Eur. Phys. J. D **24**, 111–114 (2003)
DOI: 10.1140/epjd/e2003-00156-y

THE EUROPEAN PHYSICAL JOURNAL D

Optical properties of mixed clusters: comparative study of Ni/Ag and Pt/Ag clusters

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Received 10 September 2002

Abstract. The optical properties of mixed $(\mathrm{Ni}_{0.5}\mathrm{Ag}_{0.5})_n$ and Pt/Ag clusters are investigated in the size range 2−5 nm. Low Energy Ion Spectroscopy (LEIS) experiments show that the cluster surface is entirely covered by silver atoms for the two systems. The optical spectra of Ni/Ag clusters exhibit a large Surface Plasmon Resonance (SPR), damped and widened when the cluster size decreases, in agreement with a classical model assuming a core-shell geometry and including the reduction of the conduction electron mean-free path in the silver shell. For Pt/Ag clusters, no SPR emerges in the size range 2−5 nm, although it is predicted within a classical model, a pronounced SPR appearing only for clusters larger than 10 nm in diameter.

PACS. 36.40.Vz Optical properties of clusters – 36.40.-c Atomic and molecular clusters – 78.66.Bz Metals and metallic alloys

1 Introduction

Simple metal particles exhibit specific properties due to electronic and dielectric confinements. In the nanosized range, the photoabsorption spectra are dominated by the surface plasmon resonance band whose position and width depend on the intrinsic properties of the clusters and the surrounding medium [1]. The study of bimetallic particles is of double interest since they yield size-dependent properties and mirror original features of alloys. Depending on the thermodynamic properties of both components, mixed particles can form either homogeneous alloys or segregated core-shell structures. An insight into bulk properties of both constituent materials (Wigner-Seitz radius (r_s), surface energies) and their corresponding binary phase diagrams brings indications about the possible structure of the composite clusters. In general, one expects the metal component with the lower surface energy to accumulate preferentially at the surface. However, in the case of systems in solutions like colloids, one has to be careful with such simple rules because the kinetics of reduction as well as the surface adsorbed ions and the surrounding medium come also into play.

The present work intends to compare the optical properties of mixed Ni/Ag and Pt/Ag clusters in the size range 2−5 nm. Concerning the bulk properties of these materials, the phase diagram of Ni/Ag shows that Ni and Ag are immiscible over the entire composition range. One can suppose that the silver atoms will move onto the cluster surface for both systems since the surface energy of silver is the lower one and that the resulting structure will be a core/shell one. As for the Pt/Ag phase diagram, several alloys are present, so the assumption of a core/shell structure has to be taken with caution. Moreover, the atomic Wigner-Seitz radii of Ag and Ni are noticeably different ($r_s(\mathrm{Ag}) = 3.02$ a.u. and $r_s(\mathrm{Ni}) = 2.6$ a.u.) and a pronounced lattice mismatch is expected whereas they are closer for Pt and Ag ($r_s(\mathrm{Pt}) = 2.9$ a.u.). To our knowledge, no study has been performed on Ni/Ag clusters, except a recent Low-Frequency Raman Scattering experiment, that shows that the acoustic mode frequencies of the Ni/Ag particles are in agreement with a core/shell structure in which the silver interacts only weakly with the nickel core. The observed vibrational quadrupolar modes are attributed to the vibration of the silver shell alone [2]. Besides, a lot of works on Ni/Ag films emphasize the low interaction between Ag and Ni atoms [3]. Concerning the optical properties of Pt/Ag clusters, a few

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studies deal with clusters produced by chemical way. For instance, Pt/Ag clusters prepared by simultaneous reduction of bimetallic salts [4] yield optical absorption corresponding to Ag-core/Pt-shell structures. Such a morphology seems to be ruled by the kinetics of reduction. On the other hand, Torigoe *et al.* [5] produced small bimetallic colloids (2−5 nm in diameter) and conclude from High Resolution Transmission Electron Microscopy (HRTEM) analysis (lattice spacing measurements) that the particles are alloyed (namely, both metals are homogeneously mixed within the particles). Optical spectra exhibit a plasmon resonance which blue-shifts with increasing Pt proportion. However, the authors think that silver colloids nucleate first, and then platinum settles onto the silver surface. This mechanism of formation suggests that the systems should form a core/shell structure or perhaps a stacking of nanodomains. The only technique that could provide a information about the alloying is the HRTEM but unfortunately the lattice spacing of silver and platinum are nearly similar. Moreover, the lattice spacing that they obtain for the mixed particles is near the silver one [5]. Besides, calculations based on a tight-binding scheme, in order to study the surface segregation in $(\mathrm{Pt}_{0.5}\mathrm{Ag}_{0.5})_n$ cubooctahedra show that Ag atoms segregate onto the surface of the cluster [6]. The extent of this segregation is found to be less for smaller particles

In this paper are reported the size dependence of the absorption spectra in $(\mathrm{Ni}_{0.5}\mathrm{Ag}_{0.5})_n$ clusters (Sect. 3.1). The experimental results are interpreted within a classical approach, assuming a core/shell geometry. Results concerning Pt/Ag clusters for two different compositions are also presented (Sect. 3.2). Unlike Ni/Ag clusters, Pt/Ag ones do not exhibit any plasmon resonance in this size range, although it is expected within the Mie theory assuming a core/shell geometry.

2 Experiments

Clusters are produced by a laser vaporization source using a continuous flow of helium [7]. Briefly, a frequency double Nd:YAG pulsed laser ($\lambda = 532$ nm) is focused onto a metallic rod of the alloy $\mathrm{M}_x\mathrm{Ag}_{1-x}$ to be studied (M = Ni or Pt and x is the atomic concentration of Ni or Pt) and produces a bimetallic plasma. It is further cooled by the He gas and combines into clusters that expand through a conical nozzle. The cluster beam is then collimated by a skimmer into a high vacuum chamber (10^{-7} mbar) and the particles are co-deposited with the transparent alumina matrix [7] (evaporated thanks to an electron gun) on various substrates depending on the measurements to be performed. By varying the He pressure or by using a mixture He–Ar, one can change the mean cluster size. On the other hand, the metal volumic concentration is kept below 5% to minimize the cluster coalescence.

By Energy Dispersive X-ray (EDX) and Rutherford Backscattering (RBS) [8] analyses, the relative atomic composition $\mathrm{Ni}_x\mathrm{Ag}_{1-x}$ of the target is recovered in the samples, suggesting that the average stoichiometry of the clusters is also the same. Concerning the Pt/Ag system, the situation is different. For composite rods $\mathrm{Pt}_{0.5}\mathrm{Ag}_{0.5}$ and $\mathrm{Pt}_{0.25}\mathrm{Ag}_{0.75}$ RBS analysis of the samples leads to the values $x = 0.3$ and $x = 0.18$, respectively. Similar discrepancies are deduced from EDX analysis. Therefore, Chemical analyses (Inductively Coupled Plasma (ICP)) of powders, directly extracted from the rod target, have been performed to check the exact stoichiometry of the alloy and compositions of $\mathrm{Pt}_{0.42}\mathrm{Ag}_{0.58}$ and $\mathrm{Pt}_{0.21}\mathrm{Ag}_{0.79}$ were found instead of $\mathrm{Pt}_{0.5}\mathrm{Ag}_{0.5}$ and $\mathrm{Pt}_{0.25}\mathrm{Ag}_{0.75}$. Finally, one can conclude that if the average cluster film stoichiometry is consistent with the one of the target in the case of the $\mathrm{Pt}_{0.25}\mathrm{Ag}_{0.75}$ alloy, the non negligible enrichment in silver remains obvious in clusters produced from the $\mathrm{Pt}_{0.5}\mathrm{Ag}_{0.5}$ alloy. The size distributions of the samples are analyzed by Transmission Electron Microscopy (TEM). Clusters appear almost spherical and randomly distributed in the transparent matrix. Absorption measurements are performed with a Perkin-Elmer spectrophotometer, under Brewster incidence with *p*-polarized light (in order to get rid of the multiple reflexions in the thin composite film), in the energy range 1.55−4.51 eV (275−800 nm) [9].

3 Results and interpretation

3.1 $(\mathrm{Ni}_{0.5}\mathrm{Ag}_{0.5})_n$ clusters

In order to determine the surface composition of $(\mathrm{Ni}_{0.5}\mathrm{Ag}_{0.5})_n$ clusters, Low Energy Ion Scattering experiments (LEIS) have been performed on supported clusters under ultra high vacuum. The results which will be detailed in a forthcoming paper [9] show that the cluster surface is entirely composed of silver. In view of the immiscibility of both materials, these results highly suggest that the Ni/Ag system forms a core-shell structure.

The size evolution of the absorption spectra is displayed in Figure 1. A surface plasmon resonance (SPR) is clearly observed in the same spectral range as the one obtained for pure silver clusters, but it appears broadened and damped. The main features of the size dependence are the increasing widening and damping with decreasing size whereas no clear shift of the SPR is noticed.

We have previously developed a semi-classical model to calculate the optical response of mixed clusters like the Au/Ag alloys [10]. This model requires to separate the contribution of the delocalized conduction *s*-electrons that are quantum-mechanically treated from the contribution of the banded *d*-electrons that are described as a classical polarizable medium. Nickel is a transition metal for which it is not possible to extract a Drude component in the dielectric function since the s and d bands are hybridized. Therefore, this model cannot be applied here. Consequently, only a classical model can be introduced to interpret our results. In the very upper part of Figure 1 is reported the theoretical absorption of $(\mathrm{Ni}_{0.5}\mathrm{Ag}_{0.5})_n$ clusters, assuming a core/shell geometry [11]. If the calculated absorption band is found larger than in the case of pure silver clusters, it is still less important than the experimental broadening. It can be explained by the neglect of inhomogeneous effects in the samples (size, shape and local

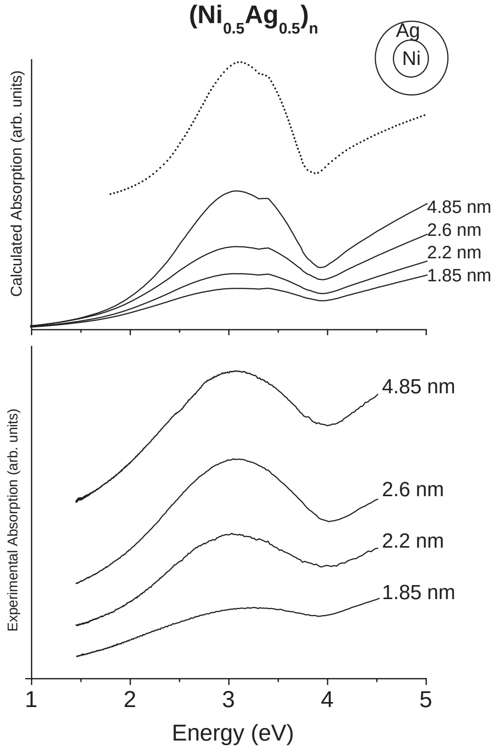

Fig. 1. Optical absorption of $(\mathrm{Ni}_{0.5}\mathrm{Ag}_{0.5})_n$ clusters. Lower part: experimental spectra obtained under Brewster incidence for different optical diameters $D_{opt} = \sqrt[3]{\langle D^3\rangle}$. Upper part: core-shell model involving the experimental dielectric functions of bulk Ni and Ag (dotted line) and core-shell model including the surface scattering-limited mean-free-path contribution in the silver shell for the sizes corresponding to experiment (black lines).

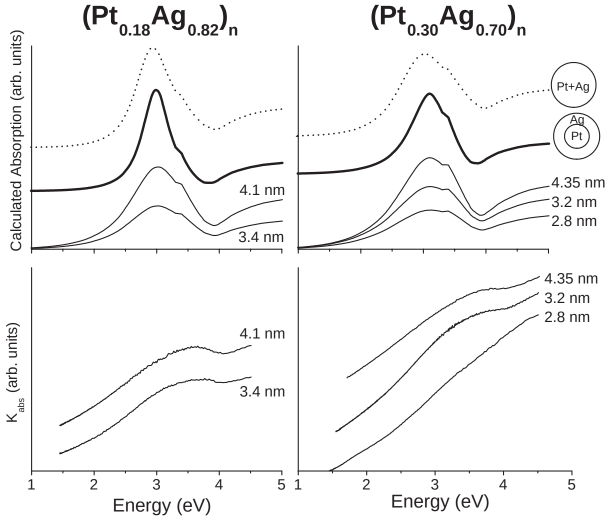

Fig. 2. Optical absorption of $(\mathrm{Pt}_{0.18}\mathrm{Ag}_{0.82})_n$ and $(\mathrm{Pt}_{0.3}\mathrm{Ag}_{0.7})_n$ clusters. Lower part: experimental spectra obtained under Brewster incidence for different optical diameters. Upper part: classical model assuming that the dielectric function of the particles is the weighted average of those of both constituents (dotted line). Core-shell model involving the experimental dielectric functions of Pt and Ag (bold line) and core-shell model including the surface scattering-limited mean-free-path contribution in the silver shell for the sizes corresponding to experiment (black lines).

porosity), but also by the use of the bulk dielectric functions of both materials which underestimate the damping constant Γ characterizing the conduction electron scattering rates in the particle. Moreover, the chemical calculations are only sensitive to the cluster composition but independent of their size. Nevertheless, one can notice that the theoretical SPR remains in the same spectral range as the one obtained experimentally. In order to introduce a more realistic damping constant and to interpret the size evolution of the optical spectra, the surface scattering-limited mean-free-path contribution has been included in the silver dielectric function parametrized as the sum of a Drude formula and an interband transition contribution [1,9]. The mean free path of the silver conduction electrons in the shell is assumed to be, as proposed by Granqwist and Hunderi [12]: $l_{path} = \sqrt[3]{(R-R_c)(R^2-R_c^2)}$ where R_c and R denote respectively the core and total cluster radii. No finite size effect is included in the Ni-core, described merely by its bulk experimental dielectric function.

Theoretical results are compared to experiment in Figure 1. One can see that the damping and broadening are well-reproduced by the model in spite of its crudeness. Actually, for a small amount of silver in small clusters, the silver shell is incomplete and the model is less appropriate. However, one can conclude that the properties of the composite particles remain related to those of constituents, namely, the dielectric function of the mixed system and those of Ni and Ag are closely correlated. The system is surely not an alloy with its intrinsic dielectric function. A more exhaustive study of $(\mathrm{Ni}_x\mathrm{Ag}_{1-x})_n$ clusters will be reported in a forthcoming paper [9].

3.2 $(\mathrm{Pt}_x\mathrm{Ag}_{1-x})_n$ clusters

The surface composition of Pt/Ag clusters produced from an alloy $\mathrm{Pt}_{0.5}\mathrm{Ag}_{0.5}$ has been investigated by LEIS experiments. The results prove that the cluster surface is mainly composed of silver, like in Ni/Ag clusters. Nevertheless, the presence of alloys in the phase diagram casts doubts on a perfect core/shell geometry, the LEIS analysis proving only that at least one monolayer of silver covers the cluster surface. The absorption spectra of the $\mathrm{Pt}_{0.3}\mathrm{Ag}_{0.7}$ clusters produced from a $\mathrm{Pt}_{0.5}\mathrm{Ag}_{0.5}$ alloy are given on the right side of Figure 2. They do not show a marked SPR in the size range 2–5 nm. By increasing the silver proportion inside the clusters (left side of Fig. 2), one can see that the SPR, although more apparent, is much more damped compared to the one observed in Ni/Ag clusters. The theoretical absorption of these systems, assuming a core/shell geometry, is reported in the upper part of Figure 2 and for both compositions, a large resonance band is expected. Calculations have been also performed assuming an homogeneous dielectric function equal to the volumic weighted

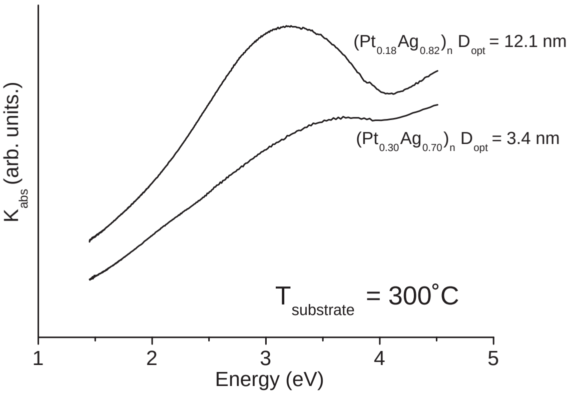

Fig. 3. Experimental absorption spectra of Pt/Ag clusters embedded in alumina and deposited on a silica substrate kept at 300 °C.

average of the constituent ones. In this case the SPR is enlarged but does not disappear as observed experimentally. Including the surface scattering-limited mean-free-path in the silver shell strenghtens the damping but cannot explain the experimental results. In order to increase the mean cluster size in the samples, clusters have been deposited on a substrate kept at a constant temperature of 300 °C. This technique favours the coalescence and actually, the size distribution of $(\mathrm{Pt}_{0.18}\mathrm{Ag}_{0.82})_n$ clusters is shifted to larger sizes (mean size of about 10.5 nm in diameter), the shape of the clusters remaining spherical. However, in the case of $(\mathrm{Pt}_{0.3}\mathrm{Ag}_{0.7})_n$, the mean size was hardly modified. This difference may be explained by a less efficient coalescence of clusters when the proportion of Pt is larger owing to the higher melting temperature of this element as compared to silver. The corresponding absorption spectra of these two samples are given in Figure 3. A pronounced SPR appears for clusters of 12 nm in optical diameter, blue-shifted compared to the Mie theory. This can be explained by a possible change of the alumina matrix index when deposited at 300 °C. For $(\mathrm{Pt}_{0.3}\mathrm{Ag}_{0.7})_n$ clusters, the SPR remains damped and similar to the one observed for clusters deposited at room temperature. Therefore, one can suppose that the emergence of the SPR is correlated to the size variation. Finally, we indeed observe the plasmon resonance when the size increases drastically. At these large sizes, the segregation of silver is perhaps more efficient. Another possibility is that the resultant dielectric constant of the formed alloy is such as the plasmon resonance emerges only at large sizes, as it is observed in pure copper clusters [13].

4 Conclusion

The size dependence of the optical properties of $(\mathrm{Ni}_{0.5}\mathrm{Ag}_{0.5})_n$ clusters has been investigated. LEIS experiments provide the undisputed evidence that the surface of the clusters is covered by silver atoms, suggesting that the geometry of the system is a core-shell one. The optical properties of this system are found to be intermediate between those of pure silver and pure nickel clusters, with a surface plasmon resonance band enlarged and blue-shifted compared to pure silver clusters. This feature can be understood by the mixing of the silver conduction collective electron excitation with those involving the nickel *s-d* band electrons. The size effects (damping and widening of the SPR) are well reproduced within a classical model assuming a core-shell geometry and including the reduction of the conduction electron mean free path in the silver shell. To conclude, this mixed system remains closely connected with the dielectric functions of its constituents. As for Pt/Ag clusters, the SPR is strongly flattened in the size range 2−5 nm. The comparison between the two systems Ni/Ag and Pt/Ag clusters, in view of the quite similar theoretical predictions obtained within a given model, permits to conclude that the geometry of Pt/Ag particles is probably not a core/shell one, even if their surface is entirely composed of silver. These results do not agree with those of Torigoe *et al.* [5] who found a well-developed SPR in Pt/Ag clusters of same size, assumed by the authors to form alloys. In fact, the chemical synthesis is not the more convenient to produce an alloyed structure except if they anneal their samples. In our source, clusters are produced from a hot plasma cooled by the inert gas and this way of formation is in favour of the mixing of both constituent atoms. Moreover, our results prove that the dielectric function of the Pt/Ag system is not simply correlated to those of its constituents as it is the case for Ni/Ag. EXAFS experiments would permit to probe the neighbouring of the atoms inside the particles. Besides, Monte Carlo simulations will be performed in order to have an idea of the possible structure of this system. Current work is planned towards these directions.

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