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Absorption spectrum of the trimer silver cluster Ag_3^{2+} and metal nanoparticles in microemulsion

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Abstract

Classical quantum simulation suggests the formation of Ag_3^{2+} [Chem. Phys. Lett. 389 (2004) 150]. We present the effect of water pool radii on the transient absorption spectra of initial silver clusters. Experimental evidence for the formation of Ag_3^{2+} in microemulsion system is reported for the first time. The surface plasmon absorption band of stable silver clusters obtained by bombardment of electron pulses in water-in-oil microemulsions showed absorption maximum at 405 nm. The transmission electron micrograph studies showed the presence of silver nanoparticles having an average size of 10 nm.

1. Introduction

A variety of methods to prepare metal nanoparticles have been reported in the literature. At present the search of methods, which can give monodisperse nanoparticles, is actively pursued [1–3]. Microemulsions are currently being explored for making ultrafine particles of metals and semiconductors for many reasons. The main reason for using microemulsion in the preparation of nanoparticles is that they promise a medium of controlling particle size as well as their distributions. This is because of the reason that they consist of water droplets of nanometer size, which are dispersed in a continuous medium. Microemulsions are used as micro/nanoreactors because they can exchange the content of their water pools by a collision process. It has been suggested that the rate of exchange/communication between two droplets is very fast. It occurs only when an energetic collision between the two droplets is able to establish a water channel between the droplets or the droplets coalesce and reform. It requires a change in the surfactant film or curvature of droplets. This process is thermodynamically unfavourable and has not been governed by diffusion-controlled process. Thus, interchange of nuclei becomes more difficult as the nuclei grow.

Pileni and co-workers [4] have used extensively inverse micelles and microemulsions for the preparation of nanoparticles. It was found that if the organic medium was isooctane, spherical size of nanoparticles was obtained, while replacing isooctane by cyclohexane lead to the formation of small silver clusters.

Information regarding the kinetics of particle formation is of critical importance to know the mechanism of the growth process of the particles. Pulse radiolysis is an important technique by which the initial processes can be probed easily. In addition, the role played by the water pool radii in microemulsion in the growth kinetics of the metal particles is also important to control the size and distribution of particles. So far only little information is available in the literature on this aspect [5]. In the present study, the reduction of silver ions was studied in water/sodium dodecyl sulfate/cyclohexane/1-pentanol by the pulse radiolysis technique. Formation

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of metal nanoparticles was characterized by UV–Vis absorption and transmission electron microscopy.

2. Experimental

2.1. Materials

The surfactant sodium dodecyl sulfate (SDS), obtained from SISCO, India, and spectrograde cyclohexane and 1-pentanol obtained from Spectrochem, India, were used as received. All other chemicals were of Analytical Reagent grade or equivalent.

2.2. Pulse radiolysis

The pulse radiolysis set-up consists of an electron linear accelerator (Forward Industries, England) capable of giving single pulses of 50 ns, 500 ns or 2 μs of 7 MeV electrons. The pulse irradiates the sample contained in a 1 cm × 1 cm Suprasil quartz cuvette kept at a distance of approximately 12 cm from the electron beam window, where the beam diameter is approximately 1 cm. Further details of the LINAC can be seen elsewhere [6]. An aerated 10^{-2} mol dm^{-3} KSCN solution was used for dosimetry and $(SCN)_2^-$ radical was monitored at 475 nm. The absorbed dose per pulse was calculated assuming $G\varepsilon[(SCN)_2^{\bullet -}] = 2.6 \times 10^{-4}$ m^2 J^{-1} at 475 nm [7]. The dose employed in the present study, unless otherwise stated, was typically 67 Gy per pulse.

Microemulsions were prepared by adding de-ionized nanopure water (conductivity 0.06 μS cm^{-1}) obtained from Barnstead (USA) water system, to SDS, followed by the addition of cyclohexane and 1-pentanol. Solutions were optically clear after vigorous shaking. All microemulsions were thoroughly purged with high purity N_2 (>99.99%) prior to irradiation.

In the present study microemulsions of representative w_0 (w_0 = [water]/[surfactant]) values 16, 36 and 60 were used. Hydrated electrons (e_{aq}^-) and other radicals, such as $H^{\bullet}$ and $^{\bullet}OH$, were generated in the water pools of microemulsion by the electron pulse. In the microemulsion, the rate constants of $H^{\bullet}$ and $^{\bullet}OH$ with the 1-pentanol and surfactant are sufficiently high, and hence, scavenging of these radicals occurs. The reaction of surfactant with e_{aq}^- is 4–5 orders of magnitude slower than that with $H^{\bullet}$ and $^{\bullet}OH$. Transmission electron micrographs were taken using a JEOL JEM-2000FX electron microscope.

2.3. Characterization

Samples for transmission electron microscopy (TEM) were prepared by putting a drop of the colloidal solution on a copper grid coated with a thin amorphous carbon film. Samples were dried and kept under vacuum in a desiccator before putting them in a specimen holder. TEM characterization was carried out using a JEOL JEM-2000FX electron microscope. Particle sizes were measured from the TEM micrographs. The particle size was calculated by taking at least 100 particles. Absorption measurements were carried out on a Jasco V-530 spectrophotometer. The UV–Visible absorption spectra were recorded at room temperature using a 1 cm quartz cuvette.

3. Results and discussion

Microemulsions were prepared by adding nanopure water to SDS, followed by addition of cyclohexane and 1-pentanol. All microemulsions were bubbled with N_2 prior to irradiation. On irradiation of the microemulsion the hydrated electrons are produced via the following reactions [8]

$$C_6H_{12} \rightsquigarrow C_6H_{12}^{+} + e^- \quad (1)$$

$$H_2O(\text{water pools}) \rightsquigarrow e_{aq}^-,\ {}^{\bullet}H,\ {}^{\bullet}OH,\ H_3O^+ \quad (2)$$

The H and $^{\bullet}OH$ radicals produced are scavenged by 1-pentanol. However, the yield of hydrated electrons in the microemulsion is lower than that in pure water. It increases as w_0 increases (w_0 = [H_2O]/[SDS]). The details of the system are given elsewhere [9]. The rate constants for the reaction of Ag^+ ions with e_{aq}^- were measured at different w_0 to see the effect of water droplet size on the reactivity of silver ions. The reaction of Ag^+ with e_{aq}^- was monitored at 700 nm. It was observed that the bimolecular rate constant for the reaction of e_{aq}^- with Ag^+ increased as w_0 increased. The results are compiled in Table 1. The variation in rate constants can be explained on the basis of ionic strength of the solution. At lower w_0, the local concentration of Ag^+ is high and therefore the ionic strength is high. As w_0 increases, both the local concentration of Ag^+ and the ionic strength decrease. Hence the bimolecular rate constant for the reaction of e_{aq}^- with Ag^+ increases.

3.1. Reduction of Ag^+ in solutions of different w_0

Fig. 1 shows the time-resolved absorption spectra of the transient species obtained at four different times in N_2-bubbled microemulsion solution (w_0 = 36) contain-

Table 1
Effect of w_0 on the size of silver nanoparticles and bimolecular rate constants for the reaction of e_{aq}^- with Ag^+

w_0	$k_2 \times 10^{-8}$ (mol^{-1} dm^3 s^{-1})	Size (nm)
16	0.52	8 ± 2
36	0.82	10 ± 2
60	25.2	20 ± 2

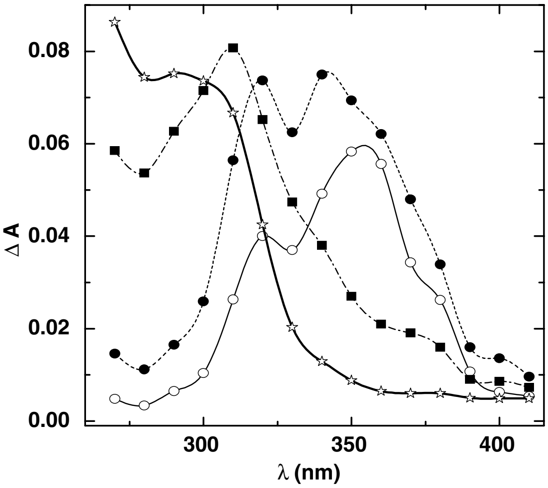

Fig. 1. Time-resolved transient absorption spectrum obtained in N_2-bubbled microemulsion solution ($w_0 = 36$) containing 6.0×10^{-3} mol dm^{-3} $AgClO_4$. (○) 0.6 μs; (●) 0.8 μs; (■) 2 μs; (☆) 16 μs after the electron pulse. Dose = 40 Gy.

ing 6.0×10^{-3} mol dm^{-3} Ag^+. Time-resolved absorption spectra were measured up to 410 nm as the contribution of electron tail increases enormously at higher wavelengths. It was observed that the e^-_{aq} absorption at 700 nm decreases substantially on increasing the concentration of Ag^+. Concomitantly the increase in the rate of 355 nm absorption band due to the transient formation of Ag^0 was observed. It can be seen from Fig. 1 that with time the absorption due to the formation of other transient intermediates build up at lower wavelengths. It can be seen from Fig. 1 that as soon as Ag^0 is formed it reacts with Ag^+ to give Ag_2^+ that shows absorption maxima at 320 and 340 nm. It is important to mention here that in aqueous solution the absorption maximum for Ag_2^+ is reported at 310 and 320 nm. It appears that in microemulsion the absorption band of Ag^0 remains similar to that reported in aqueous solution while that of Ag_2^+ shifts towards higher wavelength [1]. The observed red shift in the absorption maximum could be due to the change in the polarity of the surroundings. However, as SDS is negatively charged there also exists a possibility that Ag_2^+ is bound to the surfactant layer. Hence, it may affect its energy levels. Indeed we have observed the red shift in the absorption spectrum of Ag_2^+. It is known that spectrum of silver particles shifts towards red on adsorption of organic molecules. This suggests that the presence of the palisade layer affects the energy levels of silver clusters. This further shows that the surfactant layer provides some complexation to the silver clusters.

Very recently, Janata [10] has shown that in aqueous solution Ag_2^+ reacts with Ag^+ to give Ag_3^{2+}, which has absorption maximum at 260 and 310 nm. It can be seen clearly in Fig. 1 that 2 μs after the electron pulse a clear absorption band is observed at 310 nm. On comparing the results obtained in microemulsion with that reported in aqueous solution [1,10] it can be inferred that the observed two paths are due to the following reactions (Eqs. 3 and 4). This is followed by the decay of the transients formed.

$$Ag_2^+ + Ag^+ \rightarrow Ag_3^{2+} \tag{3}$$

$$Ag_2^+ + Ag_2^+ \rightarrow Ag_4^{2+} \tag{4}$$

The spectra in Fig. 1 are not spectra of single species, but superimpositions of the absorption bands of at least four species present in different concentrations. Hence, due to the overlapping of the bands the growth and decay kinetics of the transients could not be determined quantitatively. Similar results were obtained in microemulsion with $w_0 = 16$.

Fig. 2 shows the time-resolved absorption spectra of the transient species obtained at four different times in N_2-bubbled microemulsion solution ($w_0 = 60$) containing 2.0×10^{-4} mol dm^{-3} Ag^+. On comparing the results obtained in Fig. 2 with that of Fig. 1 it can be seen that the processes remain similar on changing the w_0 value. The significant difference was observed in the decay kinetics of the higher silver aggregates. In this microemulsion, the use of 1-pentanol as a co-surfactant results in an increase in the viscosity of the interfacial region and in the water core. Therefore, at low 1-pentanol/cyclohexane ratio the microemulsion system becomes more rigid [11]. Due to the rigidity of the matrix the exchange rate between water droplets decreases. This in turn should affect the aggregation processes of initial clusters formed in the droplets. On comparing Figs. 1 and 2 it can be seen that the peaks of the initial clusters of silver are well-resolved in $w_0 = 36$ as compared to that

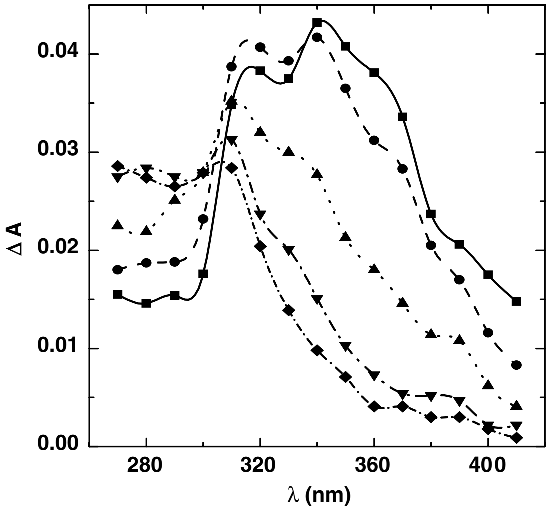

Fig. 2. Time-resolved transient absorption spectrum obtained in N_2-bubbled microemulsion solution ($w_0 = 60$) containing 2.0×10^{-4} M $AgClO_4$. (■) 1.3 μs; (●) 2.6 μs; (▲) 5 μs; (▼) 10 μs; (◆) 16 μs after the electron pulse. Dose = 40 Gy.

in $w_0 = 60$. As droplet size or w_0 increases it acts like a continuum, that is, bulk water. Due to this the diffusion of the species is faster. This could be the reason for observing a distinct absorption band of Ag_3^{2+} in $w_0 = 36$ and 16 (results not shown) as compared to that in $w_0 = 60$. Very recently, Dubois et al. [12], using theoretical calculations, have confirmed the existence of Ag_3^{2+} despite the fact that it has large charge repulsion and only one valence electron. This could be one of the reasons for not getting any shift in the transient spectrum of Ag_3^{2+}.

3.2. Stabilization of silver clusters in the presence of low silver ions

The time-resolved absorption spectrum obtained on reduction of silver ions on pulse irradiation by 2 μs electron pulse, dose 140 Gy, of N_2 -bubbled microemulsion solution ($w_0 = 60$) containing 2.5×10^{-5} mol dm^{-3} Ag^+. The concentration of e^-_{aq} produced by a 2 μs electron pulse was 10^{-5} mol dm^{-3}. Thus, e^-_{aq} has reacted with all or nearly all of the Ag^+ ions present in the solution. It was observed that the stabilization of silver clusters do not take place in the absence of excess silver ions and no increase in optical absorbance due to the formation of other clusters of silver was observed within the time window of our experimental conditions.

3.3. Formation and stabilization of silver nanoparticles

Long-lived clusters were prepared by reducing Ag^+ ions by trains of 500 ns electron pulses in N_2-bubbled microemulsion solution containing 1.0×10^{-3} mol dm^{-3} Ag^+ at different w_0. Fig. 3a shows a representative optical absorption spectra obtained after irradiation by electron pulses in $w_0 = 36$. None of the bands observed at short time scales could be observed at these slow time scales. However, we do observe a broad band at 410 nm, which probably correspond to larger aggregates of Ag_n, due to out-of-plane dipole resonance. It is important to mention here that the silver particles showed almost similar stability under inert conditions or when exposed to air. A representative TEM image of silver particles is shown in Fig. 3b. The corresponding diffraction pattern is shown in Fig. 3c, which corresponds to fcc structure of Ag. It can be seen that the particles were spherical in shape having an average diameter of around 10 nm.

3.4. Alloy of Cd and Ag

One-electron reduction potentials of Cd^{2+}/Cd^+ and Ag^+/Ag^0 are close to −1.8 V vs. NHE [1]. Therefore, there exists a possibility that the two may form alloy rather than core–shell type of particles. Kinetic traces obtained for N_2-bubbled microemulsion solution ($w_0 = 36$) at 360 nm show that electron transfer from Cd^+ to Ag^+ takes place under the conditions where selectively Cd^{2+} is reduced by e^-_{aq} (Fig. 4a).

For the formation of alloy it is necessary that the reduction of both metal ions takes place simultaneously. Therefore, the equal concentration of metal ions was taken for making the mixed particles. On bombardment with trains of 500 ns electron pulses in N_2-bubbled microemulsion solution ($w_0 = 36$) containing 1.0×10^{-3} mol dm^{-3} Cd^{2+} and 1.0×10^{-3} mol dm^{-3} Ag^+, black precipitate was observed. TEM studies revealed the presence of particles of the size of around 25 nm (Fig. 4b). On comparing with Fig. 3b it can be seen that particle size has increased in the case of mixed particles.

Diffraction pattern of a particular particle reveals the presence of two different types of metals (Fig. 4b). It is known that studies of TEM and diffraction methods can be used to determine the change in lattice parameters that results from the alloying process [13]. However, the mechanism of alloying of small particles is still not

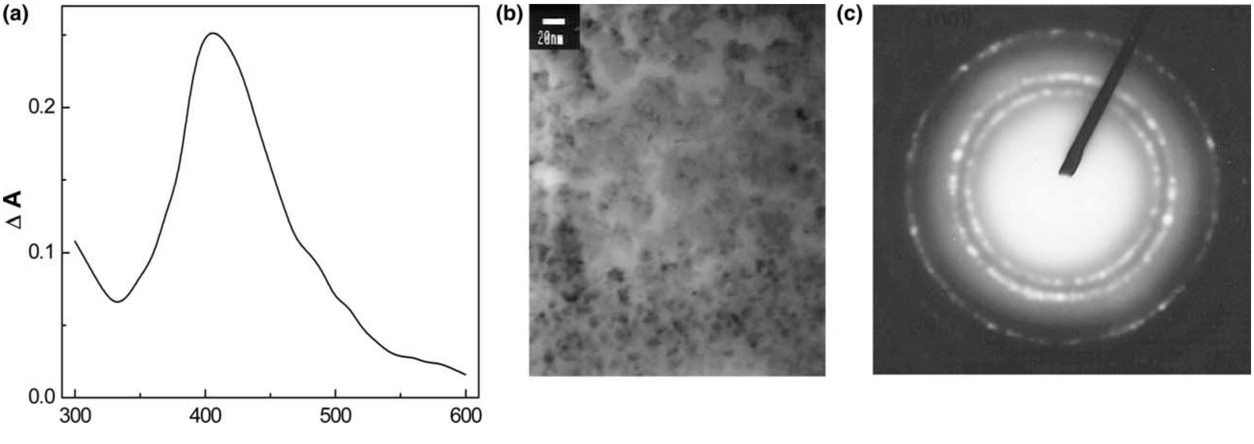

Fig. 3. (a) Absorption spectrum of silver metal sol obtained, on irradiation (dose = 0.7 kGy), in N_2-bubbled microemulsion ($w_0 = 36$) solution containing 1.0×10^{-3} M $AgClO_4$. (b) TEM picture of Ag nanoparticles. Other conditions are the same as in Fig. 3a. (c) Diffraction pattern of silver nanoparticles.

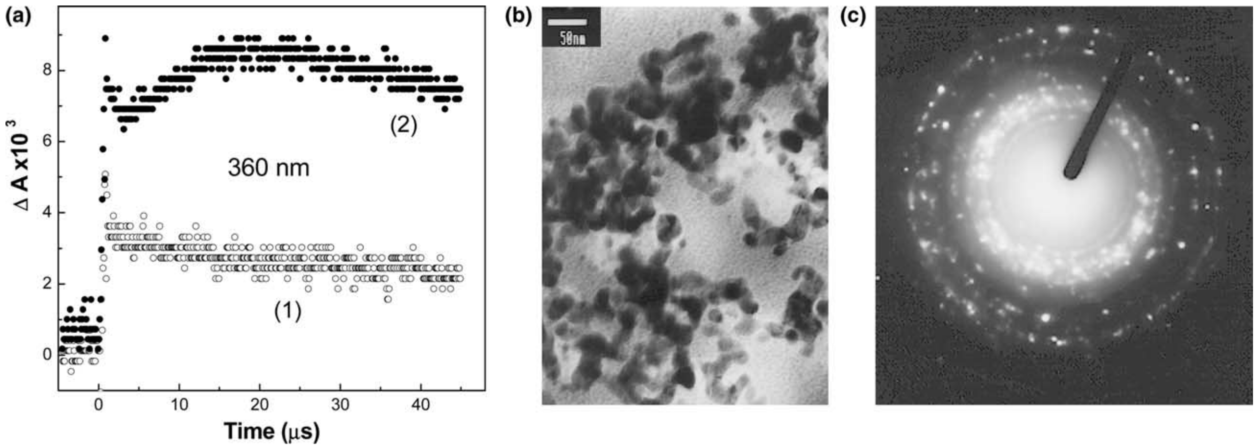

Fig. 4. (a) Kinetic traces obtained for N_2-bubbled microemulsion solution ($w_0 = 36$, dose = 46 Gy) at 360 nm containing (1) $CdSO_4$ (1×10^{-2} mol dm^{-3}) only (2) $CdSO_4$ (1×10^{-2} mol dm^{-3}) and $AgClO_4$ (4.9×10^{-4} mol dm^{-3}). (b) TEM picture of Ag/Cd nanoparticles prepared by irradiating N_2-bubbled microemulsion solution ($w_0 = 36$) containing 1.0×10^{-3} M $CdSO_4$ and 1.0×10^{-3} M $AgClO_4$. Dose = 12 kGy. (c) Diffraction pattern of Ag/Cd nanoparticles.

clear. Kinetic considerations indicate that, for the two metals to mix, the diffusion coefficients need to be many orders of magnitude larger than that the bulk materials [13]. It is suggested that, in addition to the collisional energy and the striking coefficient, the rates of nucleation and growth were determined mainly by the collisions between the atoms [2–4]. In electron beam irradiation the reduction rate was so large that most of the ions are reduced before the formation of the nuclei and therefore the probability of the effective collisions between the atoms is higher. Due to this the probability of alloying increases and the resultant particles would have more monodispersity. Since the difference in the mean diameter of Ag nanoparticles (10 nm) and mixed particles (25 nm) was large enough to distinguish, the nearly mono-dispersion of bimetallic systems suggested that they were not physical mixtures of the individual metallic nanoparticles and bimetallic nanoparticles were really formed. Thus, it appears that in microemulsion, one can get alloy particles of Cd and Ag.

4. Conclusion

It has been shown that initial silver aggregates get well-resolved in microemulsion droplets. The studied microemulsion also provides a medium (microreactor) to stabilize small silver particles. In addition, the slow diffusion of the water droplets can be exploited for making alloy particles.

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