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

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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 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.

- **Total atoms:** 10
  - Surface atoms: 10
  - Percent surface: 100%

- **Total atoms:** 92
  - Surface atoms: 74
  - Percent surface: 80%

- **Total atoms:** 792
  - Surface atoms: 394
  - Percent surface: 50%
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

- molecule
- nanoparticle
- bulk metal

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.

<table>
<thead>
<tr>
<th></th>
<th>Z=79</th>
<th>Z=47</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization potentials (eV)</td>
<td>1st:</td>
<td>9.225</td>
</tr>
<tr>
<td></td>
<td>2nd:</td>
<td>20.5</td>
</tr>
<tr>
<td>Electron affinity (eV)</td>
<td></td>
<td>2.039</td>
</tr>
<tr>
<td>Heats of atomization (kJ/mol)</td>
<td>368</td>
<td>285</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td></td>
<td>1063</td>
</tr>
<tr>
<td>A-A distance in f.c.c. cells (Å), 25°C</td>
<td>2.8840</td>
<td>2.8894</td>
</tr>
</tbody>
</table>

Radial contraction
<\textit{r}>_R/<\textit{r}>_{NR} for gold 6s orbital.

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

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

Biomedical Applications

Nonlinear optics

Nanoelectronics

Drug delivery

Imaging agent

Photothermal therapy

Targeting

Radiotherapy

DOI: 10.3390/ijms21072480
Bimetallic nanoparticles including Au

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.

DOI: 10.1002/ppsc.201800111

doi:10.3390/catal6070097

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

Nanoparticles and some preparation methods

**Resistive evaporation method** is a physical vapor deposition technique where vaporized molecules travel from the source to the substrate forming a thin-film coating.

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

**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.

**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.

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

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 Absorption Spectroscopy 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

\[ I = I_0 e^{-\mu(E)d} \]

\[ \chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2 \sigma_j^2}}{k R_j^2} \sin[2kR_j + \delta_j(k)] \]
XAS studies on mono and bimetallic Au NPs: a Short Review
XAS and L$_3$ edges

XANES spectra and 5d orbital occupancy

5d elements

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

DOI: 10.1038/ncomms13481

Monometallic Au nanoparticles
**XANES and EXAFS of Au/mylar**

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.

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**EXAFS data analysis**

\[
\Delta R = - \frac{4}{3} K R_b f \frac{1}{D}
\]

**Contractions explained with a macroscopic liquid drop model**

\[\Delta R = \text{contraction} \quad f = \text{surface stress} \quad R_b = \text{bulk NN distance} \quad D = \text{nanoparticle diameter}.\]

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EXAFS of Au/mylar

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.

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.
AuCu/\text{C} nanoparticles (Au)\text{core}@("Cu)\text{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.

\[
\begin{align*}
\text{Conversion (\%)} & \quad \text{Time (min)} \\
\hline
\text{Au/C} & \quad \square \\
\text{Au13Cu1/C} & \quad \red{\circ} \\
\text{Au4Cu1/C} & \quad \blue{\triangle} \\
\text{Au1Cu1/C} & \quad \green{\downarrow} \\
\text{Au1Cu17/C} & \quad \pink{\uparrow} \\
\text{Cu/C} & \quad \blue{\uparrow}
\end{align*}
\]

Increase of the intensity of the white line indicates the presence of d-holes confirming a charge transfer from Au to Cu.

AuPd
XANES and EXAFS of AuPd/Al$_2$O$_3$ and AuPd/TiO$_2$ NPs

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.

XANES and EXAFS of AuPd/Al₂O₃ and AuPd/TiO₂ NPs

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.

AuAg
XANES and EXAFS of AuAg/Al$_2$O$_3$ 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.

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)

<table>
<thead>
<tr>
<th>Coordination shell</th>
<th>N</th>
<th>R (Å)</th>
<th>σ² (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au Foil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-factor = 0.007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au-Au (I)</td>
<td>12</td>
<td>2.871 (6)</td>
<td>0.0031 (6)</td>
</tr>
<tr>
<td>Au-Au (II)</td>
<td>6 (fixed)</td>
<td>4.066 (8)</td>
<td>0.0044 (9)</td>
</tr>
<tr>
<td>Au/Al₂O₃ SOL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-factor = 0.007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au-Au (I)</td>
<td>7.6</td>
<td>2.828</td>
<td>0.007</td>
</tr>
<tr>
<td>Au/Al₂O₃ SMAD</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>R-factor = 0.006</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Au-Au (I)</td>
<td>8.2</td>
<td>2.844</td>
<td>0.006</td>
</tr>
<tr>
<td>Au-Ag (I)</td>
<td>0.8</td>
<td>2.845</td>
<td>0.008</td>
</tr>
<tr>
<td>Au-Au (II)</td>
<td>4.0</td>
<td>4.030</td>
<td>0.011</td>
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<tr>
<td>Au/Ag/Al₂O₃ SOL</td>
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<tr>
<td>R-factor = 0.008</td>
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<tr>
<td>Au-Au (I)</td>
<td>10.8</td>
<td>2.863</td>
<td>0.0047</td>
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<tr>
<td>Au-Au (II)</td>
<td>5.4</td>
<td>4.057</td>
<td>0.0075</td>
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<tr>
<td>Au/Ag/Al₂O₃ SMAD</td>
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<tr>
<td>R-factor = 0.009</td>
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<tr>
<td>Au-Au (I)</td>
<td>9.1</td>
<td>2.862</td>
<td>0.0045</td>
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<tr>
<td>Au-Ag (I)</td>
<td>1.7</td>
<td>2.862</td>
<td>0.0055</td>
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<tr>
<td>Au-Au (II)</td>
<td>4.4</td>
<td>4.056</td>
<td>0.0079</td>
</tr>
</tbody>
</table>

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