Structural and Energetic Properties of Au@Ag and Ag@Au Core-Shell Nanoparticles

Ronei Miotto

Centro de Ciências Naturais e Humanas
Universidade Federal do ABC
Santo André, SP, Brazil
Email: `ronei.miotto@ufabc.edu.br`

L. H. Santos, F. D. Kiss, and A. C. Ferraz

Instituto de Física
Universidade de São Paulo
São Paulo, SP, Brazil

Abstract—Using first principles density functional calculations, the stability and structural properties Au@Ag and Ag@Au core shell nanoparticles is explored. Our data shows that the growth of Au shell layers on an Ag core nanoparticle is more likely to happen than the growth of Ag shell layers on an Au core nanoparticle. Our structural analysis indicates that lower coordinated sites experience a bigger contraction when compared to the metallic 12 coordinated sites. In addition, our structural and energetic data for homonuclear Au and Ag nanoparticles indicate that dispersion forces do not decisively influence these properties.

Keywords–nanoparticle; core-shell; dispersion forces

I. INTRODUCTION

Metal nanoparticles (Nps) show size and shape-dependent optical and electronic properties that are appreciable different from those observed for bulk metals. These has lead to extensive investigations involving metallic nanoparticles as building blocks for nanoscale materials and devices. In particular, gold and silver nanoparticles have been extensively explored in a variety of fields, including catalysis, food industry, environmental conservation, fluorescence biosensors, glucose biosensors, nucleic acids-based biosensors, protein-based biosensors, drug delivery vehicles and cancer therapeutic agents [1].

Since gold presents high biocompatibility, chemical stability, and easy surface modification, it is often considered to be more suitable for biomedical applications [1]. Silver, on the other hand, presents higher plasmonic efficiency and superior magnetic enhancement in the visible range and it is more attractive for optoelectronics, photovoltaics, and sensing [1]. In order to combine these properties, a great deal of attention has been devoted to the synthesis of core shell and alloy bimetallic NPs. The main idea is to tune the NPs optical catalytic properties and making them useful in other fields, such as taggants for security applications [2].

The AuAg system is of particular interest since the Surface Plasmon Resonance (SPR) band might be tunable between ~520 nm for Au and ~410 nm for Ag [2]. These interesting physical and chemical properties appear because of the combination of two kinds of metals and their fine structures, evolving new surface characteristics. With a view to contribute to a better understanding of the surface properties of these complex systems, in this work we explore the stability and structural properties Au@Ag and Ag@Au core shell NPs. In addition, the influence of dispersion (van der Waals) interactions in the core shell properties is also discussed.
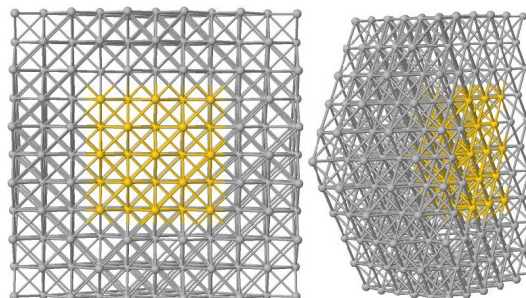

Figure 1. Schematic representation of a 561 atoms nanoparticle, with 2 gold core layers (gold atoms) and 3 silver shell layers (gray atoms), refered as 3Ag@2Au for simplicity.

The paper is structured as follows. In Section II, we briefly describe our theoretical approach. In Section III, our results for Au@Ag and Ag@Au core shell NPs are discussed and compared to available theoretical and experimental works. Finally, a summary is presented in Section IV.

II. THEORETICAL MODELING

Cube-octahedral nanoparticles with 147, 309, 561 and 923 atoms are modeled considering an extended bulk with a face centered cubic (FCC) crystalline packing properly cut to give the desired geometry, following the procedure described in [3]. These nanoparticle's sizes where chosen in order to guarantee that the studied systems can properly represent the nanoparticle's properties [3]. By construction, our nanoparticles are similar to onions, i.e., the growth of a nanoparticle is done by layers. This is consistent with the experimental findings by Maenosono and co-workers [4] suggesting that the shell layers thickness can be closely controlled. The 561 atoms nanoparticle, for example, has 5 layers. Core shell nanoparticles are then constructed by the exchange of a complete layer of atoms. Following this picture, for a 561 atoms nanoparticle, for example, 3Ag@2Au indicates a nanoparticle with 2 gold core layers and 3 silver shell layers. The 3Ag@2Au nanoparticle is schematically represented in Figure 1.

Our simulations are performed considering the supercell scheme and a vacuum region greater than 10 Å between the images. The ionic potentials are described by ultra-soft pseudopotential [5][6][7] and the electron-electron exchange-correlation interactions are described within density functional theory (DFT) considering the generalized gradient approximation as proposed by Perdew and Wang (PW91) [8]. Spin

polarization effects, as considered in the Vienna Ab-initio Simulation Package (VASP) [9][10], are explicitly treated. The single-particle orbitals are expressed in a plane waves base with energy up to 290 eV, considering only the Γ point inside the Brillouin zone. Increasing the number of **k**-points or the basis set results in changes in total energies, atomic distances and vibrational modes smaller than 0.05%, 0.1% and 0.8%, respectively. The atoms are assumed to be on their low energy position when the forces are smaller than 10 meV/Å. Dispersion forces, indicated by vdW for short, are taken into account by a simple pair-wise force field, as proposed by Grimme [11]. The C6 and R0 vdW parameters for gold (silver) are 40.62 (24.67) and 1.772 (1.639), respectively. Formation energy per atom is obtained using

$$E_f = \frac{E_{system} - (N_{Ag} \times \mu_{Ag} + N_{Au} \times \mu_{Au})}{N_{tot}}, \qquad (1)$$

where E_{system} is the total energy of a given configuration, N_{Au} and N_{Ag} are the total number of Au and Ag atoms, respectively, μ_X is the chemical potential of atom X and $N_{tot} = N_{Au} + N_{Ag}$, i.e., the total number of atoms in the system.

III. RESULTS AND DISCUSSION

In the first step of our study, we investigate the influence of the inclusion of dispersion forces (vdW) on the energetic and structural properties of different sized homonuclear nanoparticles. Figure 2 presents the energy per atom for different gold and silver nanoparticles, bare surfaces and metallic bulk against their mean coordination number. Nanoparticles with 147, 309, 561 and 923 atoms have coordinations numbers 8.98, 9.63, 10.05, and 10.35, respectively. The bare 001 and 111 coordination numbers are 10.67 and 11.00, while the bulk coordination number is 12. It is clear from this figure that both gold and silver have similar linear regression coefficients: 0.23 and 0.21, respectively, when vdW is included and 0.13 in both cases when dispersion forces are not included. In other words, the effect of vdW is different for different sized nanoparticles. When vdW is included, the overall change in energy per atom is smaller for smaller nanoparticles. This is probably related to the fact that smaller nanoparticles also have smaller coordination numbers. In other words, since smaller nanoparticles have a smaller percentile number of ideal 12-coordinated sites, vdW interactions are more relevant in the description of the lower coordinated sites. This is consistent with previous observations of smaller energy differences for atomic adsorption, e.g., noble gases [12], on metallic surface sites with different coordinations when vdW interactions are considered.

In Table I, we compare the average bond contraction for homonuclear Ag nanoparticles as a function of its coordination sites considering (vdW) or not (no vdW) dispersion forces. The average bond contraction, in %, was found comparing the average bond distance between a given atom site and its first neighboring atoms for the ideal bulk NP and the relaxed one. The mean value is obtained considering all studied nanoparticles. It is clear from this table that lower coordinated sites experiences a bigger contraction when compared to the metallic 12 coordinated sites. Similar contraction patterns are observed for Au nanoparticles. The inclusion of dispersion forces only slightly decreases the observed contractions. Our
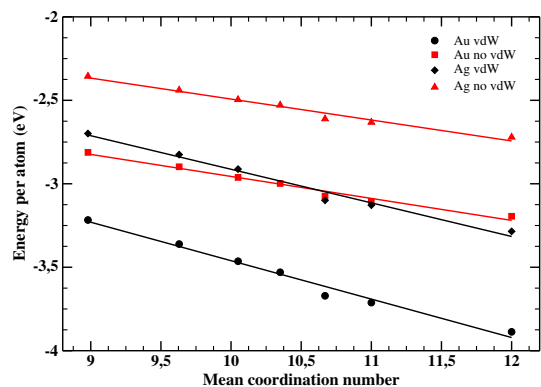

Figure 2. Energy per atom, in eV, for different gold and silver nanoparticles, bare surfaces and metallic bulk against their mean coordination number. The solid lines are linear regression fits.

TABLE I.   AVERAGE BOND CONTRACTION, IN %, OF SILVER NPS FOR DIFFERENT COORDINATION SITES CONSIDERING (VDW) OR NOT (NO VDW) DISPERSION FORCES.

site	average contraction (%)	
	vdW	no vdW
c5	3.5	4.3
c7	2.1	2.6
c8	1.1	1.5
c9	0.9	1.0
c12	1.1	1.2

structural and energetic data for homonuclear Au and Ag nanoparticles indicate that dispersion forces do not decisively influence these properties. Therefore, in the following discussion, we will present only the results obtained for one set of calculations and comment on the other.

In Figure 3, we present the difference in formation energies, or energy gain in eV, (no vdW) when a new shell is adsorbed on the top of a 147 nanoparticle (corresponding to 3 atomic layers). We consider both Ag and Au cores covered by additional Au or Ag shell layers. Our calculations indicate that starting from an Au core, it is always less favorable to encapsulate it with one or more Ag shell layers rather than adding an additional Au shell layer. For an Ag core nanoparticle, on the other hand, the addition of Au shell layers is always more favorable than the growth of a bigger homonuclear Ag nanoparticle. In other words, our data indicates that the growth of an Au shell layer on an Ag core nanoparticle is more likely to happen than the growth of Ag shell layers on an Au core nanoparticle. Similar results were obtained for larger (306 and 561) nanoparticles. This is consistent with the experimental findings indicating that growth of Ag shells on Au cores requires a reducing agent for reducing Ag(I) to Ag(0). In contrast, growth of Au shells on Ag can often be accomplished by galvanic exchange or transmetalation reactions that oxidize Ag(0) to Ag(I) dissolved in solution while reducing Au(III) or Au(I) to Au(0) [2]. As a consequence, Ag@Au nanoparticles are characterized by a smooth Ag shell layer, observed by Güzel *et al* [13] using Ultraviolet visible (UVVis), Reflection Absorption Infra-Red (RAIRS) and X-ray photoelectron (XPS) spectroscopy. Our findings are also consistent with other synthetic routes, such as the use of Neem (Azadirachta indica) leaf broth, proposed
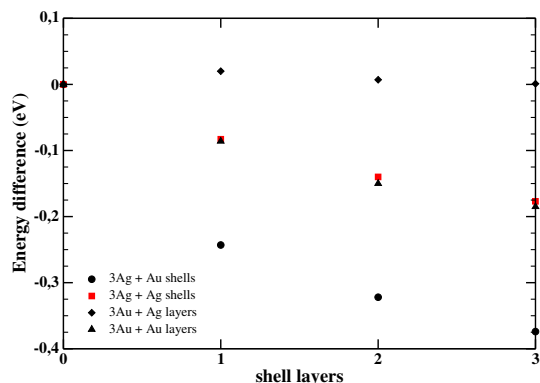
Figure 3. Formation energy difference (no vdW), in eV, when a new shell is adsorbed on the top of a 147 nanoparticle (corresponding to 3 atomic layers).

by Shankar et al. [14]. Using this approach, Shankar et al. have found that in a competitive process involving both silver and gold ions, the reduction of gold ions is accelerated. As a consequence, silver do not form a uniform layer around core gold nanoparticles, but rather form small nanoparticles that decorate them. Although small energy differences are observed when dispersion forces (vdW) are considered, the same energy pattern was found. It is important to mention that our simulations do not consider possible exchange or diffusion mechanisms, although they might play an important role in the growth process, as suggested by Shibata et al. [15].

Next, we analyze the shape of the studied nanoparticles. By construction, all unrelaxed nanoparticles considered present a cube-octahedral structure. The largest distance inside a nanoparticle is from the central atom to the c5 site. Upon relaxation, for Ag using vdW, this distance experiences a contraction ranging from 0.13 Å, or 1.5%, to 0.31 Å, or 1.8%, when the size of the nanoparticle increases from 147 to 923 atoms. A larger contraction is observed for gold nanoparticles and vdW: 0.10 Å (1.1%) and 0.43 Å (2.5%), respectively. In a similar manner, the bond angles between the c5 site and its 4 first neighbors is 300° for the unrelaxed nanoparticle. Upon relaxation, increasing the size of the nanoparticles from 147 to 923, the angles increase to 305° and 309° for silver and to 310° and 313° for gold, respectively. Therefore, our data indicates that, for pure cube-octahedral samples, gold nanoparticles are more likely to have a spherical shape when compared to silver nanoparticles. This is in agreement with TEM images obtained by Shankar et al. [14] indicating that gold and silver nanoparticles formed were predominantly spherical, although thin planar structures were also observed for the former, when Neem leaf broth was used in the nanoparticles synthesis process.

We next analyze the 3Ag@3Au, 3Au@3Ag, 2Ag@4Au and 2Au@4Ag 923 atom core-shell nanoparticles. The same contraction pattern of pure nanoparticles is observed, i.e., we observe a larger contraction for Au@Ag when compared to Ag@Au nanoparticles. Interestingly, with only 2 Au shell layers (2Au@4Ag) and vdW the distance between the c5 and the central atom (0.43 Å) is already of the same magnitude observed for the pure gold 923 atoms nanoparticle. The bond angles between the c5 site and its 4 neighboring atoms for Au@Ag nanoparticles (313°) are similar to the ones observed

for pure Au nanoparticles. In a similar manner, the bond angles for Ag@Au (309°) are close to the values observed for pure Ag nanoparticles. In other words, our data indicates that Au@Ag nanoparticles are more rounded when compared to Ag@Au nanoparticles, in a clear indication that the structural behavior of core-shell nanoparticles are dominated by the shell layers, with small influence of the core. This is consistent with the TEM images obtained by Shankar and co-workers [14] suggesting that the Ag@Au nanoparticles are predominantly spherical in morphology. In a similar manner, Güzel *et al* [13] TEM images of Au and Au@Ag NPs showed that most of these nanoparticles present a spherical shape. In addition, Shankar et al., based on a comparison of the TEM images of silver, gold, and bimetallic Ag@Au nanoparticles, suggested that the cores in the bimetallic Ag@Au nanoparticles resemble that of pure gold nanoparticles and the particles constituting the shell resemble pure silver nanoparticles in terms of both their size and shape.

IV. CONCLUSIONS

Using first principles density functional calculations, the stability and structural properties Au@Ag and Ag@Au core shell nanoparticles are explored. Our data shows that the growth of an Au shell layers on an Ag core nanoparticle is more likely to happen than the growth of an Ag shell layers on an Au core nanoparticle. Our structural analysis indicates that lower coordinated sites experience a bigger contraction when compared to the metallic 12 coordinated sites. Our structural and energetic data for homonuclear Au and Ag nanoparticles indicate that dispersion forces do not decisively influence these properties. Our data indicates that the effect of vdW is different for different sized nanoparticles. When vdW is included, the overall change in energy per atom is smaller for smaller nanoparticles. In addition, our results indicate that Au@Ag nanoparticles are more rounded when compared to Ag@Au nanoparticles, in a clear indication that the structural behavior of core-shell nanoparticles are dominated by the shell layers, with small influence of the core. In the next step of our work, the adsorption of functional groups and species on different nanoparticle's surfaces are going to be investigated.

REFERENCES

[1] A. Majdalawieh, M. C. Kanan, O. El-Kadri, and S. M. Kanan, "Recent Advances in Gold and Silver Nanoparticles: Synthesis and Applications," Journal of Nanoscience and Nanotechnology, vol. 14, no. 7, Jul. 2014, pp. 4757–4780. [Online]. Available: http://openurl.ingenta.com/content/xref?genre=article&issn=1533-4880&volume=14&issue=7&spage=4757

[2] M. S. Shore, J. Wang, A. C. Johnston-Peck, A. L. Oldenburg, and J. B. Tracy, "Synthesis of Au(Core)/Ag(Shell) nanoparticles and their conversion to AuAg alloy nanoparticles." Small (Weinheim an der Bergstrasse, Germany), vol. 7, no. 2, Jan. 2011, pp. 230–4. [Online]. Available: http://www.ncbi.nlm.nih.gov/pubmed/21213387

[3] F. D. Kiss, R. Miotto, and A. C. Ferraz, "Size effects on silver nanoparticles' properties." Nanotechnology, vol. 22, no. 27, Jul. 2011, p. 275708. [Online]. Available: http://www.ncbi.nlm.nih.gov/pubmed/21597143

[4] S. Maenosono, J. Lee, A. T. N. Dao, and D. Mott, "Peak shape analysis of Ag 3d core-level X-ray photoelectron spectra of Au@Ag core-shell nanoparticles using an asymmetric Gaussian-Lorentzian mixed function," Surface and Interface Analysis, vol. 44, no. 13, Dec. 2012, pp. 1611–1614. [Online]. Available: http://doi.wiley.com/10.1002/sia.5078

[5] D. Vanderbilt, "Optimally smooth norm-conserving pseudopotentials," Physical Review B, vol. 32, no. 12, Dec. 1985, pp. 8412–8415. [Online]. Available: http://link.aps.org/doi/10.1103/PhysRevB.32.8412

[6] ——, "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism," Physical Review B, vol. 41, no. 11, Apr. 1990, pp. 7892–7895. [Online]. Available: http://link.aps.org/doi/10.1103/PhysRevB.41.7892

[7] G. Kresse, "From ultrasoft pseudopotentials to the projector augmented-wave method," Physical Review B, vol. 59, no. 3, Jan. 1999, pp. 1758–1775. [Online]. Available: http://link.aps.org/doi/10.1103/PhysRevB.59.1758

[8] J. P. Perdew, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, "Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation," Physical Review B, vol. 46, no. 11, Sep. 1992, pp. 6671–6687. [Online]. Available: http://link.aps.org/doi/10.1103/PhysRevB.46.6671

[9] G. Kresse, "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set," Physical Review B, vol. 54, no. 16, Oct. 1996, pp. 11 169–11 186. [Online]. Available: http://link.aps.org/doi/10.1103/PhysRevB.54.11169

[10] G. Kresse and J. Furthmüller, "Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set," Computational Materials Science, vol. 6, no. 1, Jul. 1996, pp. 15–50. [Online]. Available: http://linkinghub.elsevier.com/retrieve/pii/0927025696000080

[11] S. Grimme, "Semiempirical GGA-type density functional constructed with a long-range dispersion correction." Journal of computational chemistry, vol. 27, no. 15, Nov. 2006, pp. 1787–99. [Online]. Available: http://www.ncbi.nlm.nih.gov/pubmed/16955487

[12] Q.-S. Chen, F. J. Vidal-Iglesias, J. Solla-Gullon, S.-G. Sun, and J. M. Feliu, "Role of surface defect sites: from Pt model surfaces to shape-controlled nanoparticles," Chemical Science, vol. 3, 2012, pp. 136–147.

[13] R. Güzel, Z. Ustünda, H. Eki, S. Keskin, B. Taner, Z. G. Durgun, A. A. I. Turan, and A. O. Solak, "Effect of Au and Au@Ag core-shell nanoparticles on the SERS of bridging organic molecules." Journal of colloid and interface science, vol. 351, no. 1, Nov. 2010, pp. 35–42. [Online]. Available: http://www.ncbi.nlm.nih.gov/pubmed/20701922

[14] S. S. Shankar, A. Rai, A. Ahmad, and M. Sastry, "Rapid synthesis of Au, Ag, and bimetallic Au core-Ag shell nanoparticles using Neem (Azadirachta indica) leaf broth." Journal of colloid and interface science, vol. 275, no. 2, Jul. 2004, pp. 496–502. [Online]. Available: http://www.ncbi.nlm.nih.gov/pubmed/15178278

[15] T. Shibata, B. A. Bunker, Z. Zhang, D. Meisel, C. F. Vardeman, and J. D. Gezelter, "Size-Dependent Spontaneous Alloying of AuAg Nanoparticles," Journal of the American Chemical Society, vol. 124, no. 40, Oct. 2002, pp. 11 989–11 996. [Online]. Available: http://pubs.acs.org/doi/abs/10.1021/ja026764r