

Facile Synthesis of Stable, Sub-Nanosized Silver Atomic Clusters in Microemulsions

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Metallic clusters are very important for technological applications due to their fascinating and unusual properties.^[1] However, advances in this field are mainly inhibited by the difficulty in preparing clusters with monodisperse sizes in macroscopic quantities. For this purpose different chemical approaches have been tried using dendrimers,^[2] thiol cappings,^[3] microemulsions,^[4] vesicles,^[5] etc. Most of these methods are based on well-developed techniques used before for the preparation of monodisperse nanoparticles. A classical method for the preparation of nanoparticles is the microemulsion method.^[6] With this method is possible to obtain nanodroplets of water dispersed in oil using surfactants and/or amphiphilic blockcopolymers. These nanodroplets are used as nanoreactors to obtain nanoparticles with well-defined sizes. However, there is a general belief that severe limitations have to be faced if those techniques are applied in the sub-nanometer size range. The main argument for it is that clusters are much more unstable than their larger "brothers", the nanoparticles. Therefore, it should be very difficult to have a precise control of the experimental conditions, to stop and then isolate the clusters as soon as they are formed. That claim is based on the theory of nucleation and growth. According to that thermodynamic-based idea nuclei formed during the first steps of the chemical synthesis are only stable above a particular size, critical nucleus.

Below this size the nuclei are dissolved because of their large Laplace pressure. Above that size they continuously grow in order to reduce their surface energy by different mechanisms, like autocatalysis, Ostwald ripening, etc.^[7] until their growth is stopped by templates, capping agents, etc. The results reported in this paper show that such "macroscopic" arguments are incorrect when they apply to very small clusters. Support for our claim can be already found in numerous theoretical and experimental reports for clusters prepared in the gas phase. Those studies indicated that clusters can be especially stable,^[8] due to their different and particular electronic and geometrical structures. Very recently, some of us have already shown that sub-nanometer high Pt nanoislands can be obtained by using microemulsions, which are then spontaneously arranged in several hierarchical levels.^[9] Although the hypothesis of having subnanometer clusters forming those nanoislands was put forward in that paper, no evidence was given to corroborate such idea. In this paper we report for the first time the preparation of small silver clusters, Ag_n, with $n \leq 10$, in microemulsions by using a recently introduced technique of kinetic control.^[10] Clusters with very large band-gaps (≈ 2.3 eV) prepared in this way, displaying fluorescent and molecular-like paramagnetic properties, are very stable as it has been confirmed after working with this procedure for over two years. Clusters organize in 1 atom high nanoislands when they are deposited over a substrate from the microemulsion.

A transmission electron microscopy (TEM) image of a typical sample obtained from the synthesis using water-in-oil microemulsions (Figure 1) apparently indicates the existence of a polydisperse distribution of nanoparticles with an average size of 5.3 ± 1.6 nm.

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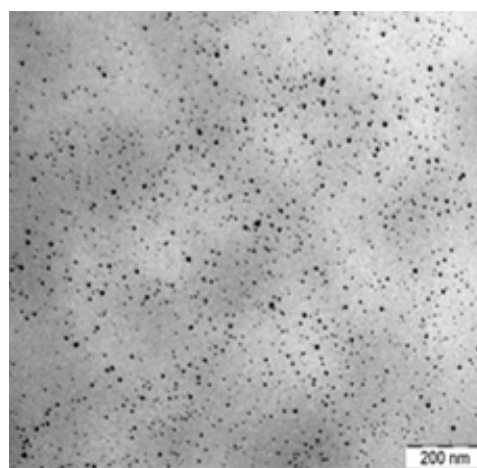


Figure 1. Typical TEM picture of Ag samples prepared in microemulsions

To check further the structure of these particles scanning tunnelling microscopy (STM) studies were carried out by depositing a drop of the same microemulsion containing particles onto an

Au(111) surface. In Figure 2 it is observed that the nanoparticles are approximately one atom high, which can be checked using the one Au atom high steps of the Au(111) substrate. The particles are actually nanoislands with a thickness of about 0.24-0.26 nm. The size of these nanoislands is in the range 3.5-5 nm, which agrees with the sizes estimated by TEM. Although very thin, the contrast of such islands would be enough to allow observation by TEM, as occurs with other metallic clusters.^[11] Therefore, inside the aqueous pools (droplets) of the microemulsion or, more likely –see later on-, at the interface, 2D monoatomic flat Ag nanoislands, instead of 3D nanoparticles, are formed.

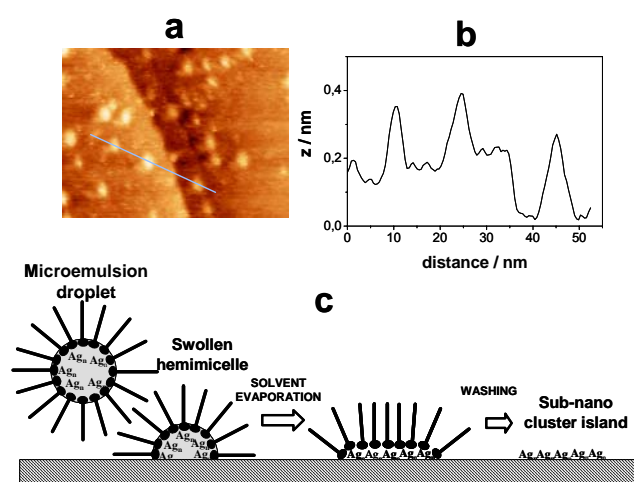


Figure 2. a) STM 86nmx65nm detailed image of Ag nanoislands produced in microemulsions. The substrate is an Au plate. b) Z-resolved profile along the line shown in a. c) Hypothetical scheme for cluster deposition.

A further corroboration that the particles obtained in microemulsions are 1 atom high cluster aggregates and not just Ag nanoparticles is given by the absence of the characteristic silver peaks expected for 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, with $n \approx \leq 10-12$ atoms, have a tendency to be planar.^[12] Thus, the STM pictures suggest that planar Ag_n clusters with $n \approx \leq 10-12$ atoms are obtained in the microemulsion (see Figure S2 in the Supporting Information). These planar clusters aggregate inside the microemulsion droplets given rise to 2D-nanoislands of approximately the same size than the water nanodroplets of the microemulsion. A hypothetical scheme of the deposition process of the clusters from droplets to 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 surfactant is eliminated (as evidenced by the good conductance observed in STM experiments) and one-atom thick Ag islands remain.

To further check the existence of small clusters, a mass spectra analysis was performed. Due to the presence of many chemicals in the microemulsion, the mass spectra analysis was done on clusters separated from them. For this purpose the microemulsion containing particles was broken adding 1 ml of dodecanethiol to an aliquot of 10 ml of the microemulsion. After that the microemulsion becomes cloudy and slow precipitation of a dark solid is observed. Isooctane is then added to the precipitate and a brown dark solution is obtained.

This fraction was analyzed by matrix-assisted laser desorption/ionization time-of-flight spectroscopy (MALDI-TOF).

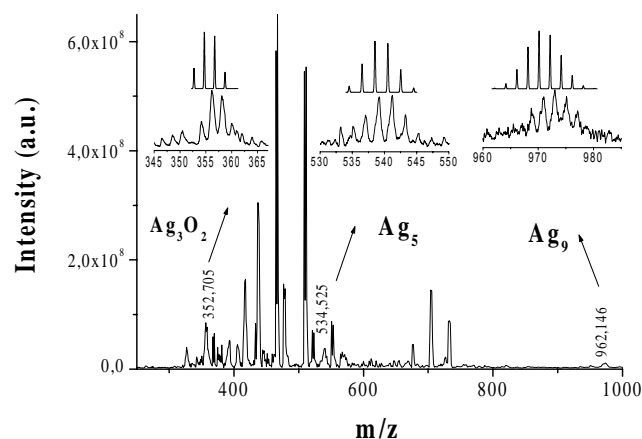


Figure 3. MALDI-TOF mass spectra (positive ions) of Ag samples prepared from microemulsions showing the presence of Ag clusters. Theoretical spectra for each cluster are shown on the top of the figure.

From a comparison of theoretical and experimental mass spectra (Figure 3) the following clusters can be identified: Ag_3O_2 , Ag_5 and Ag_9 . 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 units) between the theoretical and experimental data for Ag_3O_2 and Ag_9 which can be attributed to the presence of adsorbed protons. In all samples studied there is no peak that could be associated with the presence of the dodecanethiol bound to any cluster. Only “naked” clusters (with the exception of the oxygen bound to the Ag_3 cluster) were observed. Note that this finding is not expected in nanoparticles, because it is well-known that the sulphur atom of thiols is very reactive against Ag, both in bulk and in nanoparticles.^[14] This constitutes additional evidence that we are in the presence of a 2D agglomeration of clusters and not “true” nanoparticles. Although this is an area that needs more work, it seems that thiols are able to “extract” planar clusters from the microemulsion due to their tendency to form lamellar structures, which can host planar Ag 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 observed from their respective X-ray diffraction patterns (see Figure S3 in the Supporting Information). Cluster growth, with a transition from the 2D cluster sub-nanoislands to 3D nanoparticles destroying the thiol lamellar structure, can be observed by heating the system above 130 °C (results not shown).

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

A further identification of the clusters can be made by UV-vis spectroscopy. Figure 4 shows the slow evolution of the UV-vis spectra for a typical reaction carried out in AOT 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 shows the reproducibility of the method.

The consecutive appearance of three main bands located at around 220-230 nm, 250-270 nm and 400-450 nm is observed. The final UV-vis spectrum recorded after 5 days at room temperature remains stable for about one month. The stability can be increased for months if the non-reacted Ag (I) ions are eliminated from the reaction medium or the particles are separated from the microemulsion by the thiol procedure described above. Keeping the unperturbed microemulsion at room temperature, the formation of new bands (associated with larger clusters) can be observed after ca. one month.^[15] Finally, after approximately 1 and 1/2 month, the appearance of typical Ag nanoparticles, as it can be deduced from its X-ray diffraction pattern (results not shown), is observed.

Usually, the band, which slowly appears at around 400 nm is interpreted as the characteristic plasmon band of Ag nanoparticles. However, the STM, AFM, XRD and Mass Spectra results clearly indicate that this band does not correspond to nanoparticles. It is now established that when the size of the particles is reduced below 2-3 nm, the plasmon band disappears and a continuous increase of absorption is observed in the UV-vis spectrum as the wavelength is decreasing.^[16] For very small clusters ($n < 10-20$ atoms) the appearance of molecular-like discrete bands, like those observed in Figure 4, is expected.^[17] If one considers the onset of the UV-vis absorption (~ 550 nm, i.e., 2.3 eV) as the HOMO-LUMO band-gap,^[18] the clusters produced in the microemulsions would be smaller than approximately 10 atoms^[19] which nicely agrees with the results showed above. Moreover, clusters display fluorescence (see inset in Figure 4) with a strong emission band centred at 350 nm (3.54 eV). Because of the large discrepancies found in the literature, an unambiguous assignation of the cluster size from the absorption and emission bands cannot be carried out at this moment, but the UV fluorescence emission clearly points out again to the presence of very small Ag clusters in the samples.

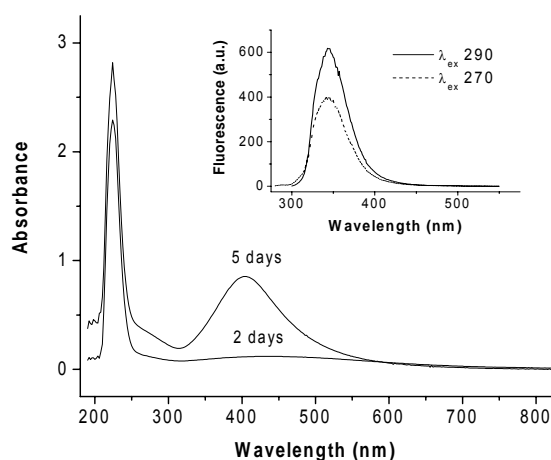


Figure 4. UV-vis spectra of Ag samples prepared in microemulsions, at two different times after preparation. The inset shows the fluorescence emission observed for the final Ag clusters obtained after 5 days.

Redox properties of thiol extracted clusters (and redispersed in dichloromethane) were investigated (see Figure 5) by differential pulse voltammetry (DPV) using a Pt microelectrode ($\phi = 40 \mu\text{m}$). Besides the central redox couple corresponding to Ag (I) ions present in the samples, the results 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, observed at 1.5 V. This indicates that the band-gap of the clusters should be $\sim > 2.9$ V. This value is larger than the HOMO-LUMO band-gap estimated by UV-vis spectroscopy (2.3 V). The difference, $\Delta \approx > 0.6$ V, is due to the electron-hole ($e-h$) Coulomb energy,^[20] which is only important for small nanoparticles. In the simplest approximation, $\Delta = e/C$, where e is the elementary charge and C the capacitance of the nanoparticle. Then, from the obtained $e-h$ Coulomb energy of the clusters, one can deduce (assuming $C=4\pi\epsilon\epsilon_0r$; ϵ = dielectric constant of the surrounding media: dichloromethane, 9; ϵ_0 = permittivity of vacuum; r = particle radius) that their size should be $\approx < 0.3$ nm, 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 obtained for these small silver clusters, $C \approx < 0.3$ aF, is approximately less than a half of that reported by the Murray's group for larger Au_{38} clusters.^[21] Therefore, the great redox stability observed for the microemulsion synthesized clusters agrees again with its very small size.

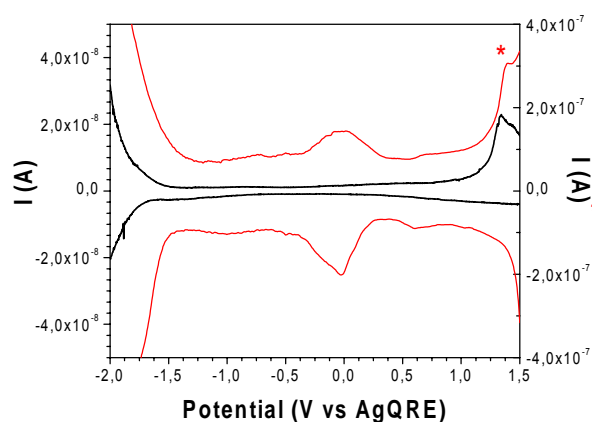


Figure 5. Differential pulse voltammograms of silver clusters prepared in microemulsions (red line) and of a blank solution of 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ (black line) at 20 mV/s and 25 °C.

A last proof that the particles prepared in microemulsions are not “true 3D nanoparticles”, but clusters showing properties very different than nanoparticles is given by the observation of their unusual magnetic properties. For this purpose, some preliminary electron paramagnetic resonance (EPR) measurements at 9 GHz between 120 K and 300 K were performed. Spectra showing a well-resolved sextuplet with $g_n = 2.0$ and a hyperfine splitting of $A_n \approx 9$ mT were obtained (see Figure 6). Superimposed to it, a broad paramagnetic signal was found. The presence of this sextuplet is not expected in nanoparticles/nanoislands. It may be associated to an entity with $S=1/2$ interacting with 5 Ag

nuclei ($I=1/2$), as it would be the case for Ag_5 clusters. However, more work is needed before the EPR spectra could be well characterized. The different chemicals used on the synthesis and the microemulsion do not give an EPR signal. Thus, magnetic impurities are not responsible for the EPR spectra. Moreover, the EPR signal disappears after approx. one and half month, when the clusters growth and “true 3D nanoparticles” are formed. According to previous studies^[22] done on γ -irradiated Ag-loaded zeolites and frozen aqueous glasses of silver salts, the paramagnetic EPR signal can be associated to the presence of small Ag clusters. The intensity of the EPR spectra increases somewhat as the temperature is lowered in accordance with the magnetization measurements taken on those samples. No other change as a function of temperature was observed in the spectra, suggesting that the synthesized magnetic clusters are stable for this temperature range. At this moment we cannot carry out a precise assignment of the signal, because the geometry, and the values of g and A for the clusters are not known. In a first tentative assignment of the EPR signal, one could associate the Ag_5 cluster with the resolved EPR sextuplet, the splitting being due to the interaction with 5 equivalent silver nuclei as given by the formula $2nI+1$ (where n = number of equivalent interacting nuclei and I = nuclear spin quantum number). The observed hyperfine splitting constant approximately agrees with^[22b] $A_n = 64/n = 12.8$ mT, taking $n=5$ as the number of Ag atoms in the cluster. However, the intensities are not in the ratio 1:5:10:10:5:1 indicating that the 5 Ag nuclei in the cluster may not be equivalent.

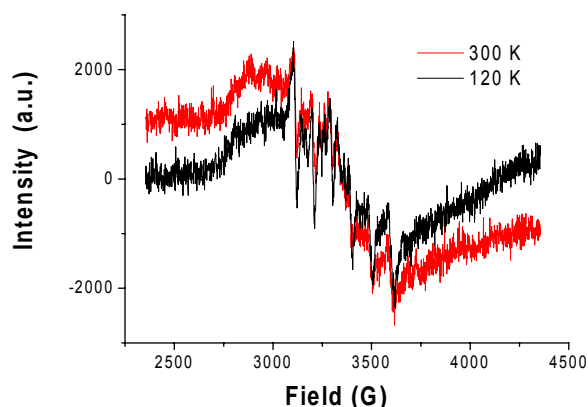


Figure 6. EPR signal at two different temperatures of Ag clusters prepared in microemulsions.

In summary, it has been shown that by using microemulsions one can obtain small Ag_n clusters, with $n < 10$. Moreover, the clusters remain very stable in the microemulsion, probably due to their large HOMO-LUMO band-gap (approx. 2.3 eV). By comparison of the band-gaps deduced from optical and electrochemical techniques, one can obtain a value of ≈ 0.6 V for the Coulomb charging energy, which corresponds to a cluster capacity of about 0.3 aF. Clusters have special preference to go to the interface

when the microemulsion is broken and cannot be extracted from it using conventional solvents, instead it can be done with the above described thiol “trick”. Finally, the present results show that scaffolds, such as dendrimers, zeolites, solid matrices, etc., **are not needed** for the preparation of clusters. **There is no need** either for thiols (typical capping molecules) to protect the clusters, as it was recently reported in the thermal-induced synthesis of gold clusters.^[23] A simple kinetic control based on the use of small reaction rates is enough for the synthesis of stable clusters. That can be done using small reaction constants and small concentrations, as those provided by mild reducing agents and microemulsion droplets, respectively. Clusters prepared by this simple method display novel properties, like fluorescence and a paramagnetic molecular-like behaviour, which could find new interesting applications using them either directly or as sub-nano building blocks. It is thinkable that, by further tuning of the kinetic control, one could prepare clusters of other sizes/geometries with different properties, and also to apply the same idea to prepare clusters of other materials, which can open a new broad sub-nano area of great technological interest with many potential applications, like catalysis, biosensors, etc.

Experimental Section

Silver clusters were synthesized in water-in-oil microemulsions containing silver nitrate (AgNO_3 , 99%, Aldrich) and sodium hypophosphite monohydrate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, 99%, Fluka) as a mild reduction agent. Microemulsions were prepared using a mixture of water/sodium bis(2-ethylhexyl) sulfosuccinate/isooctane having a molar ratio of water to AOT equal to 6. AOT (96%, Aldrich) concentration, based on the overall volume of the microemulsion, was fixed at 0.1 M and concentrations of metal ion and reduction agent aqueous solutions, based on the volume of aqueous phase, were kept constant at 0.1 M and 1 M, respectively. The synthetic procedure begins with the preparation of microemulsions, one of them containing sodium hypophosphite monohydrate in the aqueous phase and the other one containing silver nitrate. Silver microemulsion is then slowly added at room temperature over the sodium hypophosphite microemulsion under stirring. During the reduction process the colour of the mixture changes gradually from transparent, light yellow to dark brown.

Mass spectra were acquired using a Bruker MALDI-TOF Autoflex mass spectrometer. MALDI mass spectra were calibrated against the positive ions of peptide calibration standard II (Bruker). For the measurements we employed a silver cluster solution at a concentration of 65 mg/L, after precipitation with dodecanethiol and redispersion in isooctane. The sample preparation was made by the dried droplet method on a ground steel target without any matrix, and the long lifetime nitrogen (N_2) laser was used for desorption/ionization into the reflectron time-of-flight mass spectrometer.

AFM of the sample surface morphology in air was performed by using a Veeco Multimode Nanoscope 4 controller. The photographic images were recorded in tapping mode with a 5 nm radius tip. Silicon wafers were used as substrate after been cleaned by an ultrasonic bath in methanol and distilled water. The AFM sample was prepared by dropping the clusters solution with thiol onto to a cleaned piece of silicon wafer to form a thin film and allowing the solvent to evaporate.

STM images (constant current mode) were taken with a Nanoscope IIE (Digital Instrument, Santa Barbara, CA) using commercial and electrochemically etched Pt-Ir tips. All images were acquired in air. Typical tunneling currents and applied voltages to obtain good-quality images were 0.6-0.8 nA and 0.3-0.6 V, respectively, at scan rates ranging from 0.5 to 2 Hz. Au plates (1×0.5 cm²; arranged) were used as substrate. After flame annealing, these plates consisted of micrometer-sized Au(111) preferred oriented crystals with atomically smooth terraces separated by monoatomic steps in height. The height of these steps (0.24±0.02 nm) was used to calibrate the piezotube of the STM in the z direction. Several STM samples were prepared and investigated, and different sites over each modified surface were analyzed. Before performing the STM measurements the samples were abundantly washed with acetone and finally with milli-Q water.

TEM images were taken by a Philips CM-12 microscope, operating at 100 kV. Samples were prepared by placing a drop of microemulsion on a Formvar coated copper grid and allowing the solvent to evaporate at room temperature.

X-ray diffraction studies were performed between 10° and 90° on a Philips 1710 diffractometer using Cu K α radiation.

Voltammetric studies were performed with an Autolab PGSTAT 20 potentiostat in 0.1M Bu₄NPF₆ (tetrabutylammonium hexafluorophosphate) in CH₂Cl₂ solutions that were degassed with N₂ and blanketed in N₂ atmosphere. The working electrode was a 0.4 mm Pt disk (polished with Al₂O₃ and cleaned electrochemically by potential cycling in 0.1 M H₂SO₄ solution); the reference and counter electrodes were an Ag wire quasi reference electrode and a Pt wire, respectively. Background potential scans in electrolyte solutions were carried out to check for any spurious peaks.

EPR spectra were recorded on a Bruker EMX instrument (Frequency ≈9.5 GHz; Power ≈ 200 mW).

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