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Stable Silver Clusters and Nanoparticles Prepared in Polyacrylate and Inverse Micellar Solutions

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Silver clusters and nanoparticles were prepared by reduction of silver nitrate by sodium borohydride in water, in the presence of polyacrylate ions, and in inverse micellar solutions consisting of Laureth 4 and water. The kinetics of formation of Ag_4^{2+} aggregates and Ag_9^+ in the presence of polyacrylate ions could be observed by the stopped-flow technique, and the characteristic UV absorption spectra of the respective stable clusters were recorded. The formation of these species was critically dependent on the manner in which reactants were combined. The silver nanoparticles prepared in the inverse micellar solutions using different mixing procedures were characterized via UV−vis spectra, dynamic light scattering, and transmission electron microscopy. The results showed that the procedure of adding aqueous sodium borohydride solution into the inverse micellar solution containing silver nitrate gave the most uniform spherical silver nanoparticles. The reaction kinetics of this procedure was investigated through UV−vis spectra, which indicated that the generation of silver nanoparticles occurred in parallel with the disappearance of smaller clusters, and was characterized by a single exponential with a time constant of about 18 s, followed by aggregation into much larger particles.

Introduction

Nanoparticles of metals have been investigated extensively in recent years due to their novel material properties which differ greatly from the bulk substances.[1,2] Among them, silver nanocrystallites have been widely studied[3-10] due to their application potential in catalysis[11] and photographic processes,[12] and as the substrates for surface-enhanced Raman spectroscopy.[13]

The early events, from formation of silver atoms and clusters to ultrafine particles in solution, are still poorly understood. Research on silver clusters was first carried out with silver vapor or in supersonic beams in vacuo,[14] as well as in matrices at low temperatures.[15] The first observation of silver clusters in dilute aqueous solutions at room temperature was made from pulse radiolysis studies.[16,17] The ability to produce and stabilize such clusters and resulting nanoparticles in appreciable amounts using simple solution chemistry will enhance our fundamental knowledge of primary nucleation events, at the same time providing chemical species for novel applications ranging from catalysis to multiphoton laser spectroscopy.

A variety of methods to prepare the metal nanoparticles have been reported in the literature, which include chemical reduction in aqueous media without[18,19] and with stabilizers,[9,20] radiation chemical reduction,[16,17,21] thermal decomposition in organic solvents,[22] Langmuir−Blodgett films,[23,24] etc. Pileni et al.[5,7,8,25,26] used inverse micelles or microemulsions as microreactors for

the preparation of nanoparticles. Friberg[27,28] and Guo et al.[29,30] extended the scope by applying lyotropic liquid crystals as the template for particle formation.

Wang et al.[9] prepared silver hydrosols through reduction of silver nitrate ($AgNO_3$) by sodium borohydride ($NaBH_4$) in an aqueous medium, and stabilized the particles by sodium oleate, and then obtained the organosols using a solvent exchange method. Instead of $NaBH_4$, Bright et al.[10] used citrate and ethylenediaminetetraacetic acid (EDTA) as the reducing agents. Liz-Marzán et al.[6] produced silver nanoparticles through reducing $AgNO_3$ in ethanol simply by nonionic ethoxylated surfactants. Barnickel et al.[3] obtained silver nanoparticles by mixing two sets of water/cyclohexane/pentaethylene glycol dodecyl ether water-in-oil (W/O) microemulsions with $AgNO_3$ solubilized in one set and $NaBH_4$ as the reducing agent in the other set. Pileni et al.[5,7,8] obtained silver nanoparticles in W/O microemulsion with the application of functionalized surfactant, silver bis(2-ethylhexyl) sulfosuccinate (Ag(AOT)). It was found that if the organic medium was isooctane, spherical silver particles of several nanometers, $(Ag^0)_n$, were obtained, while replacing isooctane by cyclohexane led to the unusual product, Ag_4^{2+} clusters.[5,7,8]

Information regarding the kinetics of particle formation is of critical importance in controlling the size and distribution[31] and has so far been investigated very little for this system. In this study, the reduction of silver ions by sodium borohydride was investigated in water and poly(acrylic acid) by the stopped-flow technique, and the same, much slower process was carried

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out in microemulsion media. For the latter purpose, our attention was focused on the commercial nonionic surfactant Laureth 4 (or Brij 30), poly(4)-oxyethylene lauryl ether, since it has been extensively investigated by us,[32] and it can provide an inverse micellar solution when mixed with small amount of water, and a lamellar liquid crystal (LLC) phase with increasing amount of water. Therefore, if the silver nanoparticles are produced in the inverse micellar solution, they can be further captured in the LLC structure by simply adding the required amount of water to the system. In this contribution, we focus on the synthesis of silver nanoparticles using the inverse micellar solution of Laureth 4 as the template, and using the $AgNO_3$ and $NaBH_4$ solutions as the aqueous phase.

Experimental Section

Materials. $AgNO_3$ and $AgClO_4$ were obtained from J.T. Baker (Phillipsburgh, NJ), and $NaBH_4$ was from Sigma (St. Louis, MO), both of analytical grade. Laureth 4 (Brij 30) was from Uniqema (Wilmington, DE). Sodium salt of poly(acrylic acid), MW = 2100, was from Aldrich Chemical Co. (Milwaukee, WI). All materials were used as received. Aqueous solutions of $AgNO_3$ or $AgClO_4$ and $NaBH_4$ were prepared using degassed, preboiled deionized water. Since borohydride can, catalyzed by metallic ions, react directly with water to form hydrogen,[33] freshly prepared aqueous solutions were prepared, and kept on ice if necessary, in all the experiments.

Preparation of Particles. The preparation of silver clusters in water and in the aqueous solution of polyacrylate ions was made by mixing the solution containing the silver salt (and the polyanion) and that containing $NaBH_4$ in the stopped-flow apparatus (vide infra). For the reaction in microemulsions, the composition of the inverse micellar solution used is 8 wt % water and 92 wt % Laureth. The concentration of the aqueous solution is 5.4×10^{-3} M for $AgNO_3$, and 2.7×10^{-2} M for $NaBH_4$ (based on the initial water phase). Three different procedures were employed all with magnetic stirring during the mixing process. Procedure 1 was mixing two inverse micellar solution containing $AgNO_3$ and $NaBH_4$ respectively. Procedure 2 involved adding aqueous $NaBH_4$ solution into the inverse micellar solution containing $AgNO_3$, while in procedure 3, $NaBH_4$ was contained in the inverse micellar solution and the aqueous solution of $AgNO_3$ was added. The important observation was that all three procedures led to the same final composition. The silver particles prepared were found to be insensitive to air, so the syntheses in microemulsions were performed in the presence of air at room temperature.

Measurements. The UV−vis spectra of the silver particles were recorded on a HP 5425 diode array spectrophotometer using the inverse micellar solution without silver as the background, and the fast kinetics was obtained while the solution in the UV cell was stirred by a magnetic stirrer. Samples for dynamic light scattering (DLS) were prepared by diluting several drops of the inverse micellar solution into 2 mL of water under vigorous stirring. The DLS measurements were performed on a Brookhaven Instruments system with a 514.5 nm argon ion laser (model 85 Lexel Laser) as the light source. Intensity correlation data were analyzed by the CONTIN method, and the diffusion coefficients were represented in terms of apparent radii by Stokes equation. For electron microscopy, a few drops of the inverse micellar solution was diluted into 1 mL of ethanol, and the resulting ethanol solution was placed onto a carbon-coated copper grid and allowed to evaporate. Micrographs were recorded using a JEOL JEM-1200EX transmission electron
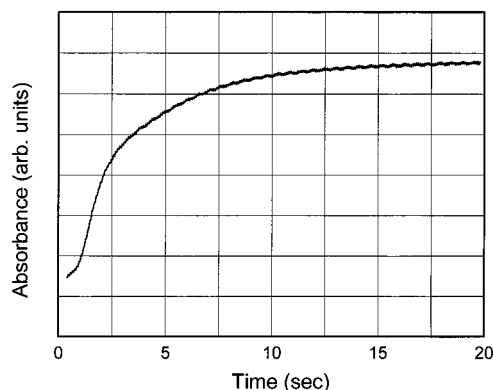

Figure 1. Formation of Ag particles in aqueous solution by stopped-flow kinetics monitored at 390 nm. $[AgNO_3] = 0.002$ M; $[NaBH_4] = 0.0002$ M.
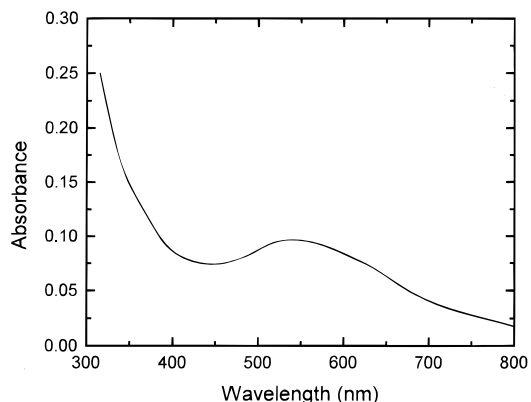

Figure 2. Absorption spectrum of aggregated Ag_4^{2+} clusters stabilized by polyacrylate anions. $[AgClO_4] = 0.001$ M; $[NaBH_4] = 2.5 \times 10^{-5}$ M; $[polyacrylate] = 0.01$ M.

microscope (TEM). Stopped-flow experiments were performed using an instrument described earlier.[34]

Results and Discussion

The formation of silver particles in pure aqueous solutions is shown in Figure 1. The time constant for this process is about 1.8 s. In pure aqueous solutions, it was not possible to trap small silver clusters definitively. Hence, reactions were carried out in the presence of poly(acrylic acid) as a growth modifier.[35] The rationale behind this strategy is to keep the nucleating sites as far apart as possible, achieved due to the strong electrostatic repulsion of the negatively charged polyacrylate anion which was in large excess and contained bound Ag^+ ions. Henglein and co-workers have performed a rather detailed investigation of the reduction of silver ions in the presence of poly(acrylic acid)s using the solvated electron as the reducing agent.[35] With the high time resolution available by this technique, spectra of silver species from monatomic to a few nanometers could be observed. In the present stopped-flow study, the relatively fast formation of a colored species could be observed at 540 nm (Figure 2) with a time constant of about 70 ms. This process can be ascribed to the rapid formation of Ag_4^{2+} which aggregates to larger species. It was originally thought that Ag_4^{2+}−poly(acrylic acid) had an absorption maximum at 480 nm,[35a] but this was later[35b,c] ascribed to a possible dimer of Ag_4^{2+}. On the basis of current information[35] it is reasonable to assume that the species absorbing at the longer wavelength of 540 nm is probably larger than an Ag_4^{2+} dimer, consisting of approximately equal numbers of silver atoms and ions. In the absence of experiments such as X-ray crystallography, the exact identity
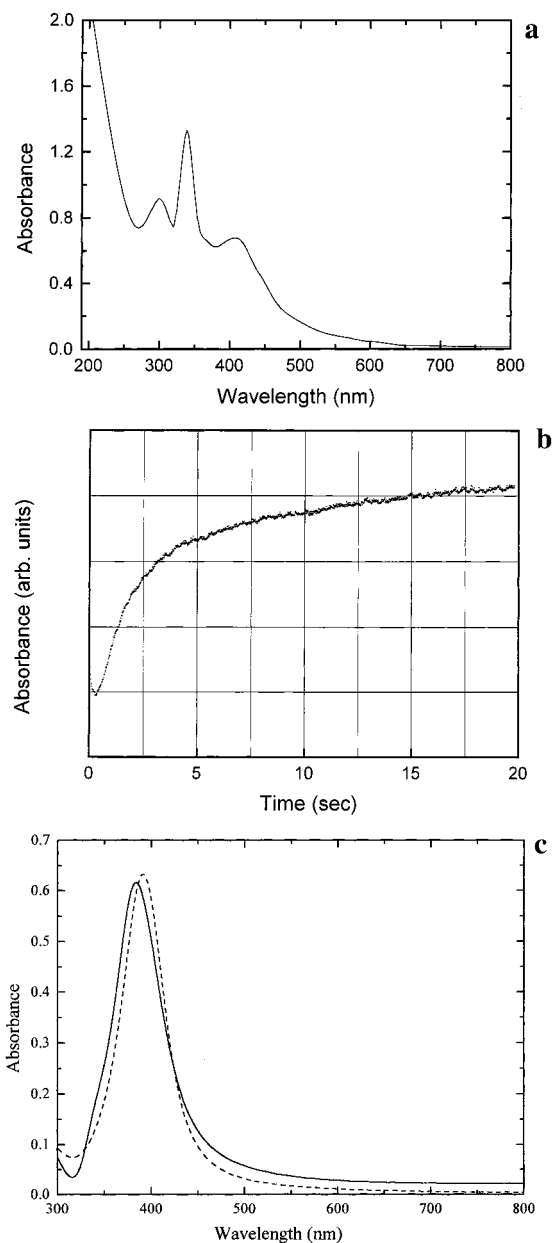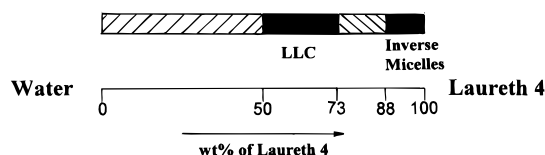
Figure 4. Binary phase diagram of Laureth 4 and water. LLC = lamellar liquid crystal.

corresponding time constant of 1.6 s, followed by a second slower process due to the formation of larger clusters and silver nanoparticles. It is interesting to note the similarity between silver cluster species produced by sodium borohydride reduction in the present study with earlier reports[35] in which radiolytic methods were used. This finding supports the model[35] in which the reducing agent creates an initial burst of silver atoms, which aggregate (with the inclusion of silver ions) to produce clusters and eventually colloidal silver. The aggregation is greatly influenced by the presence of a growth modifier such as poly-(acrylic acid).

In addition to particle preparation, it is important for many commercial applications to achieve a well-defined array of the resulting nanoparticles. For this purpose, the combination of controlling the formation of particles in a self-assembling system, e.g., microemulsion or liquid crystal, can be very advantageous. Consequently, the Laureth 4−water system was used to produce the silver nanoparticles. The binary phase diagram is illustrated in Figure 4.[32] Laureth 4 has almost no water solubility as shown in the left side in Figure 4. It can dissolve water to a maximum of 12% to form inverse micellar solution, and a higher water content gives a lamellar liquid crystal (LLC) phase between 27 and 50% water. Liz-Marzán et al.[6] used several nonionic surfactants of the Brij series in their preparation of silver particles, including Brij 72, Brij 92, and Brij 97. Compared with those, Laureth 4, or Brij 30, is of medium hydrophobicity, which is more hydrophobic than Brij 97 (poly(10)-oxyethylene oleyl ether), while more hydrophilic than Brij 72 (poly(2)-oxyethylene stearyl ether) and Brij 92 (poly(2)-oxyethylene oleyl ether). In the inverse micellar solution the water pools contained may provide a large number of reaction sites which are separated and isolated from one another by the nonaqueous medium with a high viscosity, through controlling the location and communication of the reaction components.[25,26,36]

Upon mixing of the two inverse micellar solutions, or the inverse micellar solution with water, in procedures 2 and 3, a slight yellow color appeared in the resulting solution, indicating the reduction of silver cation into its metal form.[3,19] For procedure 1, no coloration was observed immediately after mixing, and the solution turned slightly yellowish 10 min later. In all three cases the color grew a little darker with time, and the dispersions containing silver particles were stable for at least 1 month.

Shown in Figures 5−7 are the UV−vis spectra of the silver nanoparticles in the three procedures. In Figures 6 and 7, a strong absorption band at 420 nm is seen, which corresponds to the plasmon peak associated with relatively large spherical silver nanoparticles.[5,33,37,38] In addition, the band is stronger and more symmetric in Figure 6 than that in Figure 7, indicating that there are more particles formed in protocol 2, and they are more monodisperse than those in procedure 3. This band decreases with time, accompanied by gradual red shift and severe broadening, showing the onset of particle aggregation.[4,19,39] In Figure 5 a broad band centered at 400 nm appears at the beginning, the intensity of which increases in the first 10 min,
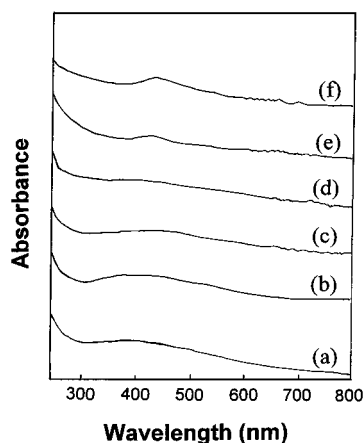

Figure 3. (a) Absorption spectrum of Ag_9^+ clusters stabilized by polyacrylate anions. $[AgClO_4] = 2.5 \times 10^{-4}$ M; $[NaBH_4] = 2.5 \times 10^{-4}$ M; [polyacrylate] = 0.01 M. (b) Formation of predominantly Ag_9^+ clusters by stopped-flow kinetics monitored at 340 nm. $[AgClO_4] = 2.5 \times 10^{-4}$ M; $[NaBH_4] = 2.5 \times 10^{-4}$ M; [polyacrylate] = 0.01 M. (c) Absorption spectra of silver nanoparticles obtained using 1×10^{-4} M $[AgClO_4]$ and 0.005 M $[NaBH_4]$. Dashed curve (- - -) in water, full curve (—) in the presence of 0.01 M polyacrylate.

of this species cannot be determined. The formation of atomic silver and smaller clusters was too fast to be observed.

At more dilute silver ion concentrations, Ag_9^+ was found to predominate (Figure 3a), based on the prominent peak at 340 nm. Absorption bands at 310 and 345 nm have been attributed to a "magic" silver cluster, Ag_9^+, of special stability.[35a,b] The formation kinetics at 340 nm reveals a double-exponential curve (Figure 3b). At this wavelength, there is overlap of the absorption band due to larger colloidal silver particles (Figure 3c), which can vary with the size and distribution of particles. Compared with aqueous solutions, in the presence of 0.01 M polyacrylate ions, the peak maximum is blue-shifted by 7 nm to 384 nm (Figure 3c). Consequently, the major amplitude in Figure 3b can be attributed to the Ag_9^+ cluster, with the

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Figure 5. UV−vis spectra of the silver particles formed in procedure 1: (a) 5 min; (b) 10 min; (c) 30 min; (d) 1 h; (e) 3 h; (f) 24 h.
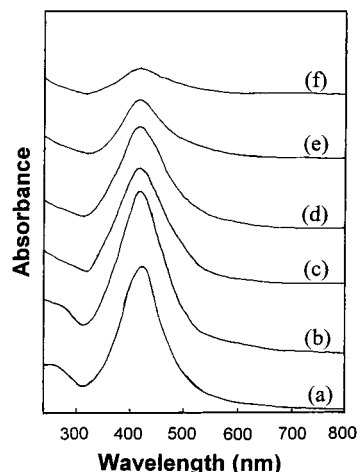

Figure 6. UV−vis spectra of the silver particles formed in procedure 2: (a) 5 min; (b) 10 min; (c) 30 min; (d) 1 h; (e) 5 h; (f) 24 h.
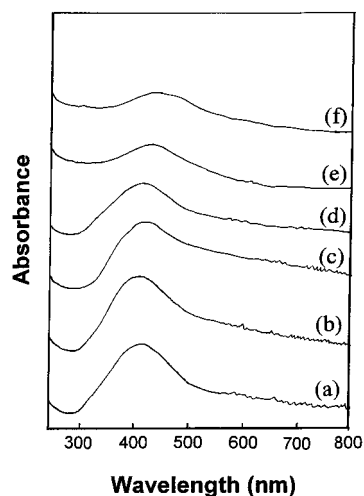

Figure 7. UV−vis spectra of the silver particles formed in procedure 3: (a) 5 min; (b) 10 min; (c) 30 min; (d) 1 h; (e) 3 h; (f) 24 h.

and after that the spectra change very little with time. In all of the three cases the spectra show no change after 24 h. The results of UV−vis spectra are in good agreement with the visual observation of the color change of the corresponding mixing procedures (vide supra). It should be pointed out that procedure 2 is differentiated from the other two by having an extra
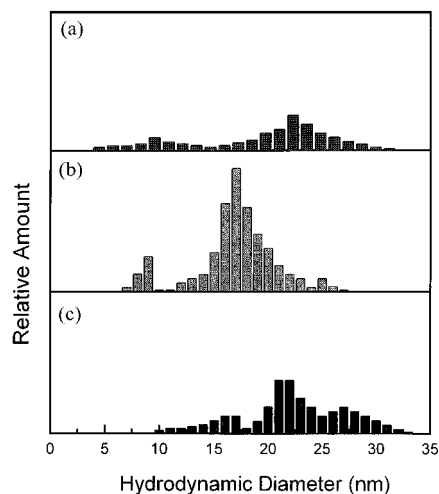

Figure 8. Size distribution of the silver particles at 24 h of the three procedures obtained from the dynamic light scattering measurements: (a) procedure 1; (b) procedure 2; (c) procedure 3.

small absorption peak at ca. 270 nm at early stages of the reaction, spectrum a in Figure 6, which will be discussed in detail later.

Figure 8 illustrates the DLS size distribution of the silver nanoparticles 24 h after the initial mixing. The average hydrodynamic diameters for the three procedures are 25, 17, and 23 nm, respectively. The yield (relative amount) and monodispersity of the particles from procedure 2 are superior to those from procedures 1 and 3. Figure 9 gives the TEM microphotos of these nanoparticles; they confirm the DLS results. It is noteworthy that procedure 2 results in morespherical particles, Figure 9b, as compared with Figure 9, a and c.

From the above it is clear that among the three procedures of producing silver nanoparticles, procedure 2 is the most effective, whereas procedure 3 is better than 1, which is explained as follows.

In procedures 2 and 3, the aqueous solution of one reaction component is added into the inverse micellar solution. Since the final composition is still an inverse micellar solution, the mixing causes the inclusion of the aqueous solution into the water pools of the inverse micelles, leading to direct contact of the two reaction components, which is a thermodynamically favorable, and thus a spontaneous, process. In procedure 1, the two inverse micellar solutions have the same water content, and the mixing will not bring direct contact of the two reaction components as in the other two procedures. The contact of the reaction components in this protocol relies on the exchange of the water content through either the transient short-lived dimer process or the single component exit process.[25,36] Therefore, in contrast to the direct reaction in water pools in procedures 2 and 3, the reaction in procedure 1 is closely related to the mechanism of transfer of reactants between the droplets and the nature of diffusion and collision of droplets in the highly viscous inverse micellar solution,[36,40] and hence it is not surprising that procedure 1 is less effective than the other two.

The difference between procedures 2 and 3 may originate from the different location of the two reacting ions, Ag$^+$ and BH$_4^-$, in the initial solutions. Barnickel et al.[3] proposed that the oxo groups from the polyether may form hydroperoxides with oxygen from the air. These oxides have both oxidizing and weakly reducing properties, and Barnickel et al. suggested that Ag$^+$ can be reduced to Ag^0 by these hydroperoxides,[3] which
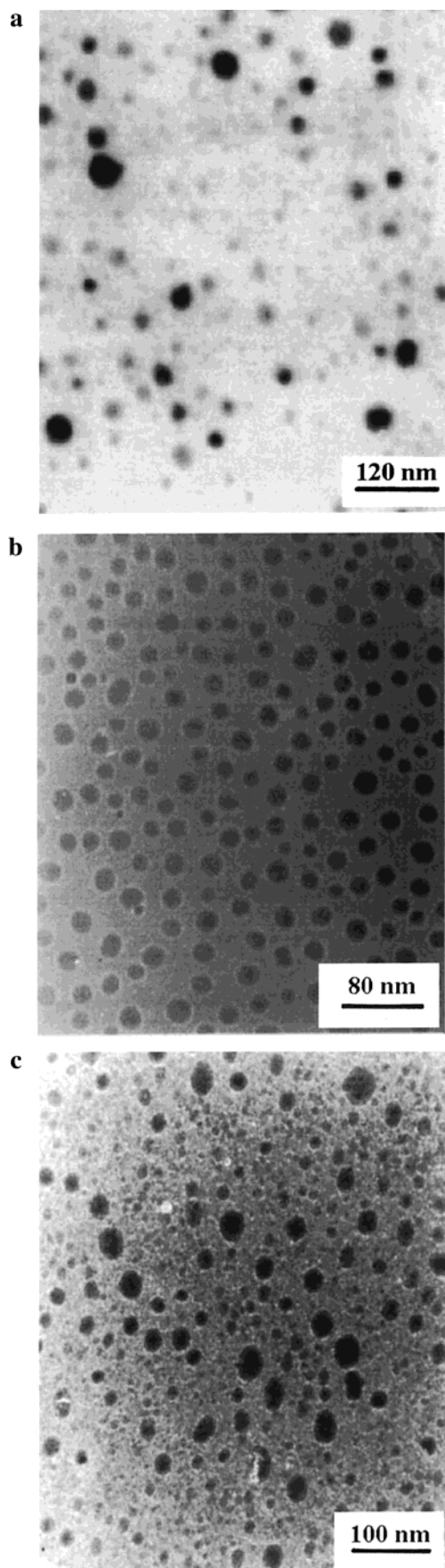
Figure 9. Transmission electron micrographs of the silver particles at 24 h of the three procedures. (a) procedure 1; (b) procedure 2; (c) procedure 3.
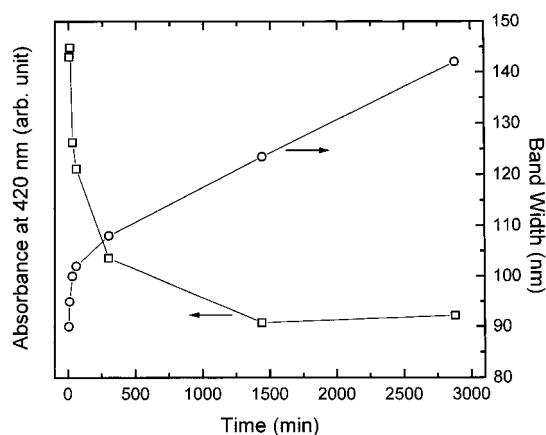

Figure 10. Time dependence of the absorbance and bandwidth of the absorption peak centered at $\lambda = 420$ nm of the silver nanoparticles in procedure 2.

was later confirmed by Liz-Marzán et al.[6] In our study, $NaBH_4$ is applied as the reducing agent and the reducing capacity of hydroperoxides is suppressed. However, in procedure 3, the aqueous $NaBH_4$ has been used to make the inverse micellar solution. Since the BH_4^- ions stay in the surroundings of Laureth 4 for a certain period of time before they react with Ag^+ ions, there is a possibility that they may be oxidized by the hydroperoxides formed by Laureth 4; especially the polyether in our study, i.e., Laureth 4, is in such an excess as compared with cases in the literature: Barnickel et al. used about $10-25$ wt % surfactant,[3] and for Liz-Marzán et al. the typical surfactant concentration was much lower than 10 wt %.[6] As a result, the reducing capacity of $NaBH_4$ in procedure 3 is less than in procedure 2, although the final composition of $NaBH_4$ is exactly the same in the two cases. Another possible reason is that in procedure 2, the availability of the Ag^+ ions would be restricted: they are probably adsorbed near the water/oil interface, which provides easy access to the BH_4^- ions when they move into the water core, driven by the thermodynamic preference. Ultimately, the growth of the silver clusters or nanoparticles is influenced more by the presence of Ag^+ rather than BH_4^- ions. Additional experiments would be required to differentiate between the two possibilities.

Considering these features it is reasonable to conclude that procedure 2 enables the direct contact of the two reactants and ensures the complete reaction between them, and the following analysis is founded on this assumption. Based on Figure 6, the time dependence of the absorbance and bandwidth at the absorption maximum is obtained, which is plotted in Figure 10. The absorbance decreases rapidly, and the bandwidth of the maximum absorption increases with time, showing that the nanoparticles are aggregating into larger particles.[4,19,39] The silver nanoparticles at 24 h, Figure 9b, are much larger than the particles at 10 min, Figure 11. The DLS measurements of the particles at different times are presented in Figure 12, which confirm the aggregation process as well. The mean diameter is 8 nm at 10 min, which increases to 10 nm at 1 h, and 17 nm at 24 h; meanwhile, the size distribution is continuously increasing with time.

However, in the microemulsion media, following the reduction of Ag^+, the growth of metal silver atoms, Ag^0, into the nanoparticles, $(Ag^0)_n$, is missing from Figure 10. In order to understand the reaction kinetics in detail, UV−vis spectra in shorter time scale are recorded, as shown in Figure 13.

From Figure 13, two absorption bands are observed, one at 420 nm and the other at 270 nm. The absorption at 270 nm is
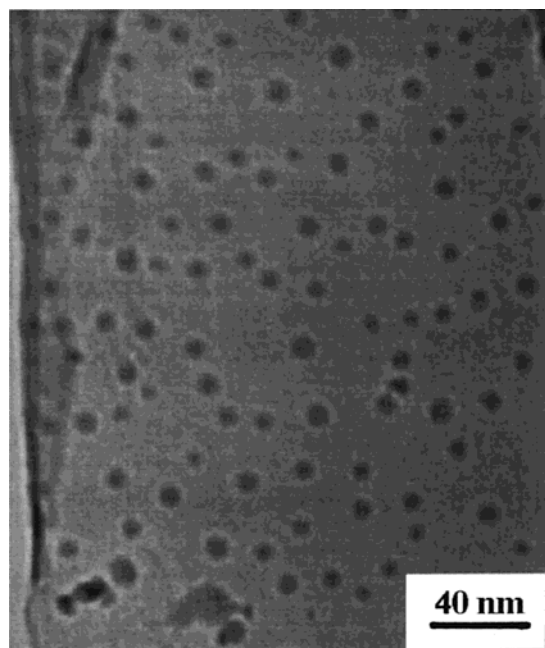
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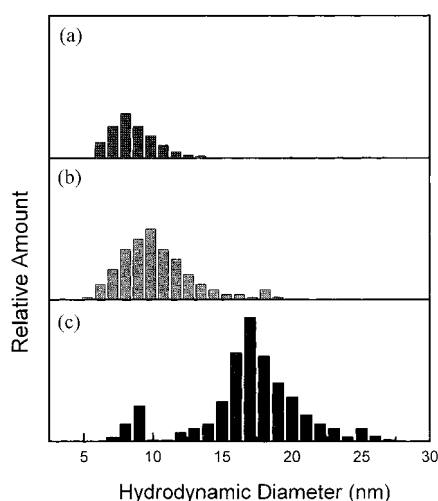**Figure 11.** Transmission electron micrograph of the silver particles at 10 min of procedure 2.

Figure 12. Size distribution of the silver particles in procedure 2 obtained from the dynamic light scattering measurements. The relative amount is plotted in the same scale. (a) 10 min; (b) 1 h; (c) 24 h.
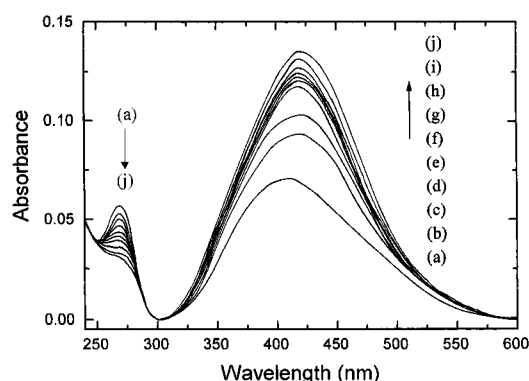

Figure 13. UV−vis spectra of the silver particles formed in procedure 2: (a) 12 s; (b) 24 s; (c) 36 s; (d) 48 s; (e) 60 s; (f) 72 s; (g) 84 s; (h) 96 s; (i) 108 s; (j) 120 s.

due to Ag_4^{2+} and small clusters.[5,41−43] The absorbance at 420 nm increases up to 90 s after which time it is relatively constant. Concurrently, the 270 nm band decreases in the time scale
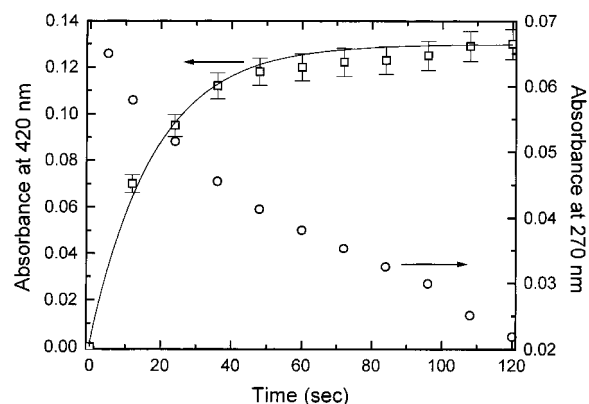

Figure 14. Time dependence of the absorbance of the absorption peaks centered at 420 and 270 nm of the silver nanoparticles in procedure 2. The solid line is the single exponential fit of the data: $A_{420} = 0.13 \times (1 - e^{-t/18})$.

investigated. The absorbance at 420 and 270 nm is plotted against time (Figure 14). The solid line in the figure is a fit by first-order kinetics. The exponential fit gives a time constant of 18 s. This value is much smaller than those obtained by using the nonionic surfactant itself as the reducing agent, which ranged from tens to thousands of minutes.[6] This is not unexpected since BH_4^- is a much stronger reducing agent than hydroperoxides. Therefore, the Ag^+ ions were reduced to form Ag_4^{2+} and other small clusters immediately after mixing, and these precursors transform into relatively lager spherical silver nanoparticles characterized by a single exponential.

Conclusions

From the pulse radiolysis[16] and the present study, the formation of small silver clusters is found to be an extremely rapid process in aqueous solutions, in the presence of polyacrylate ion, and in microemulsion media. Following the initial burst of small clusters, the subsequent aggregation kinetics determines the size and distribution of final particles.

In microemulsions, monodisperse spherical silver nanoparticles can be prepared by adding the aqueous solution of $NaBH_4$ into the inverse micelles of Laureth 4 which contain $AgNO_3$ solution as the aqueous component. Ag^+ ions are reduced by $NaBH_4$ first into Ag_4^{2+} and other small clusters, which transform into nanoparticles with a time constant of 18 s. After 5 min the nanoparticles begin to aggregate. The larger nanoparticles are stable for more than a month because of the protection of the surfactant molecules at the interface. No oil medium is necessary for the preparation.

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