

Electrum, the Gold-Silver Alloy, from the Bulk Scale to the Nanoscale: Synthesis, Properties and Segregation Rules

Grégory Guisbiers^{1,*}, Rubén Mendoza-Cruz^{1,2}, Lourdes Bazán-Díaz^{1,2}, J. Jesús Velázquez-Salazar¹, Rafael Mendoza-Perez¹, José Antonio Robledo-Torres³, José-Luis Rodríguez-Lopez³,
Juan Martín Montejano-Carrizales⁴, Robert L. Whetten¹, Miguel José-Yacamán¹

¹Department of Physics & Astronomy, University of Texas at San Antonio, One UTSA Circle,
San Antonio, TX 78249, United States of America

²Institute of Physics, Universidad Nacional Autónoma de México, A. P. 20-364 Distrito Federal
C.P. 01000 Mexico City, Mexico

³Advanced Materials Department, IPICYT, A.C., Camino Presa San José 2055, Lomas 4^a Secc.
78216 San Luis Potosi, Mexico

⁴Institute of Physics, Universidad Autónoma de San Luis Potosi, Alvaro Obregón 64000, Centro,
San Luis Potosi, Mexico

*E-mail: gregory.guisbiers@physics.org

1. TEM characterization

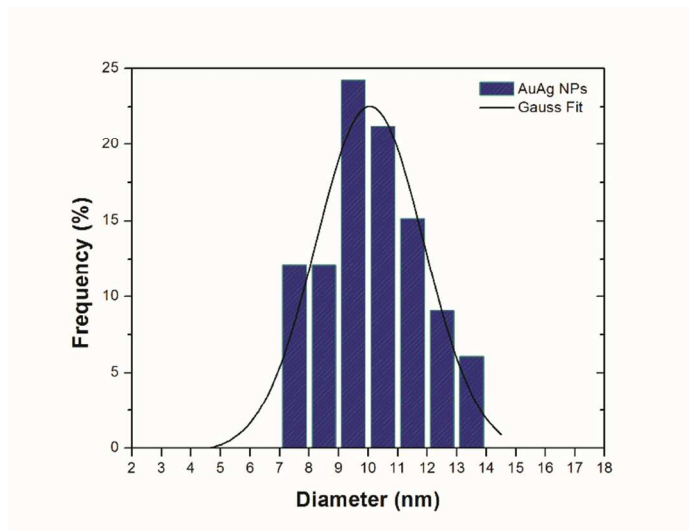


Figure S1. Size distribution of the synthesized Au-Ag nanoparticles. The average diameter is 10.2 ± 1.6 nm.

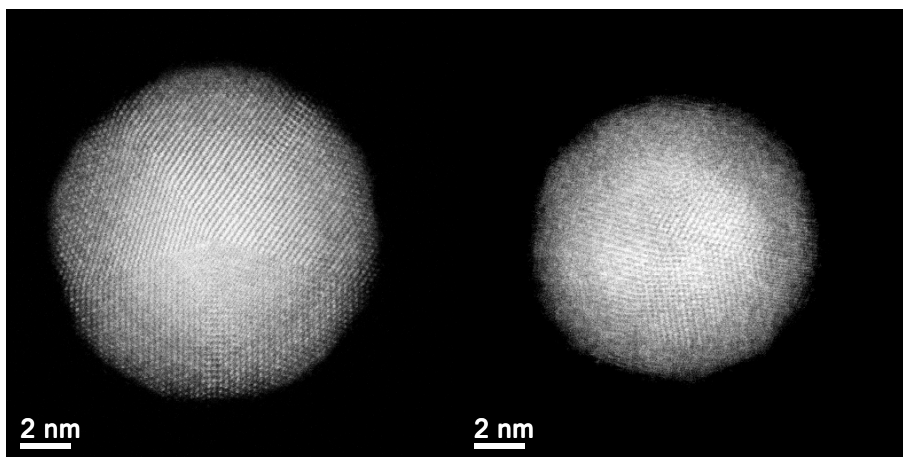


Figure S2. HAADF-STEM images of Au-Ag nanoparticles (co-reduction at 50:50 molar ratio). The contrast in the images is dependent on the average atomic number of the present elements. The brighter center and the faint outer shell evidence an Au-rich core and an Ag-rich surface.

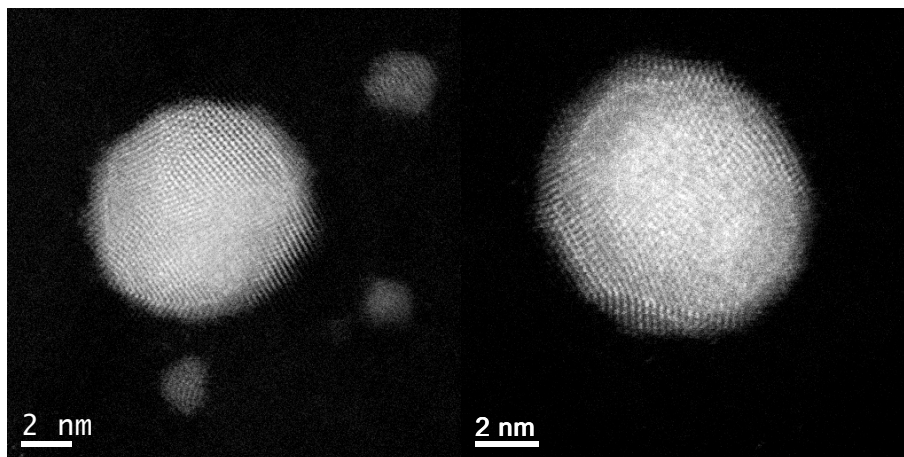


Figure S3. HAADF-STEM images of Au-Ag nanoparticles (co-reduction at 25:75 molar ratio). Notice the contrast difference at the surface of the particle.

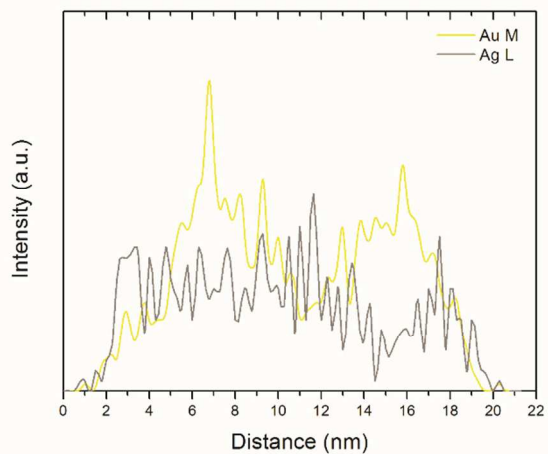
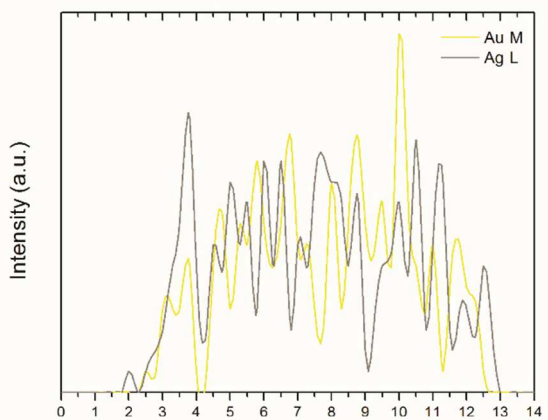
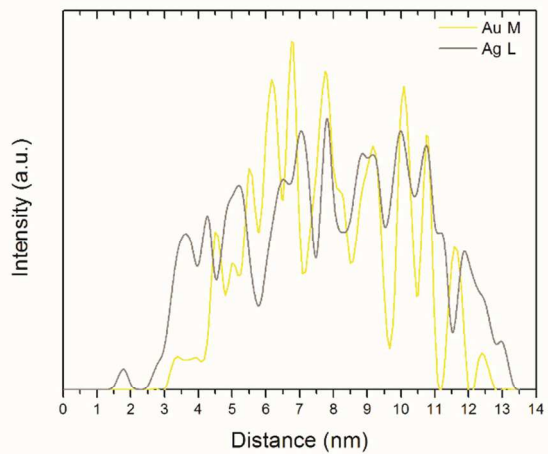
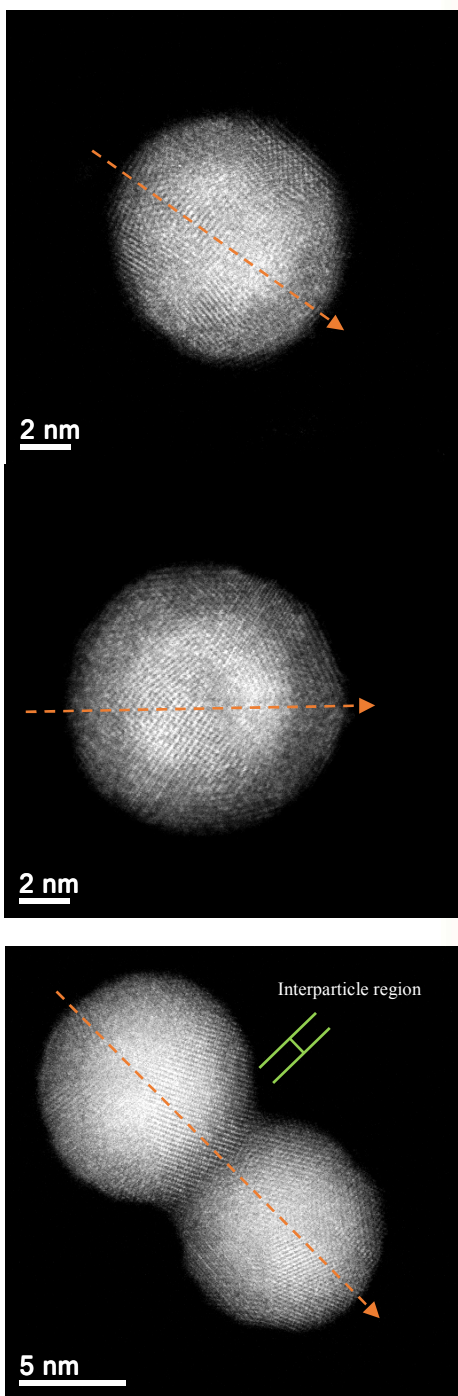


Figure S4. HAADF-STEM images and the corresponding EDS line-scans of different Au-Ag nanoparticles. It is obvious that Au signal is predominant at the center and Ag signal is predominant at the edges of the nanoparticles.

2. Segregation rules

Rigorously, we have to apply the Hume-Rothery rules¹ to determine the miscibility of the alloy.

When applying the Hume-Rothery rules, the miscibility is determined by the following factors:

- The crystal structure
- The atomic radii
- The valence
- The electronegativity

These rules indicate that the alloy is preferred when the crystal structure, atomic radii, valence and electronegativity are similar. Quantitatively, the miscibility can be determined by looking at the bulk phase diagram (total miscibility, partial miscibility or immiscibility). In the case of total miscibility or partial miscibility (ordered phases, or even having the presence of eutectic points), then the first and second rules apply. The first segregation rule says that the element with the highest melting temperature goes to the surface. And the second segregation rule applies only when the two melting temperatures are similar i.e. the segregated element is the one with the lowest surface energy. To be considered similar, the difference between the two melting points should be less than 10% of the highest melting temperature. In the case of total immiscibility, the first segregation rule is de-activated and only the second segregation rule applies.

In the **Au-Ag** alloy (totally miscible), Ag goes to the surface. In this case, Au and Ag have almost the same melting temperature ($\Delta T_{m,\infty} = 102 \text{ K}$, $< 10\%$), then we have to look at the second rule which says that Ag goes to the surface since Ag has the lowest surface energy compared to Au.

In the **Au-Cu** alloy (ordered phases), Au goes to the surface. In this case, Au and Cu have almost the same melting temperature ($\Delta T_{m,\infty} = 20 \text{ K}$, $< 10\%$), then we have to look at the second rule which says that Au goes to the surface since Au has the lowest surface energy compared to Cu.

In the **Cu-Ni** alloy (miscibility gap at low temperatures), Ni goes to the surface because of rule 1, since Ni has the highest melting temperature compared to Cu ($\Delta T_{m,\infty} = 371 \text{ K}$, $> 10\%$).

In the **Ag-Cu** alloy (eutectic), Ag goes to the surface. In this case, Ag and Cu have almost the same melting temperature ($\Delta T_{m,\infty} = 122 \text{ K}$, $< 10\%$), then we have to look at the second rule which says that Ag goes to the surface since Ag has the lowest surface energy compared to Cu.

In the **Ag-Ni** alloy (totally immiscible), Ag goes to the surface. In this case, rule 1 does not apply because this alloy is totally immiscible. Then, we have to look at the second rule which says that Ag goes to the surface since Ag has the lowest surface energy compared to Ni.

In the **Ag-Co** alloy (totally immiscible), Ag goes to the surface. In this case, rule 1 does not apply because this alloy is totally immiscible. Then, we have to look at the second rule which says that Ag goes to the surface since Ag has the lowest surface energy compared to Co.

In the **Pt-Au** alloy (totally immiscible), Au goes to the surface. In this case, rule 1 does not apply because this alloy is totally immiscible. Then, we have to look at the second rule which says that Au goes to the surface since Au has the lowest surface energy compared to Pt.

In the **Pt-Ni** alloy (ordered phases), Pt goes to the surface because of rule 1, since Pt has the highest melting temperature compared to Ni ($\Delta T_{m,\infty} = 313 \text{ K}$, $> 10\%$).

In the **Pt-Pd** alloy (totally miscible), Pd goes to the surface. In this case, Pt and Pd have almost the same melting temperature ($\Delta T_{m,\infty} = 213 \text{ K}$, $< 10\%$), then we have to look at the second rule which says that Pd goes to the surface since Pd has the lowest surface energy compared to Pt.

In the **Ni-Au** alloy (totally immiscible), Au goes to the Surface. In this case, rule 1 does not apply because this alloy is totally immiscible. Then, we have to look at the second rule which says that Au goes to the surface since Au has the lowest surface energy compared to Ni.

3. DDA Method

The Discrete Dipole Approximation method (DDA) developed by Purcell and Pennypacker² has been used in various fields of science, among those, the calculation of optical properties of metal nanoparticles³. The DDA method uses a point cubic arrangement, which describes an object of any arbitrary geometry. Each point represents a dipole that determine the optical response and composition of our object. The point dipole responds to the local electric field through the dipole moment. For an array of N dipoles, each dipole moment is given by the product between the polarizability, α_j , and the local electric field, E_j .

$$P_j = \alpha_j \cdot E_j$$

E_j contains the contribution of the incident electric field and the electric field induced by the other N-1 dipoles:

$$P_j = \alpha_j \cdot \left(E_{j,inc} + \sum_{i=1}^N A_{ij} \cdot P_i \right)$$

The expression A_{ij} is the matrix which couples the electromagnetic interaction between dipoles. Once the dipole moments, P_j , are calculated, we can find the values C_{ext} and C_{abs} of the extinction and absorption cross sections, respectively.

$$C_{ext} = \frac{4\pi k}{|E_0|^2} \sum_{j=1}^N \text{Im} \{ E_{j,inc} \cdot P_j^* \}$$

$$C_{abs} = \frac{4\pi k}{|E_0|^2} \sum_{j=1}^N \left[\text{Im} \{ P_j \cdot (\alpha_j^{-1})^* P_j^* \} - \frac{2}{3} k^3 |P_j|^2 \right]$$

In the last couple of equations the superscript * indicates the complex conjugate and k represents the magnitude of the wave vector of the incident beam. The scattering cross section, C_{sca} , is given by $C_{sca} = C_{ext} - C_{abs}$.

The DDA method has been coded in a program called DDSCAT^{4, 5}, we used this program for the calculations performed in this work.

The length of the edges of the NPs considered in this work are 4 and 10 nm; dimensions that exhibit dispersion effects. Indeed, dispersion effects are presented in NPs for dimensions smaller than 40 nm approximately. Therefore, a size effect correction is performed as explained in Ref.³ and Ref.⁶. The dielectric function of the NPs takes finally the following form:

$$\varepsilon(\omega, a) = \varepsilon_{bulk}(\omega) - \left[1 - \frac{\omega_p^2}{\omega \left(\omega + \frac{i}{\tau} \right)} \right] + \left[1 - \frac{\omega_p^2}{\omega \left(\omega + \frac{i}{\tau} + \frac{i}{\tau(a)} \right)} \right]$$

Where $\varepsilon_{bulk}(\omega)$ is the dielectric function of our material (gold and/or silver) in the bulk, and we will use the values reported in Ref.⁷, ω_p is the electron plasma frequency, $1/\tau$ the damping constant due to electron scattering and $1/\tau(a)$ the damping term due to size effects; for the last three terms we use the values reported in Ref.⁸.

The way to characterize the size of a NP in DDSCAT is through the effective radius, which is defined as the radius of a sphere where its volume equals the volume of the object. The effective radius (nm) of the different structures is shown into the following table.

	4 nm	10 nm
TE	1.21	3.04
CU	2.48	6.20
OC	1.93	4.83
DE	2.08	5.20
DO	4.89	12.23
CO	3.30	8.25
RD	3.61	9.02
TO	5.57	13.92
IC	3.21	8.04

The abbreviations correspond to a Tetrahedron (TE), Cube (CU), Octahedron (OC), Decahedron (DE), Dodecahedron (DO), Cuboctahedron (CO) Rhombic Dodecahedron (RD), Truncated Octahedron (TO) and Icosahedron (IC).

In all the structures, about 10^5 dipoles were used and the refractive index of the surrounding medium was set to $n = 1$. The direction of propagation of the incident light was along the $+X$ axis, and the electric field polarization was on the YZ plane.

References

1. Hume-Rothery, W.; Mabbott, G. W.; Channel Evans, K. M. The Freezing Points, Melting Points, and Solid Solubility Limits of the Alloys of Silver, and Copper with the Elements of the B Sub-Groups. *Philos. Trans. R. Soc., A* **1934**, 233, 1-97.
 2. Purcell, E. M.; Pennypacker, Cr. Scattering and Absorption of Light by Nonspherical Dielectric Grains. *Astrophys. J.* **1973**, 186, 705-714.
 3. Gonzalez, A. L.; Noguez, C. Influence of morphology on the optical properties of metal nanoparticles. *J. Comput. Theor. Nanos.* **2007**, 4, 231-238.
 4. Draine, B. T. The Discrete-Dipole Approximation and Its Application to Interstellar Graphite Grains. *Astrophys. J.* **1988**, 333, 848-872.
 5. Draine, B. T.; Flatau, P. J. Discrete-Dipole Approximation for Scattering Calculations. *J. Opt. Soc. Am. A* **1994**, 11, 1491-1499.
 6. Kreibig, U. Electronic Properties of Small Silver Particles - Optical-Constants and Their Temperature-Dependence. *J. Phys. F Met. Phys.* **1974**, 4, 999-1014.
 7. Johnson, P. B.; Christy, R. W. Optical Constants of Noble Metals. *Phys. Rev. B* **1972**, 6, 4370-4379.
 8. Felidj, N.; Aubard, J.; Levi, G. Discrete dipole approximation for ultraviolet-visible extinction spectra simulation of silver and gold colloids. *J. Chem. Phys.* **1999**, 111, 1195-1208.
-