Synthesis of Ag clusters in microemulsions: A time-resolved UV–vis and fluorescence spectroscopy study

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Abstract

The combined use of the microemulsion technique and the kinetic control allows the preparation of small silver clusters. By using UV–vis and fluorescence spectroscopy the main stages by which the clusters grow, before the formation of nanoparticles, were elucidated. Transmission electron microscopy (TEM) and scanning tunnelling microscopy (STM) were used to further characterize the samples. Two main stages were clearly identified, which are associated with: (1) the formation of Ag$_n$ clusters with $n<10$, which self-aggregate into one atom high 2D nanodiscs of 3.2 nm size and (2) Ag$_n$ clusters, which self-aggregate into 3D nanostructures of 1.5 nm in size. The fluorescence properties observed with both stages show that the formed clusters are small enough to display a molecule-like behaviour.

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1. Introduction

The progression of the technology demands nowadays the synthesis of novel and small materials. At this moment a large interest is focussed in the development of procedures for the controlled synthesis of nanomaterials with different sizes and shapes. A great variety of soft chemical methods have been developed in the last decade for such purpose, but there is a lack of methods in the “last bottom region” when the dimensions are reduced down to the sub-nanometer range (clusters). Taking into account that in this range novel electronic, optical, and chemical properties may appear, which are different from both the nanoparticles and also the bulk material, this is a very important topic to be further explored. Understanding the appearance of these new phenomena as a function of the core size, core geometry and capping within this sub-nanometer scale, is a sine qua non to apply this kind of sub-nm pieces in the new technologies. One of the main reasons for the lack of synthetic methods to produce sub-nm particles is the generalized idea that clusters are much more unstable than nanoparticles. Therefore, special procedures using very reactive capping agents or nanocavities have been used so far. In general, these methods are very inefficient for the production of clusters, and only particular examples for the production of specific clusters have been reported [1–4]. We have recently developed a new strategy, which allows the production of clusters with different sizes in large quantities [5]. Moreover, it has been observed that, contrary to what is usually assumed [6], clusters are very stable even without using special protecting agents.

Metal nanoparticles show exciting electronic properties exhibiting size-tuneable plasmon absorption bands. These optical properties depend on the structure, size, geometry of the particles and also on the kind of the surrounded media [7–9]. It has been observed that the Mie theory can be used to explain the optical features observed in these systems. However, when the particles are below 1–2 nm ($A_n$, with $n \approx 100–200$ atoms per particle) the plasmon band disappears [10,11] and is replaced by a continuous increase of the absorption band as the energy is increased, remembering the optical properties of semiconductors.

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For very small clusters some new features, remembering the optical properties exhibited by molecules, become evident [12,13].

In the present work we report the preparation of silver clusters by the microemulsion technique. The main idea behind this technique is that by a suitable control of the synthesis parameters one can produce tailor-made materials down to the sub-nm scale [14]. Single phase microemulsions are colloidal “nano-dispersions” of water-in-oil (or oil-in-water) stabilized by a surfactant film. These dispersions are thermodynamically stable, isotropic and transparent. The nanosized water droplets, spontaneously formed in the reverse microemulsions, can be used as nanoreactors for processing nanomaterials [15–19]. The water nanodroplets are dispersed in the continuous oil phase and stabilized by surfactant molecules, which are adsorbed at the water/oil interface. Random collisions between droplets allow exchanging of their contents via rapid fusion/fission transient processes, but the size of the exchanged species can be drastically reduced using appropriate rigid surfactant films. In this way the formation of relatively monodisperse nanoparticels can be achieved [20]. As we have recently shown [14], this technique is also very suitable for the production of sub-nanometer particles (clusters) because (1) very small concentration of reactants can be provided inside the nanoreactor pools and (2) clusters by the microemulsion technique. The main idea behind this technique is that by a suitable control of the synthesis parameters one can produce tailor-made materials down to the sub-nm scale [14]. Single phase microemulsions are colloidal “nano-dispersions” of water-in-oil (or oil-in-water) stabilized by a surfactant film. These dispersions are thermodynamically stable, isotropic and transparent. The nanosized water droplets, spontaneously formed in the reverse microemulsions, can be used as nanoreactors for processing nanomaterials [15–19]. The water nanodroplets are dispersed in the continuous oil phase and stabilized by surfactant molecules, which are adsorbed at the water/oil interface. Random collisions between droplets allow exchanging of their contents via rapid fusion/fission transient processes, but the size of the exchanged species can be drastically reduced using appropriate rigid surfactant films. In this way the formation of relatively monodisperse nanoparticels can be achieved [20]. As we have recently shown [14], this technique is also very suitable for the production of sub-nanometer particles (clusters) because (1) very small concentration of reactants can be provided inside the nanoreactor pools and (2) nanodroplets offer an “almost planar interphase” (in comparison with the cluster sizes) for stabilizing very small clusters, \( (4n, n < 10–15) \), which have a tendency to be planar [21]. Another important factor to be taken into account for the preparation of clusters is the reducing agent to be used. The most commonly used reducing agents for the preparation of monodisperse nanoparticles are sodium borohydride and hydrazine. These strong reducing agents favour the formation of monodisperse nanoparticles through a fast nucleation process. However, we have observed that, contrary to the case of nanoparticles, to favour the formation of clusters a mild reducing agent has to be used. In this work we have used a less common reducing agent, namely sodium hypophosphite, which is very adequate for achieving narrow cluster size distributions. We will report here on the temporal evolution of silver clusters produced in AOT-microemulsions, based mainly on time-resolved UV–vis and fluorescence studies.

2. Experimental section

Silver clusters were synthesized in inverse microemulsions containing silver nitrate (AgNO\(_3\), 99%, Aldrich) and sodium hypophosphite (NaH\(_2\)PO\(_2\) H\(_2\)O, 99%, Fluka), which were prepared by mixing the required amounts of the corresponding aqueous solutions into a solution of sodium bis (2-ethylhexyl) sulfosuccinate (AOT, 96%, Aldrich) in isoctane (99%, Aldrich), being the molar ratio of water to AOT (\( w_o \)) equals to 6. For all reactions, the AOT concentration, referred to the overall volume of the reverse microemulsion solution, was fixed at 0.1 M. The concentration of metal ions and reduction agent, based on the volume of aqueous solution, were kept constant at 0.1 and 1 M, respectively. Both microemulsions were mixed slowly under shaking conditions at room temperature. In the whole process the colour of the microemulsion solution changed from transparent, light yellow, dark brown to colourless, and finally the typical yellow colour of the nanoparticles appeared. We have focussed our study to the evolution of the system before the final formation of nanoparticles is achieved.

Different techniques were employed to characterize the silver cluster system. Diverse samples were followed during several weeks and its evolution was followed by transmission electron microscopy (TEM) using a Philips CM-12 microscope, operating at 100 kV. UV–vis absorption spectra were recorded on a diode-array Hewlett-Packard HP8452 spectrophotometer. The morphology of these structures was evaluated using scanning tunnelling microscopy (STM) with a Nanoscope IIE (Digital Instrument, Santa Barbara, CA). 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 \( (1 \times 0.5 \text{cm}^2) \) were used as substrate. Fluorescence spectra were acquired on a Variant Cary Eclipse spectrotlfluorimeter. Influence of AOT and solvent was subtracted from the emission spectra.

3. Results

Absorption spectroscopy in the UV–vis region allows us to follow the evolution of the cluster formation in the microemulsion medium. In situ UV–vis measurements were recorded directly in microemulsions at room temperature. The whole process was study through a period of 6 weeks. This period can be shortened performing the experiments at high temperatures giving the same results. The spectroscopic behaviour of the samples is shown in Fig. 1.

It can be observed that, at the beginning of the reaction (Fig. 1a) only a peak centred at 220–230 nm is observed. The solution at this stage is transparent and do not change with time during the first 2 days. After 5 days major changes in the spectrum are observed (Fig. 1c) with the formation of new absorption bands located at 250–270 nm and 400–450 nm. At this intermediate stage, Ag\(_n\) clusters, with \( n < 10 \) showing fluorescent and magnetic properties can be extracted, as has been reported before [14,22,23]. This intermediate stage is stable for approx. 1 month. After that a new stage (Fig. 1f) is attained with the disappearance of the yellow colour and the appearance of a new band located at 287 nm. This stage is stable during approx. 2 months, before the appearance of the final stage showing finally the formation of 3D nanoparticles.

The appearance of different species with characteristic absorption bands are accompanied by changes in the fluorescence emission spectra. Different behaviours are observed (Figs. 1d’ and g”) corresponding to the stages 1d and 1g. However, no fluorescence is found in the final
nanoparticles obtained after approx. 2 months. For silver particles in the first stage, fluorescence emission maxima at 330 and 314 nm are observed for excitations at 230 and 270 nm, respectively (Fig. 1d). For the second stage, excitation at 230 nm results in two emission bands at 267 and 319 nm, whereas by excitation at 290 nm a broad emission band is observed at 316 nm (Fig. 1g).}

Fig. 2 shows TEM pictures corresponding to the stages 1d and 1g. The samples for TEM examinations were prepared by dropping the AOT/isooctane reverse
microemulsion solution onto a Formvar-covered copper grid and evaporated slowly. It can be seen that samples in stage 1d look larger (size = 3.20 ± 0.72 nm) than the 1g samples (size = 1.53 ± 0.2 nm).

STM analyses were carried out to examine the morphology of the silver samples corresponding to the stages 1d and 1f. Fig. 3 shows pictures of these samples prepared by dropping the corresponding solutions onto an Au (1 1 1) surface, and then thoroughly washed with acetone and milli-Q water. It can be seen that sample 1d is formed by nanodisks of only one atom height (0.24–0.26 nm) which is much smaller than the size observed by TEM. Whereas for sample 1g a mean height of 1.53 ± 0.26 nm is obtained, which agrees with the size estimated by TEM.

4. Discussion

Contrary to what happens in metal nanoparticles, a distinctive feature of small sub-nanometre Ag clusters is their strong fluorescence due to their lower density of electronic states [22–26]. Therefore, the presence of fluorescence in samples 1d and 1g can be taken as an evidence for the formation of small Ag sub-nm clusters in these samples. In a previous publication [14] we have studied in detail the clusters formed in stage 1d, concluding that they are formed by planar Agn clusters with \( n < 10 \). The fact that clusters aggregate forming 2D nanoislands can be related with the relative hydrophobic character of these small clusters, tending to aggregate when they are deposited onto the hydrophilic Formvar surface of the TEM grid. Guillen–Villafuerte et al. [27] have recently shown that Pt clusters prepared in microemulsions have also a tendency to self-aggregate when they are deposited onto the Au (1 1 1) surface forming ordered arrangements in several hierarchical levels. They also have shown that TEM images, offering only two-dimensional projections of the samples, cannot be used to distinguish the true morphology of the particles. In our case, the existence of 2D cluster aggregates of planar clusters can explain the differences in sizes observed by TEM and STM for sample 1d. The stage 1g shows a nearby related fluorescence behaviour, and can therefore also be identified with the presence of small Agn clusters. Although \( n \), the number of atoms per cluster, should be in this case somehow larger than for the stage 1d, because they are formed at a later stage in the evolution of the sample, the value of \( n \) should be also \( < 10–12 \). The reason for that is the observance of only high energy absorption and emission bands in this sample. In this case, TEM and STM pictures agree, which can be taken as a proof that 3D particles are formed. However, a particle of 1.5 nm in size should have around 100 atoms, which does not agree with their absorption/emission properties. Again, the presence of 3D cluster aggregates could explain the results. The different aggregation behaviour (2D/3D) for the two stages (1d/1g) could be related to differences in the planar/non-planar geometry of the clusters, but this is a matter which deserves a much detailed study.

The different fluorescent behaviours observed for the stages 1d’ and 1g’ are summarized in the scheme shown in Fig. 4 for the three main excitation wavelengths. Assuming that one cluster has only one main specific absorption and emission peak [22,28], one can see that in both stages there are, at least, two different fluorescent clusters. The cluster, with an absorption maximum located at 230 nm, is common

Fig. 3. STM image showing silver clusters with a planar morphology deposited onto an Au plate. Au triangular terraces separated by monatomic steps in height (clearly seen in the left upper corner) can be compared with the silver island height.

Fig. 4. Schematic diagram of energy levels explaining the fluorescent emission spectra observed for silver clusters synthesized in microemulsions. Energy values are given in eV (and nm inside parenthesis).
to both stages, but the emissions are different. On the other hand, the other fluorescent peak is located at approximately the same emission wavelength although the absorption is red shifted for the 1g sample. Moreover, it is observed an electronic transfer (ET) (or charge transfer (CT)) for the 230 nm absorption band in the 1g sample. Because the results show that, although some common clusters may be present in both stages (e.g. clusters showing an absorption at 230 nm), they are somehow different because, in general, their absorption and emission wavelengths are different. It is also observed that there is, at least, one non-fluorescent cluster in the 1d stage, namely, the cluster absorbing at 430 nm. One of the main clusters identified before by EPR in the 1d stage is the paramagnetic Ag$_5$ cluster [14]. Contrary to that, sample 1g, however, does not show any EPR signal indicating that this cluster disappears (maybe because of growing) in stage 1g. Because the absorbance at 430 nm also disappears in the later sample one is tempted to attribute this band to the Ag$_5$ cluster. The lower stability predicted for clusters with an odd number of electrons could explain both, the absence of fluorescence and the large red shift of its absorption band compared with other more stable clusters.

5. Conclusions

A simple microemulsion method is reported for the synthesis of silver sub-nm clusters. Microemulsion droplets act as stabilizing agents, as well as to control the cluster formation in a slow reduction process. Two main stages were identified in the evolution of the cluster formation using UV–vis and fluorescence spectroscopy. TEM and AFM micrographs show the formation of self-aggregated clusters. In the first stage, clusters aggregate forming by 1 atom height 2D nanoislands, whereas in the second stage, 3D aggregates are formed. Different aggregation behaviour could be related with differences in the geometry of the clusters formed at both stages. Finally, it is concluded that the fluorescence behaviour observed for both stages points to the existence of well defined energy levels, which indicate that these small clusters display a molecule-like behaviour.

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