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

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

1. Laboratorio de Magnetismo y Nanotecnología, Instituto de Investigaciones Tecnológicas, Universidad de Santiago de Compostela. 15782 Santiago de Compostela (Spain).

2. Institut d’Investigacions Químiques i Ambientals de Barcelona. Consejo Superior de Investigaciones Científicas (IIQAB/CSIC), Jordi Girona, 18-26, 08034 Barcelona, Spain


4. Department of Physics, San Diego State University, San Diego, CA 92182-1233, USA
**Experimental Section**

Silver clusters were synthesized in water-in-oil microemulsions containing silver nitrate (AgNO₃, 99%, Aldrich) and sodium hypophosphite monohydrate (NaH₂PO₂·H₂O, 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 (N₂) 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; arrandee) 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 cooper 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 Kα 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).
Figure S1. XRD comparison of clusters in the microemulsion and microemulsion without clusters.
Figure S2. STM pictures of Ag nanoparticles prepared in microemulsions and deposited on Au(111) showing the presence of 1 atom high nanoislands.

Figure S3. XRD comparison of thiol precipitated clusters and silver dodecanethiolate.
Figure S4. AFM picture of thiol precipitated Ag clusters. The substrate used was a silicon wafer.

Figure S5. AFM Z-histogram of the sub-nanometer islands observed in the Supplementary Figure 4.