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Absorption Spectra and Reactions of Colloidal Bimetallic Nanoparticles Containing Mercury

Arnim Henglein* and Chris Brancewicz

Center for Advanced Materials Processing, Clarkson University, Potsdam, New York 13699

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Silver and mercury ions are reduced in a common solution by sodium borohydride in the presence of poly(ethyleneimine). Colloidal alloy particles are formed, whose plasmon absorption band is blue-shifted with increasing mercury-to-silver ratio. The reduction mechanism is rather complex: large mercury "drops" are first formed, although silver ions are reduced simultaneously. This effect is explained by an interaction of the two metal redox systems, as silver clusters are reoxidized by mercury ions. The final particles are formed in a reaction of the mercury drops with reduced silver clusters, yielding amalgam particles smaller than the mercury drops. These processes are followed by spectrophotometric and light-scattering measurements. The alloy colloids are stable up to a mercury to silver molar ratio of 2. Upon exposure to air, part of the mercury in the alloy particles is oxidized.

Introduction

During the past few years, much attention has been paid to the preparation of bimetallic nanoparticles in colloidal solution. Most of these preparations were concerned with precious metals,[1] although several combinations of precious with base metals have also been investigated.[2] Among the noble metals, silver and mercury are of special interest with respect to the optical properties of bimetallic particles. Both metals have intense and rather sharp plasmon absorption bands: silver in water at 380 nm, and mercury slightly below 300 nm.[3] In a recent study,[4] mercury ions were radiolytically reduced in a silver sol; it was found that a mercury layer formed around the silver particles and that the absorption band of the latter shifted to shorter wavelengths. The colloids were stabilized by partly carboxylated poly(acrylamide). However, stable colloids could be obtained only if the mercury ions were added to the silver sol and reduced stepwise.

In the present study, silver and mercury ions were reduced simultaneously in solution, using sodium borohydride as the reducing agent. It was found that the bimetallic colloids were stable for days and weeks using poly(ethyleneimine) as stabilizer. The optical spectra are recorded and compared to the spectra of the "core-shell" colloids prepared previously, and some mechanistic observations are reported, too.

Experimental Section

The bimetallic colloids are sensitive to oxygen. All preparations were carried out under the exclusion of air. The reaction vessel was a 100 cm^3 round flask, which carried sidearms with an optical cuvette and a septum. Spectra could therefore be recorded and substances be added with a syringe without exposing the solution to air. The solution (50 cm^3) was flushed with pure argon, the vessel closed, and 0.1−1 cm^3 of the solution of the reducing agent added.

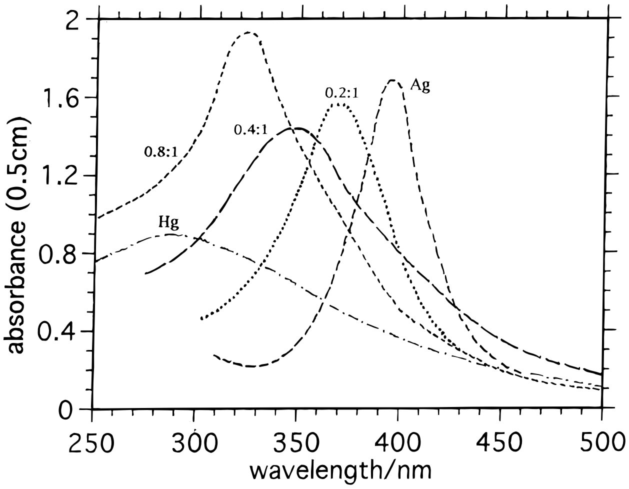

Figure 1. Absorption spectra of silver and mercury and of various bimetallic colloids up to a Hg:Ag mole ratio of 0.8:1. The Ag$^+$ concentration was kept constant (2.0 × 10^{-4} M), and that of Hg^{2+} was varied.

Samples for X-ray diffraction measurements were prepared by removing most of the solvent in a rotary evaporator, centrifuging the rest of the solution (10 000 rpm, 30 min), washing the sediment with an aqueous poly(ethyleneimine) solution, and drying after renewed centrifugation.

Mercury and silver were introduced into the solutions as perchlorates. The poly(ethyleneimine), which served as a stabilizer for both Ag and Hg particles, had a molecular weight of 50 000.

Results and Discussion

Figure 1 shows the absorption spectra of the pure silver and mercury colloids. The spectra were recorded at 10 min after the addition of the reducing agent, i.e., after a time where no more changes occurred. The overall metal concentration was 2 × 10^{-4} M in both

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(2) (a) Henglein, A. *J. Phys. Chem.* **1993**, *97*, 5457. (b) Mulvaney, P. *Langmuir* **1996**, *12*, 788.

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(4) Katsikas, L.; Gutiérrez, M.; Henglein, A. *J. Phys. Chem.* **1996**, *100*, 11203.

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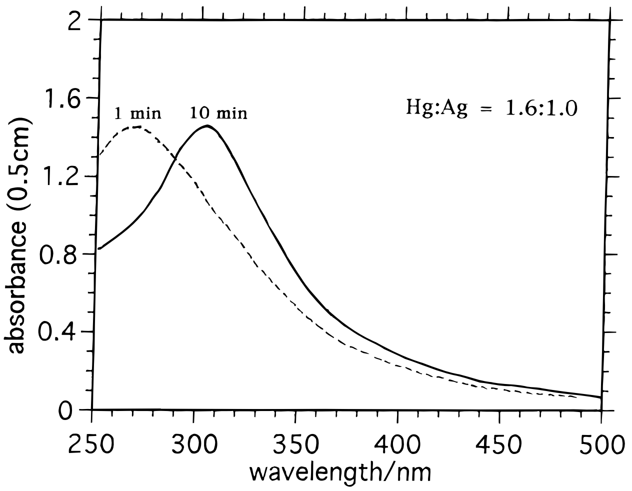

Figure 2. Absorption spectra of a solution in which the mercury-to-silver ratio was 1.6. The concentration of Ag was 1.0×10^{-4} M, that of mercury 1.6×10^{-4} M. The spectra were recorded at different times after the addition of 8.0×10^{-4} M borohydride.

cases, and the concentration of poly(ethyleneimine) was 6×10^{-4} M. The concentration of added borohydride was 8×10^{-4} M. The silver sol consisted of particles with a rather broad size distribution, 5−10 nm, as observed in the electron microscope. The mercury sol contained drops with sizes around 45 nm, as determined by light scattering. The plasmon band of silver appears at 392 nm in the presence of poly(ethyleneimine). The mercury sol exhibits a broad absorption maximum at 285 nm.

The spectra of the three mixed colloids in Figure 1 belong to solutions, which contained 2.0×10^{-4} M silver and various amounts of mercury. The mercury-to-silver mole ratio is indicated on the curves. The spectrum of a solution containing Hg and Ag at the larger ratio of 1.6:1 is shown in Figure 2. The fact that only one absorption band is present shows that no monometallic particles were present. The area of the absorption band becomes greater with increasing Hg^{2+} concentration, which is explained by the increase in total metal concentration. The plasmon absorption band shifts with increasing mercury content to shorter wavelengths. Comparing the wavelengths of the absorption bands in Figures1 and 2 with those of the previously prepared “core-shell” colloids in ref 4, one recognizes that the band positions are the same for a given Hg:Ag ratio, despite the different methods of colloid preparation.

The bimetallic particles obtained from the simultaneous reduction of silver and mercury ions can hardly be expected to be of the “core-shell” type but are expected to be alloys of silver and mercury. Figure 3A shows an X-ray diffractogram of particles obtained from a solution, which contained mercury and silver in the ratio Hg:Ag = 0.8. The typical peaks of schachnerite, $Ag_{1.1}Hg_{0.9}$,[5] are present. Figure 3B shows a diffractogram of particles from a solution, where the Hg:Ag ratio was 0.5. Only the strongest peak of silver is present, indicating that no well-defined amalgam was formed at this low ratio.

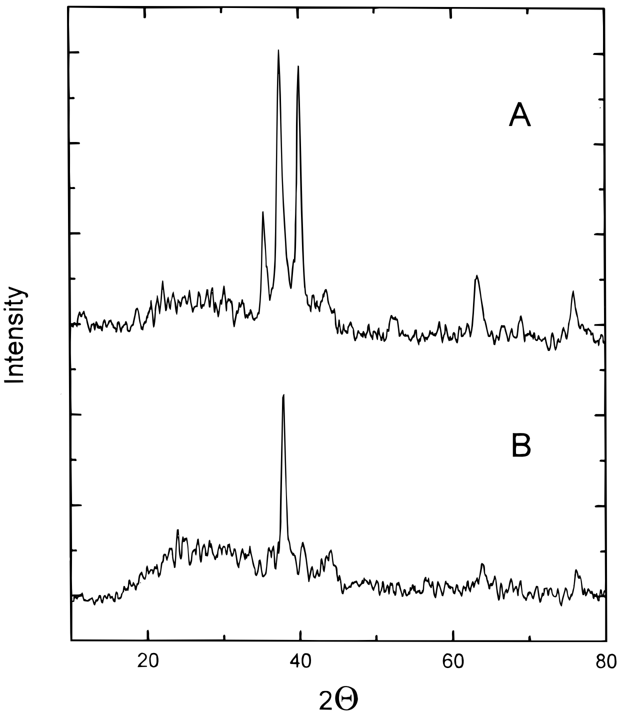

Figure 3. X-ray diffractograms of the particles obtained at different Hg:Ag mole ratios: (A) ratio 0.8:1.0; (B) ratio 0.5: 1.0.

The agreement of the previously and presently observed spectra is taken as an indication that the previously prepared “core-shell” particles also were alloys. This means that the Ag core and the Hg shell in those particles reacted with each other, the mercury atoms formed on the surface of the silver particles rapidly diffusing into the core.

The standard redox potentials of the systems Hg^{2+}/Hg (+0.85 V) and Ag^+/Ag (+0.80 V) lie rather close together. As the mercury ion is mainly present as $HgOH^+$ in neutral solution, the redox potential of the mercury system should even be slightly less positive than +0.85 V. Thus, the driving force for reduction by $NaBH_4$, which is one of the strongest inorganic reductants, should practically be equal for the two ions. As an excess of $NaBH_4$ was applied, the primary reduction processes of Hg^{2+} and Ag^+ should not be disturbed by the presence of the other ion. One would therefore expect that silver and mercury atoms are simultaneously formed and coalesce to yield larger alloy particles.

However, Figure 2 reveals that mercury and silver are reduced sequentially. At 1 min after the addition of the reducing agent, the absorption band peaks at a rather short wavelength (268 nm). This is taken as indication that particles with a larger Hg:Ag ratio are formed first, and this makes one assume that only mercury is effectively reduced in the early stages of reduction. This effect is attributed to intersystem interactions in the early stages of reduction: it is known[2a] that the electrochemical potentials of small intermediate silver clusters Ag_m ($m < 10$) are rather electronegative. Thus, reactions of the type

$$Ag_m + (m/2)Hg^{2+} \rightarrow mAg^+ + (m/2)Hg \qquad (1)$$

become possible. Reactions of this type will cease to

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(5) *Powder Diffraction File*; McClune, W. F.; Maguire, T. M., Mrose, M. E., Post, B., Weissmann, S., McMurdie, H. F., Zwell, L., Morris, M. C., Eds.; International Centre for Diffraction Data, 1981.

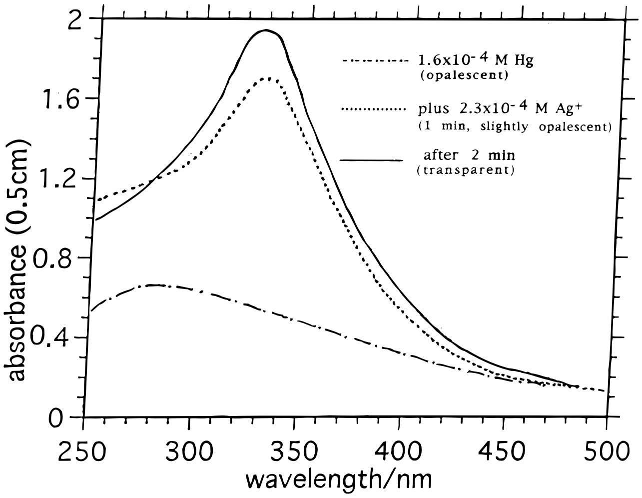

Figure 4. Absorption spectrum of a mercury colloid before and after the addition of silver ions plus $NaBH_4$.

occur when almost all the mercury ions are reduced, and the alloy formation then takes place essentially in a second stage of reaction, where reduced silver clusters react with the mercury particles formed in the first stage.

To separate temporally the two stages of reduction, the following experiment was performed: a mercury sol was produced by reducing 1.6×10^{-4} M Hg^{2+} ions. Figure 4 shows its absorption spectrum; the solution was opalescent because of the large size of the mercury drops. Silver ions (2.3×10^{-4} M) were subsequently added to the system, and borohydride added (6.0×10^{-4} M). As can also be seen from Figure 4, the absorption band of the silver−mercury alloy essentially developed during 1 min (the absorption spectrum at 1 min after the beginning of silver reduction being the shortest time possible; this was the time to put the sample into the spectrophotometer and run the spectrum). The solution was less opalescent after 1 min than the initial mercury sol. At 2 min, the absorption band was fully developed and the solution was completely transparent. It is also important to mention that no absorption at 380 nm of pure silver particles was developed at any time during the reduction.

The process was also followed by measuring the changes in the light scattering of the reacting system. The scattering intensity was measured before reduction of the added silver, and during the reduction. It was found that the mercury particles present in the beginning had a broad size distribution around 45 nm. As can be seen from Figure 5, the scattering intensity decreased rapidly during the first 100 s, i.e., the time required for the buildup of the absorption band of the alloy in Figure 4. However, the scattering intensity still decreased slightly at longer times, although the absorption band did not change. Evaluation of the dynamic scattering data revealed that the solution contained at 10^4 s mainly small particles with a mean size of 10 nm besides a very small number of larger agglomerates.

A remarkable conclusion is drawn from these findings: the large mercury "drops" present in the beginning do not simply "swallow up" the reduction products of silver. If this had occurred, the reaction should have yielded alloy particles substantially larger than the 45 nm mercury drops. Instead, the alloy particles are much smaller than the initial mercury drops. It thus seems that the silver clusters somehow pick up mercury without being incorporated into the drops. The liquid mercury drops possibly are very unstable with respect to emitting smaller droplets or even atoms into the solution, which are the true reaction partners of the silver clusters. Thus, although most of the mercury exists as large drops, the sol kinetically behaves as if the mercury was much more finely dispersed. This should be proven in more detail by a fast time-resolved study.

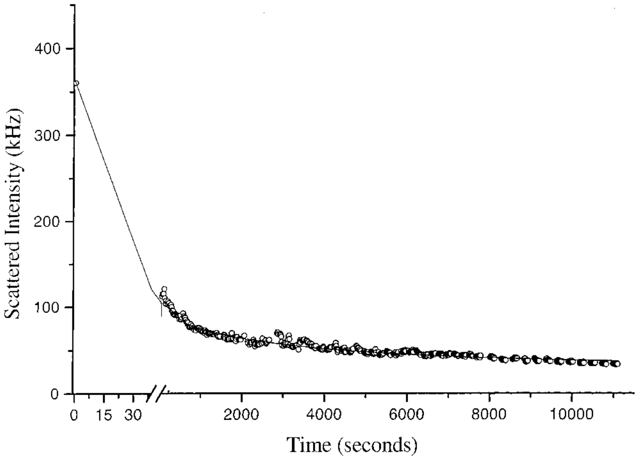

Figure 5. Temporal changes in the scattering intensity as small silver clusters react with large mercury drops. The first measurement was taken 30 s after the addition of the reducing reagent.

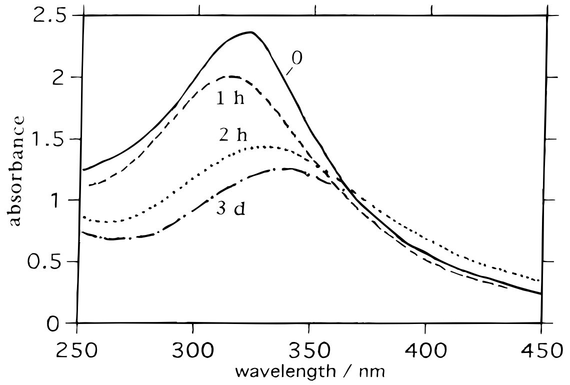

Figure 6. Absorption spectrum of a 1:1 mercury:silver colloid before and various times after the exposure of the solution to air.

A few remarks may finally be made concerning the stability of the mercury−silver colloids. In the absence of oxygen, the colloids with an Hg:Ag ratio up to 2.0 were stable for weeks. Colloids with a higher mercury content became opalescent upon aging and a precipitate was formed after a few days. The optical changes that accompany the oxidation of the amalgam colloids upon standing under air are illustrated in Figure 6. The spectrum of a colloid (Hg:Ag = 1:1) before and at several times after exposing the solution to air is shown. One can see that the plasmon band shifts to longer wavelengths. This indicates that the Hg:Ag ratio decreases upon aging under air, or, in other words, that the mercury in the amalgam is reoxidized. Three days after the exposure to air, a final stable state was reached; the solution was still transparent and stable for weeks. This is similar to the behavior of colloidal gold amalgams, which, when exposed to air, lose a large part of their mercury atoms.[6] We have also carried out a few experiments with gold–mercury colloids, which were prepared by simultaneous reduction of Hg^{2+} and $AuCl_4^-$ in a deaerated aqueous solution of mercury perchlorate and sodium tetrachloroaurate, using poly(ethyleneimine) as stabilizer. It was observed that the loss of mercury from these amalgams upon exposure to air was even more dramatic than in the case of the silver amalgams, as the absorption spectrum of the colloid became almost identical with that of a pure gold colloid after aging under air for 2 days.

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[6] Paal, C.; Steyer, H. *Kolloid Z.* **1919**, *25*, 21.