bimetallic AuAg NPs, the **XANES sensitivity can probe changes in the Au 5d charge redistribution** given by **small charge transfer from Au to Ag.**

LISA CRG Beamline - ESRF

AuAg SOL is more active than AuAg SMAD in the catalytic oxidation of glycerol in terms of activity and selectivity.

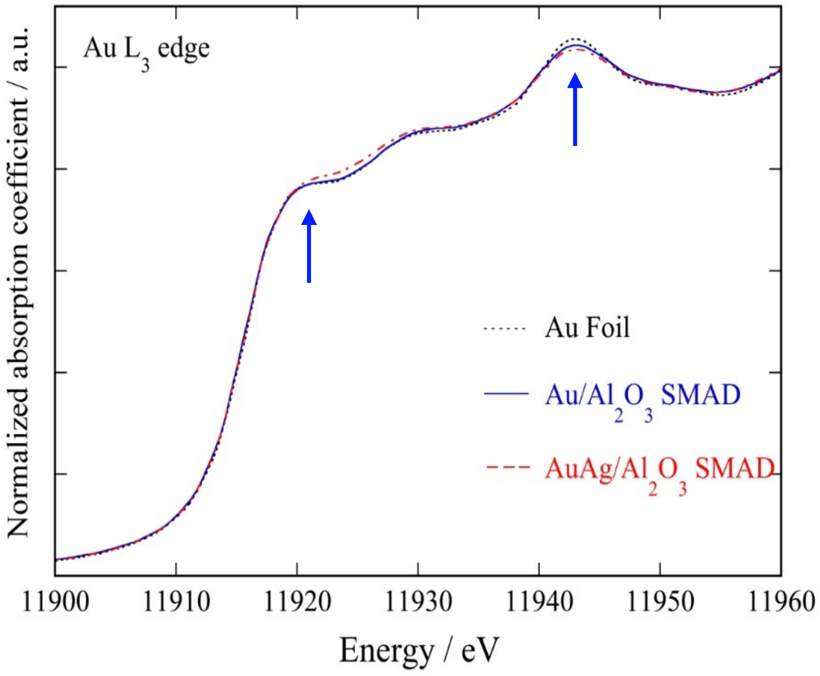


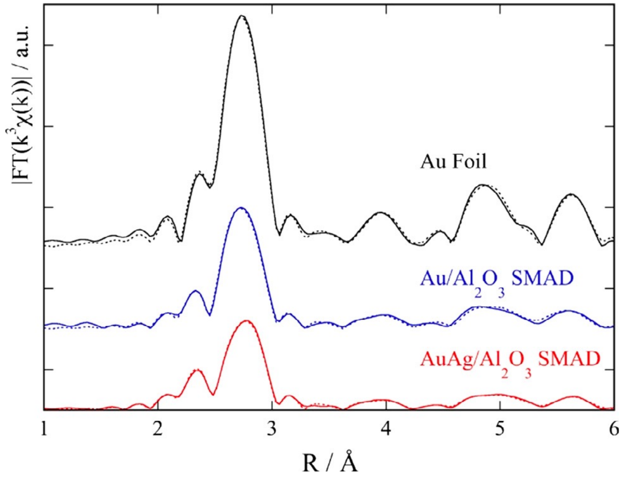
	Coordination shell	N	R (Å)	σ^2 (Å^2)
Au Foil	Au-Au (I)	12 (fixed)	2.871 (6)	0.0031 (6)
R-factor = 0.007	Au-Au (II)	6 (fixed)	4.066 (8)	0.0044 (9)
Au/Al_2O_3 SOL	Au-Au (I)	7.6	2.828	0.007
R-factor = 0.007				
AuAg/Al_2O_3 SOL	Au-Au (I)	8.2	2.844	0.006
R-factor = 0.006	Au-Ag (I)	0.8	2.845	0.008
	Au-Au (II)	4.0	4.030	0.011
Au/Al_2O_3 SMAD	Au-Au (I)	10.8	2.863	0.0047
R-factor = 0.008	Au-Au (II)	5.4	4.057	0.0075
AuAg/Al_2O_3 SMAD	Au-Au (I)	9.1	2.862	0.0045
R-factor = 0.009	Au-Ag (I)	1.7	2.862	0.0055
	Au-Au (II)	4.4	4.056	0.0079

A. Jouve et al. *Gold-silver catalysts: Effect of catalyst structure on the selectivity of glycerol oxidation*. Journal of Catalysis 368 (**2018**) 324–335

XANES and EXAFS of $AuAg/Al_2O_3$ NPs

In the bimetallic AuAg NPs, the **XANES sensitivity can probe changes in the Au 5d charge redistribution** given by **small charge transfer from Au to Ag.**





Solvated Metal Atom Deposition (SMAD)

	Coordination shell	N	R (Å)	σ^2 (Å^2)
Au Foil	Au-Au (I)	12 (fixed)	2.871 (6)	0.0031 (6)
R-factor = 0.007	Au-Au (II)	6 (fixed)	4.066 (8)	0.0044 (9)
Au/Al_2O_3 SOL	Au-Au (I)	7.6	2.828	0.007
R-factor = 0.007				
$AuAg/Al_2O_3$ SOL	Au-Au (I)	8.2	2.844	0.006
R-factor = 0.006	Au-Ag (I)	0.8	2.845	0.008
	Au-Au (II)	4.0	4.030	0.011
Au/Al_2O_3 SMAD	Au-Au (I)	10.8	2.863	0.0047
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$AuAg/Al_2O_3$ SMAD	Au-Au (I)	9.1	2.862	0.0045
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	Au-Au (II)	4.4	4.056	0.0079

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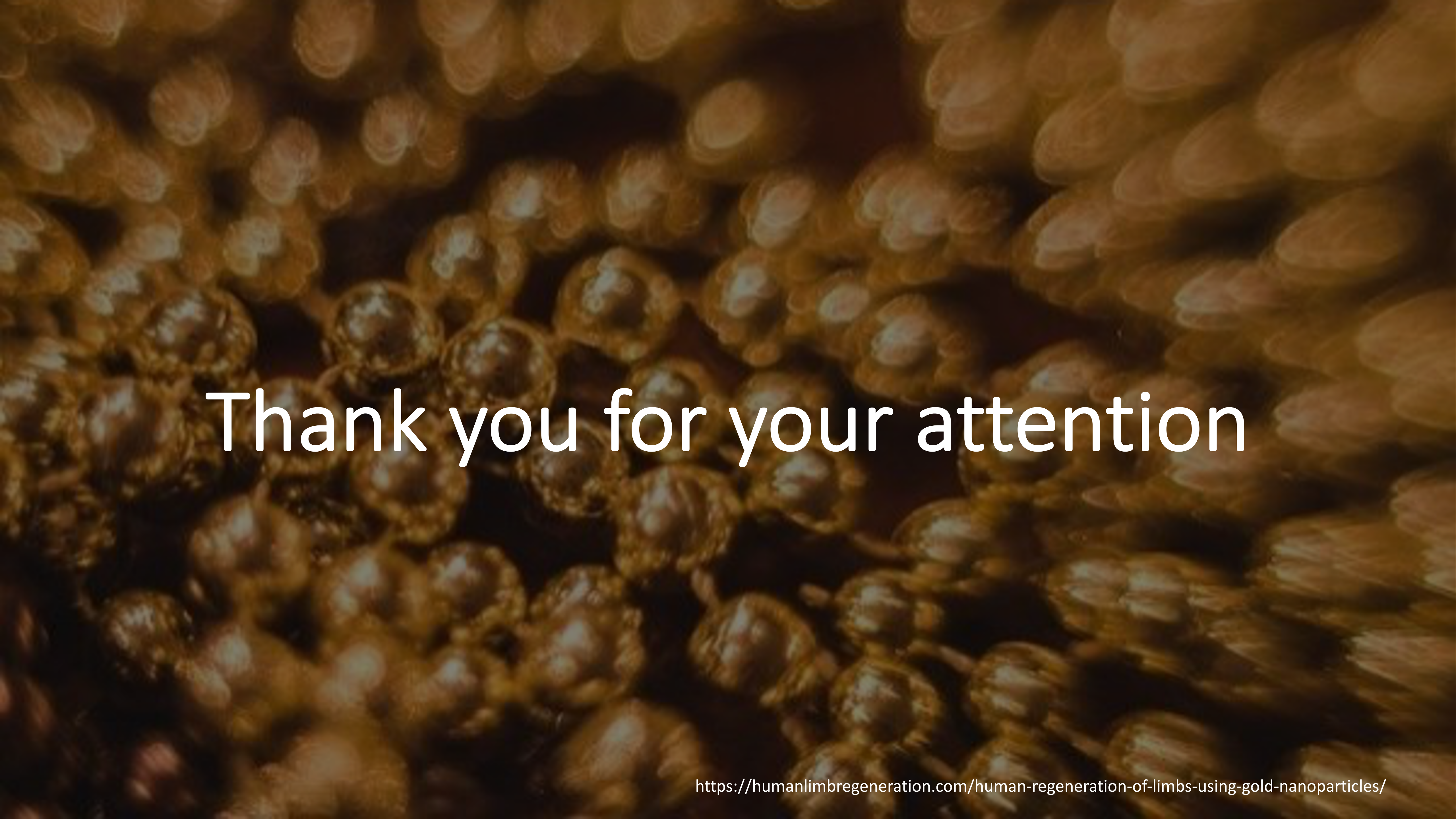
Conclusions

- XAS can give important electronic and structural information on nanoparticles

- Monometallic and bimetallic nanoparticles including Au are used in important applications in many different fields from catalysis to life science and much more and for this reason achieving information on their electronic and structural properties is really important.



Thank you for your attention

https://humanlimbregeneration.com/human-regeneration-of-limbs-using-gold-nanoparticles/