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Nanostructures

Facile Synthesis of Stable Subnanosized Silver Clusters in Microemulsions**

*Ana Ledo-Suárez, José Rivas, Carlos F. Rodríguez-Abreu, María J. Rodríguez, Elena Pastor, Alberto Hernández-Creus, Saul B. Oseroff, and M. Arturo López-Quintela**

Metallic clusters are very important for technological applications, owing to their fascinating and unusual properties.[1] However, advances in this field are inhibited by the difficulty of preparing monodisperse clusters in macroscopic quantities. For this purpose, different chemical approaches have been tried by using dendrimers,[2] thiol cappings,[3] microemulsions,[4] and vesicles.[5] Most of these methods are based on well-developed techniques used for the preparation of monodisperse nanoparticles. A classical procedure for the preparation of nanoparticles is the microemulsion method.[6] With this method, it is possible to obtain nanodroplets of water dispersed in oil by using surfactants and/or amphiphilic block copolymers. These nanodroplets are used as nanoreactors to obtain nanoparticles with well-defined sizes.

However, there is a general belief that severe limitations will be faced if such techniques are applied in the subnanometer size range, the main argument being that clusters are much more unstable than their larger "brothers", the nanoparticles. Therefore, it should be very difficult to precisely control the experimental conditions to stop and then isolate the clusters as soon as they are formed. This claim is based on the theory of the nucleation and growth of nuclei in solution. According to this theory, which is based on thermodynamics, nuclei formed during the first steps of the chemical synthesis are only stable above a particular size, the critical nucleus. Below this size, the nuclei dissolve, because of their large Laplace pressure. Above this size, the nuclei grow continuously to reduce their surface energy by different mechanisms, such as autocatalysis or Ostwald ripening,[7] until their growth is stopped by templates or capping agents, for example.

The results reported herein show that such "macroscopic" arguments are incorrect when applied to very small clusters. Support for our claim can already be found in numerous theoretical and experimental reports for clusters prepared in the gas phase. These studies indicate that clusters can be especially stable,[8] owing to their different and particular electronic and geometrical structures. Very recently, some of us showed that subnanometer-high platinum nanoislands can be obtained by using microemulsions.[9] These nanoislands then spontaneously arrange themselves on several hierarchical levels. Although the hypothesis that the nanoislands were formed by subnanometer clusters was put forward, no evidence was given to corroborate this idea. Herein, we report, for the first time, the preparation of small Ag_n clusters ($n \leq 10$) in microemulsions by using a recently introduced technique of kinetic control.[10] Clusters with very large bandgaps (ca. 2.3 eV) prepared in this way display fluorescence and molecular-like paramagnetic properties, and are very stable (as has been confirmed by working with this procedure for over 2 years). The clusters organize into one-atom-high nanoislands when they are deposited over a substrate from the microemulsions.

A transmission electron microscopy (TEM) image of a typical sample obtained from such a synthesis using a water-in-oil microemulsion apparently indicates the existence of polydisperse nanoparticles with an average size of 5.3 ± 1.6 nm (Figure 1). To further investigate the structure of these particles, scanning tunneling microscopy (STM) studies were carried out by depositing a drop of the same microemulsion containing particles onto an Au(111) surface. In Figure 2a, the nanoparticles are approximately one atom high, which can be verified by using the one-gold-atom-high steps of the Au(111) substrate (Figure 2b). The particles are actually nanoislands with a thickness of about 0.24–0.26 nm. The size of these nanoislands is in the range of 3.5–5 nm, which agrees with the size estimated by TEM. Although very thin, the contrast of these islands is great enough to allow their observation by TEM, as with other metallic clusters.[11] Therefore, inside the aqueous pools (droplets) of the micro-

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[*] A. Ledo-Suárez, Prof. J. Rivas, M. J. Rodríguez, Prof. M. A. López-Quintela
Laboratorio de Magnetismo y Nanotecnología
Instituto de Investigaciones Tecnológicas
Universidad de Santiago de Compostela
15782 Santiago de Compostela (Spain)
Fax: (+34) 981-595-012
E-mail: qfarturo@usc.es

Dr. C. F. Rodríguez-Abreu
Institut d'Investigacions Químiques i Ambientals de Barcelona,
Consejo Superior de Investigaciones Cientificas
Jordi Girona, 18–26, 08034 Barcelona (Spain)

Prof. E. Pastor, Prof. A. Hernández-Creus
Departamento de Química Física
Facultad de Química, Universidad de La Laguna
Astrofísico F. Sánchez s/n
38071 La Laguna, Tenerife (Spain)

Prof. S. B. Oseroff
Department of Physics
San Diego State University
San Diego, CA 92182-1233 (USA)

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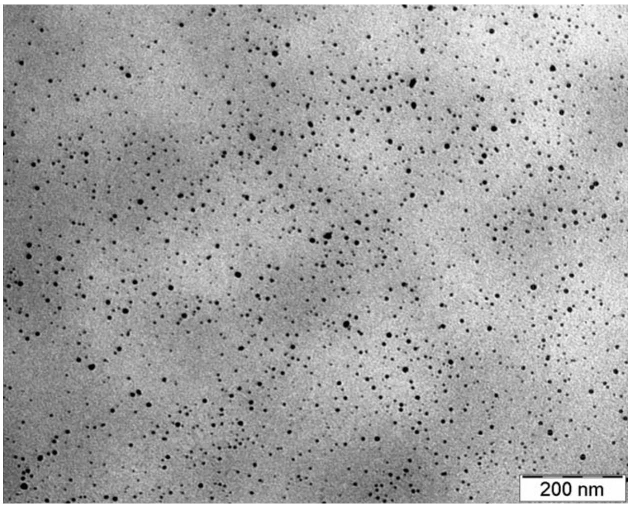

Figure 1. Typical TEM image of silver samples prepared in microemulsions.

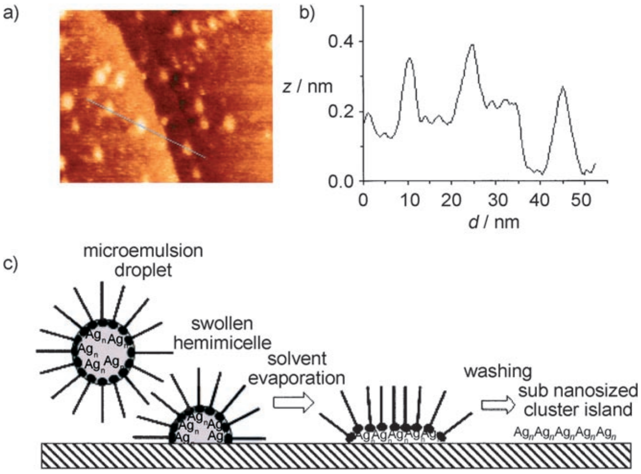

Figure 2. a) STM image (86×65 nm) of silver nanoislands produced in microemulsions after deposition onto an Au(111) surface. b) Height (*z*) profile along the line shown in (a). c) Hypothetical scheme for the deposition of nanoislands composed of subnanosized clusters onto a substrate.

emulsion or, more likely (see below), at the interface, 2D flat silver nanoislands, are formed rather than 3D nanoparticles.

A further corroboration that the particles obtained in the microemulsions are one-atom-high aggregates of clusters and not just silver nanoparticles is given by the absence of the characteristic peaks expected for silver nanoparticles of 5 nm in the X-ray diffraction pattern (see Figure S1 in the Supporting Information). From theoretical studies, it is known that small Ag_n clusters ($n \leq 10$–12) have a tendency to be planar.[12] Thus, the STM images suggest that planar Ag_n clusters with $n \leq 10$–12 are obtained in the microemulsions (see Figure S2 in the Supporting Information). These planar clusters aggregate inside the microemulsion droplets, giving rise to 2D nanoislands of approximately the same size as the water nanodroplets of the microemulsion. A hypothetical scheme for the deposition of the clusters from droplets onto the substrate is depicted in Figure 2c. The microemulsion droplets are adsorbed at the surface of the substrate, forming swollen hemimicelles.[13] Evaporation of the solvent leaves silver islands with adsorbed surfactant molecules. After washing, most of the surfactant is eliminated (as evidenced by the good conductance observed in the STM experiments), and one-atom-thick silver islands remain.

To further verify the existence of small clusters, a mass spectrometry (MS) analysis was performed. Owing to the presence of many chemicals in the microemulsions, the MS analysis was done on a separated fraction containing the silver clusters. For this purpose, a microemulsion containing the particles was broken by adding 1 mL of dodecanethiol to an aliquot of 10 mL of the microemulsion. The microemulsion became cloudy, and the slow precipitation of a dark solid was observed. Isooctane was then added to the precipitate, and a dark brown solution was obtained. This fraction was analyzed by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS.

From a comparison of the theoretical and experimental mass spectra, the following clusters could be identified: Ag_3O_2, Ag_5, and Ag_9 (Figure 3). Additional spectra (not shown) also gave evidence of the presence of Ag_2 and Ag_3 clusters. We should point out that there is some divergence (1–2 m/z units) between the theoretical and experimental data for the Ag_3O_2 and Ag_9 clusters, which can be attributed to the presence of adsorbed H^+ ions. For none of the samples studied was there a peak that could be associated with the binding of dodecanethiol to any of the clusters. Only naked clusters (with the exception of the oxygen bound to the Ag_3 cluster) were detected. Note that this finding would not be expected for nanoparticles, because it is well-known that the sulfur atoms of thiols are very reactive towards silver, both in the bulk and in nanoparticles.[14] This evidence indicates the presence of 2D agglomerations of clusters, rather than "true" nanoparticles. Although this area needs more work, it seems that thiols are able to "extract" planar clusters from the microemulsions, owing to their tendency to form lamellar

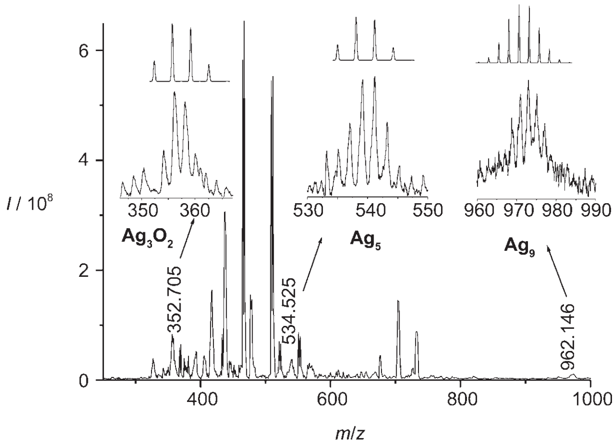

Figure 3. MALDI-TOF mass spectra (positive ions) of silver samples prepared in microemulsions, showing the presence of subnanosized silver clusters. Insets: Theoretical spectra for each cluster are shown above enlargements of corresponding sections of the experimental spectrum.

structures, which can host planar silver clusters. Indeed, the lamellar structure formed by silver thiolates is almost identical to the lamellar structure formed by the thiols carrying the embedded clusters, as suggested by their respective X-ray diffraction patterns (see Figure S3 in the Supporting Information).

Cluster growth (with a transition from the 2D nanoislands of subnanosized silver cluster to 3D nanoparticles) as the thiol lamellar structure is destroyed, can be observed upon heating the system above 130 °C (results not shown).

A further proof that thiols do not interact with the planar clusters obtained in microemulsions was obtained by atomic force microscopy (AFM). Similar to what was observed by STM directly from the microemulsions, AFM images show that the thiol-extracted silver clusters form nanoislands again (see Figure S4 in the Supporting Information). Moreover, STM and AFM gave qualitatively similar results, even though the substrates were very different, which is also a proof that the flat morphologies of the particles are not a product of interactions between the silver clusters and the substrate (see Figure S5 in the Supporting Information).

A further identification of the clusters was made by UV/Vis spectroscopy. Figure 4 shows the slow evolution of the UV/Vis spectra for a typical reaction carried out in AOT (sodium bis(2-ethylhexyl)sulosuccinate) microemulsions. In some cases, the process was accelerated by heating the system to temperatures up to 40 °C, and the same spectra were obtained, which demonstrates the reproducibility of the method.

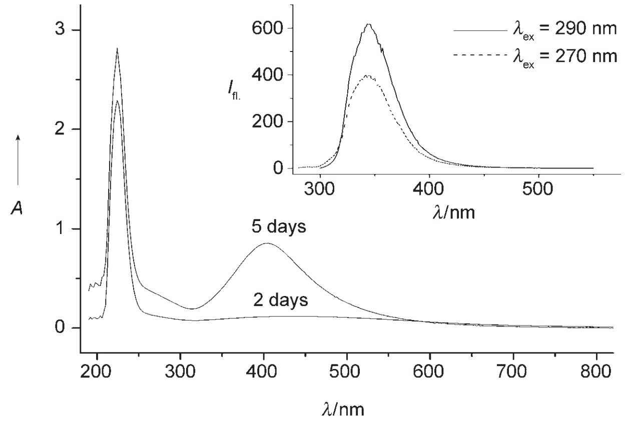

Figure 4. UV/Vis spectra of silver samples prepared in microemulsions at two different times after their preparation. Inset: Fluorescence emission spectra at two different excitation wavelengths of a sample 5 days after its preparation.

The consecutive appearance of three main bands located at $\lambda = 220$–230, 250–270, and 400–450 nm was observed. UV/Vis spectra remained unchanged from 5 days up to about 1 month indicating that the system remained stable over this time. The stability could be increased by months if the unreacted Ag^+ ions were eliminated from the reaction medium or if the particles were separated from the microemulsion by the thiol procedure described above. Upon keeping the microemulsion unperturbed at room temperature, new bands (associated with larger clusters) were observed after about 1 month.[15] Finally, after approximately 1.5 months, the appearance of typical silver nanoparticles was detected by X-ray diffraction (results not shown).

Usually, the band that slowly appears at around 400 nm in the UV/Vis spectrum is interpreted as the characteristic plasmon band of silver nanoparticles. However, the STM, AFM, XRD, and MS results clearly indicate that this band does not arise from nanoparticles. It is now established that, when the size of silver particles is reduced below 2–3 nm, the plasmon band disappears, and a continuous increase in absorption with decreasing wavelength is observed in the UV/Vis spectrum.[16] For very small Ag_n clusters ($n < 10$–20), the appearance of molecular-like discrete bands, such as those observed in Figure 4, is expected.[17] If one considers the onset of UV/Vis absorption (ca. 550 nm (2.3 eV)) as the HOMO–LUMO bandgap,[18] the clusters produced in the microemulsions would contain less than approximately 10 atoms,[19] which nicely agrees with the results discussed above. Moreover, the clusters display fluorescence with a strong emission band centered at 350 nm (3.54 eV; Figure 4, inset). Because of the large discrepancies in the literature, an unambiguous assignment of the cluster size from the absorption and emission bands cannot be made, but the UV fluorescence emission clearly points again to the presence of very small silver clusters.

The redox properties of the thiol-extracted clusters (redispersed in dichloromethane) were investigated by differential pulse voltammetry (DPV) using a platinum microelectrode ($\varphi = 40$ µm; Figure 5). Besides the central redox couple corresponding to Ag^+ ions, the voltammograms show a large central gap spanning the whole stability window of the used media, i.e., from the first oxidation peak observed as a shoulder at −1.4 V in the anodic part to the first reduction peak at 1.5 V. This result indicates that the bandgap of the clusters is approximately 2.9 eV. This value is larger than the HOMO–LUMO bandgap estimated by UV/Vis spectroscopy (2.3 eV). The difference of $\Delta \approx 0.6$ eV is due to the electron–hole Coulomb energy,[20] which is only important for small nanoparticles. In the simplest approximation, the electron–hole Coulomb energy is given by $\Delta = e/C$, where e is the elementary charge, and C is the capacitance of the nano-

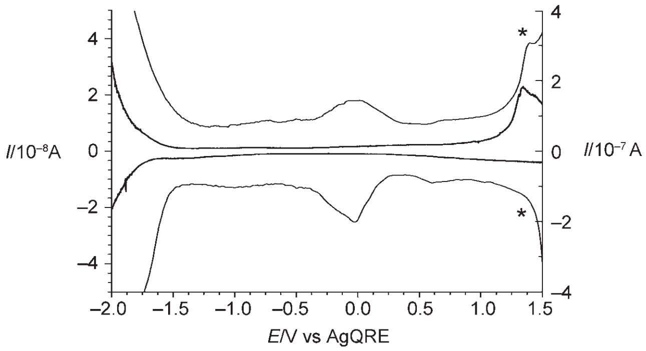

Figure 5. Differential pulse voltammograms at 20 mV s^{-1} and 25 °C of silver samples prepared in microemulsions (thin lines marked by an asterisk, right scale) and of a blank solution of 0.1 M Bu_4NPF_6 in CH_2Cl_2 (thick lines, left scale).

particle. From the electron–hole Coulomb energy of the clusters, their size can be determined to be less than approximately 0.3 nm (by assuming that $C = 4\pi\varepsilon\varepsilon_0 r$, where ε is the dielectric constant of the surrounding medium (dichloromethane), ε_0 is the permittivity of a vacuum, and r is the particle radius), which surprisingly agrees with the AFM results, in spite of the crude approximations involved in the calculations. It is interesting to note that the capacitance of approximately 0.3 aF estimated for these small silver clusters is less than half that reported for larger Au_{38} clusters by Murray and co-workers.[21] Therefore, the great redox stability observed for the microemulsion-synthesized clusters agrees with their very small size.

A last proof that the particles prepared in microemulsions are not true 3D nanoparticles, but clusters with properties very different from those of nanoparticles is given by their unusual magnetic properties. Preliminary electron paramagnetic resonance (EPR) measurements were performed at 9 GHz between 120 and 300 K. The EPR spectra show a well-resolved sextet with $g = 2.0$ and a hyperfine splitting of $A \approx 9$ mT (Figure 6). A broad paramagnetic signal is superimposed over the sextet. The presence of a sextet is unexpected for nanoparticles or nanoislands. It may be associated with an entity with $S = 1/2$ interacting with 5 silver nuclei ($I = 1/2$), as would be the case for a Ag_5 cluster. However, more work on the characterization of the EPR spectra is needed. As the different chemicals used in the synthesis and the microemulsion do not give rise to EPR signals, magnetic impurities are not responsible for the EPR spectra. Moreover, the EPR signal disappears after approximately 1.5 months, when the clusters grow to form true 3D nanoparticles. According to previous studies on γ-irradiated silver-loaded zeolites and frozen aqueous glasses of silver salts,[22] the paramagnetic signal in the EPR spectra may be associated with small silver clusters. The intensity of the EPR spectra increases somewhat as the temperature is lowered, in accordance with magnetization measurements made on the samples. No other change as a function of temperature was observed in the spectra, suggesting that the synthesized magnetic clusters are stable in this temperature range.

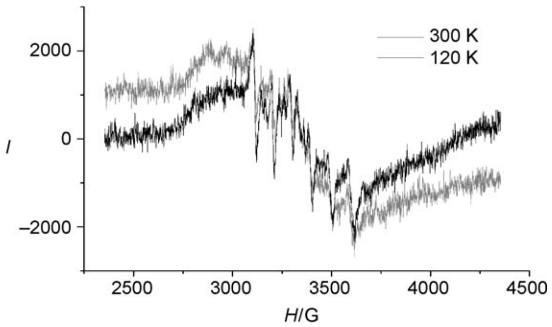

Figure 6. EPR spectra at two different temperatures of silver samples prepared in microemulsions.

We are currently unable to precisely assign the signals in the EPR spectra, because the geometry and the values of g and A for the clusters are not known. In a first tentative assignment, the resolved sextet could be assigned to an Ag_5 cluster, the splitting being due to the interaction with 5 equivalent silver nuclei, as given by the formula $2nI + 1$ (where n is the number of equivalent interacting nuclei, and I is the nuclear spin quantum number). The observed hyperfine splitting constant approximately agrees with $A = 64/n = 12.8$ mT,[22b] taking $n = 5$ as the number of silver atoms in the cluster. However, the intensities are not in the expected ratio of 1:5:10:10:5:1, indicating that the 5 silver nuclei in the cluster may not be equivalent.

In summary, we have shown that by using microemulsions small Ag_n clusters ($n < 10$) can be obtained. Moreover, the clusters remain very stable in the microemulsions, probably owing to their large HOMO–LUMO bandgap (ca. 2.3 eV). By comparing the bandgaps deduced by using optical and electrochemical techniques, a value of about 0.6 eV is obtained for the Coulomb charging energy, which corresponds to a cluster capacitance of about 0.3 aF. The clusters have a special preference to go to the interface when the microemulsion is broken and cannot be extracted from it by using conventional solvents. Instead, the clusters can be extracted with the thiol "trick" described above. Finally, the present results show that scaffolds, such as dendrimers, zeolites, and solid matrices, are not needed for the preparation of these clusters. Furthermore, there is no need for thiols (typical capping molecules) to protect the clusters, as was recently reported in the thermal-induced synthesis of gold clusters.[23] Simple kinetic control based on the use of low reaction rates is sufficient for the synthesis of stable clusters. This approach can be carried out by using small reaction constants and small concentrations, such as those provided by mild reducing agents and microemulsion droplets, respectively. The clusters prepared by this simple method display novel properties, such as fluorescence and paramagnetic molecular-like behavior, which could lead to new, interesting applications of the clusters used directly or as subnanosized building blocks. By further tuning the kinetic control, clusters of other sizes and geometries with different properties could be prepared. The same synthetic approach could also be applied to the preparation of clusters of other materials, opening a new, broad area of great technological interest with potential applications in catalysis and biosensing, for example.

Experimental Section

Experimental details can be found in the Supporting Information.

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