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Colloidal Silver Nanoparticles: Photochemical Preparation and Interaction with O_2, CCl_4, and Some Metal Ions

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The optical absorption of the colloidal nanoparticles is investigated, formed by the UV illumination of aqueous solutions containing $AgClO_4$ ((1−4) × 10^{-4} M), acetone (2 × 10^{-2} M), 2-propanol (1 M), and various polymer stabilizers. The 7 nm particles, which are produced in the presence of polyethyleneimine, possess an unusally narrow plasmon absorption band. The wavelength and shape of this band are affected by various adsorbed solutes; adsorption phenomena can therefore be studied spectrophotometrically. The changes in band shape that occur in the presence of oxygen and of carbon tetrachloride are attributed to a partial oxidation of the silver particles by these solutes. During the oxidation, the Fermi level in the nanoparticles shifts to a more positive potential, until the oxidation comes to a halt. Chemisorbed metal cations (Cd^{2+}, Ni^{2+}, Ag^{+}, Hg^{2+}) affect the plasmon absorption band of the silver nanoparticles more strongly the more electropositive is the metal. The effect is interpreted in terms of the donation of electron density from the silver particles to the adsorbed cations. In the case of Hg^{2+} ions, the electron donation leads to partial Ag oxidation and amalgam formation. UV illumination of a sol that contains Cd^{2+} ions produces Cd metal on the surface of the silver particles.

Introduction

The yellow color of aqueous silver sols is due to an intense surface plasmon absorption band, which—depending on the method of preparation—peaks in the 380−400 nm range. The absorption is a typical Mie resonance, where the electron gas in the particles undergoes a collective oscillation. The shape of this absorption band depends on the solvent, the stabilizing polymer, and in particular on chemisorbed solute molecules. Absorption effects in colloidal solution can therefore be studied spectrophotometrically.

It is most desirable for many basic studies to prepare silver nanoparticles, whose plasmon oscillation is damped as little as possible. Most methods, in which silver ions are reduced, whether chemically (by borohydride, hydrazine, etc., at room temperature or by alcohol at elevated temperatures[1]) or by γ-radiation,[2] yield particles with a damped absorption, the half-height width of the absorption band amounting to 40−100 nm. The preparation of rather perfect particles, which possess an unusually intense and narrow absorption band, has been reported using "push−pull" reduction of silver ions. In this procedure, Ag^+ ions and intermediate clusters are simultaneously reduced and reoxidized about 15 times until the final particles evolve.[3] However, this method is not readily accessible as it requires the irradiation of the solution with γ-rays under an excess pressure of hydrogen. In the present paper, a simple photochemical preparation is reported that yields silver nanoparticles with similar optical properties. Experiments on electronic interactions of the silver particles with carbon tetrachloride, oxygen, and some metal ions are also described.

Experimental Section

The aqueous solutions contained (1.0−4.0) × 10^{-4} M $AgClO_4$, 1 M 2-propanol, 0.02 M acetone, and the polymer stabilizer in various concentrations. 50 cm^3 of solution was purged with a stream of argon in a 150 cm^3 quartz vessel, which had sidearms carrying a cuvette (0.2, 0.5, or 1.0 cm optical path) and a septum. The vessel was closed and exposed to the light of a xenon−mercury lamp (Oriel Instruments; 150 W) at a distance of 30 cm. The absorption spectrum of the solution was recorded at different times during the illumination without bringing the solution into contact with air. The thickness of the optical cell used is indicated on the ordinate legend of the spectra. Samples of the solution could be withdrawn for electron microscopic investigation or substances be added via a syringe. The electron microscopic samples were prepared by putting a drop of the solution on a copper−carbon grid under an argon atmosphere and removing most of the liquid with tissue paper after 1 min. Electron microscopy was carried out with a Philips CM 12 microscope in the Hahn-Meitner Institut in Berlin, FRG.

UV illumination generates ketyl radicals via excitation of acetone and subsequent hydrogen atom abstraction from 2-propanol:

$$CH_3COCH_3{}^* + (CH_3)_2CHOH \rightarrow 2(CH_3)_2\dot{C}OH \qquad (1)$$

These radicals are strong reductants, the electrochemical

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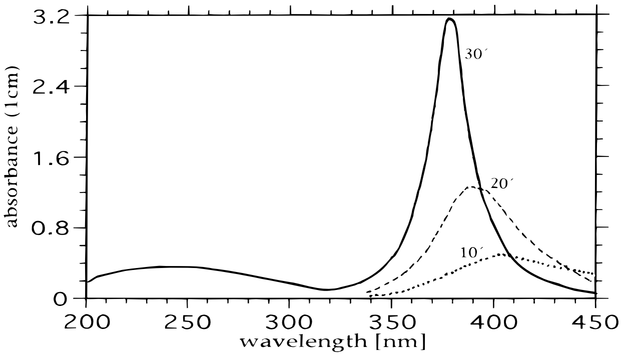

Figure 1. Absorption spectrum of a solution containing 2 × 10^{-4} M polyethyleneimine as stabilizer at various minutes of UV illumination. [$AgClO_4$] 1.1 × 10^{-4} M; [2-propanol] 1.0 M; [acetone] 2.0 × 10^{-2} M. The 260 nm absorption of acetone was compensated by the nonilluminated solution in the reference beam of the spectrophotometer.

potential of the redox system

$$(CH_3)_2\dot{C}OH \rightleftharpoons CH_3COCH_3 + H^+ + e^- \qquad (2)$$

being −1.3 V.[4,5] The radicals disappear either by reacting with each other ($2k = 1.5 \times 10^9\ M^{-1}\ s^{-1}$)[6] or with the silver ions:

$$(CH_3)_2\dot{C}OH + Ag^+ \rightarrow (CH_3)_2CO + H^+ + Ag^0 \qquad (3)$$

Results

Formation of the Silver Sols. Various polymer stabilizers were tried: polyethyleneimine, sodium polyphosphate, sodium polyacrylate, and poly(vinylpyrrolidone). Nanoparticles with the most narrow size distribution and best optical properties were obtained using polyethyleneimine. A typical absorption spectrum is shown in Figure 1. Nevertheless, we also show in Figures 2−4 the spectra that were obtained with the other polymers to demonstrate how important is the choice of the stabilizer. In these figures, the absorption spectrum of a 1.1 × 10^{-4} M Ag^+ solution is shown at various times of UV illumination. The first trace of a yellow color was observed after an induction period of about 1 min. In the beginning of reduction in the presence of polyethyleneimine (Figure 1), particles are formed which absorb at wavelengths longer than the final ones. In the case of polyphosphate (Figure 2), the early products absorb almost at the same wavelength as the final ones. With sodium polyacrylate and poly(vinylpyrrolidone) as stabilizers (Figures 3 and 4), long-wavelength absorptions in the beginning are especially pronounced. After 30 min, no additional changes were observed upon further illumination; it is concluded that all silver ions had been reduced at 30 min. When additional silver perchlorate was then introduced into the solution, further illumination led to an increase in absorption.

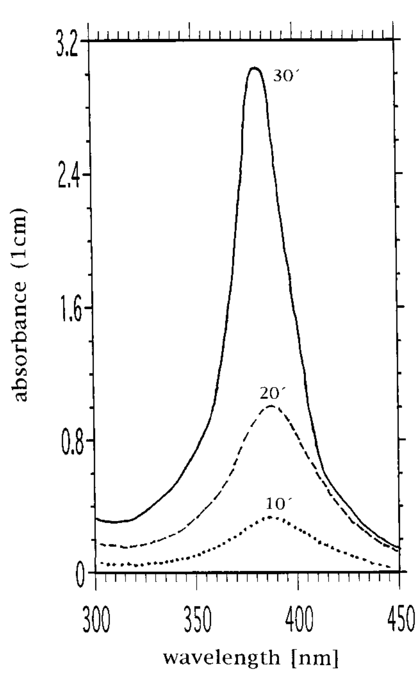

Figure 2. Absorption spectrum of a solution containing 1.1 × 10^{-4} M sodium polyphosphate as stabilizer at various minutes of UV illumination. Other concentrations as in Figure 1.

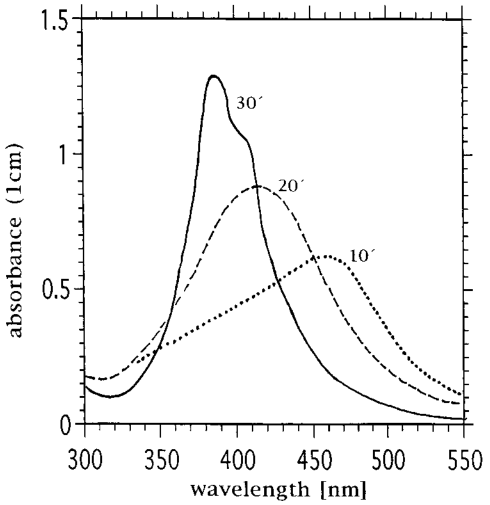

Figure 3. Absorption spectrum of a solution containing 1.1 × 10^{-4} M sodium polyacrylate as stabilizer at various minutes of UV illumination. Concentrations as in Figure 1.

In the cases of polyethyleneimine (Figure 1) and polyphosphate (Figure 2), the final spectrum consists of a very narrow and intense plasmon absorption band slightly below 380 nm. This band is practically completely separated from a very much weaker band at shorter wavelengths (Figure 1), which is attributed to the 4d → 5s,p interband transitions in the particles. A comparison with the particles prepared by push−pull reduction (Figure 1 in ref 3) shows that nanoparticles in Figures 1 and 2 have a similarly narrow absorption band. Figure 5 shows an electron micrograph of spherical silver particles formed in the presence of polyethyleneimine, which have a rather narrow size distribution with a mean size of 7 nm.

In the case of polyacrylate (Figure 3), the solution had a gold-yellow color after 10 min, which turned into a weaker yellow at longer illumination times. The final absorption band is broad, peaking at 385 nm, and there also is a shoulder at 410 nm. Poly(vinylpyrrolidone) is a good stabilizer for silver particles in ethanol.[7] It is

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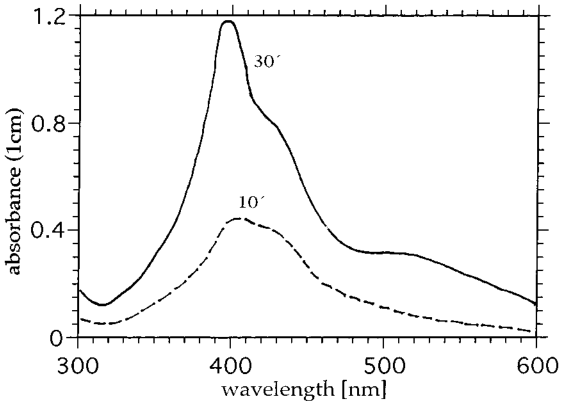

Figure 4. Absorption spectrum of a solution containing 5 × 10^{-3} M poly(vinylpyrrolidone) as stabilizer at various minutes of UV illumination. Concentrations as in Figure 1.

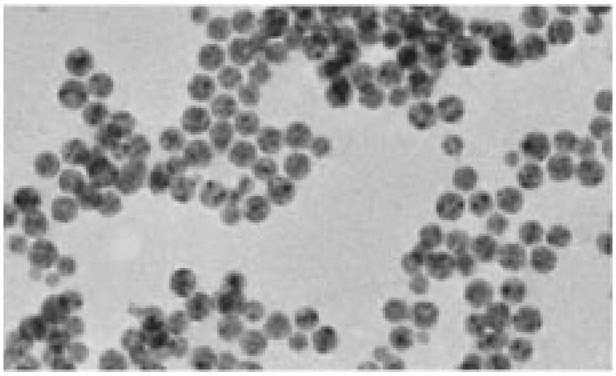

Figure 5. Electron micrograph of the silver particles formed in a 4.0 × 10^{-4} M $AgClO_4$ solution the presence of 6.0 × 10^{-4} M polyethyleneimine. Mean particle size 7 nm. Standard deviation 5 nm.

less efficient in water and had therefore to be used in much higher concentration than the other polymers. The color of the solution was brown-red after 10 min and turned into a dark brown after 30 min (Figure 4). The final absorption spectrum contained a peak at 397 nm and two shoulders at 420 and 500 nm. The longer-wavelength absorptions are possibly due to a strong particle−particle interaction. Particle clusters were seen in the electron microscope, when polyacrylate or poly(vinylpyrrolidone) was used as the stabilizer.

The following experiments were carried out with solutions containing polyethyleneimine, PEI, as stabilizer. This polymer forms a complex with silver ions, which absorbs below 240 nm. Clear sols were obtained for solutions with the molar ratio [PEI]/[Ag^+] larger than or equal to 1.0. In the case of smaller ratios, the sols were more or less opalescent. At the ratios of 1−2 mostly used, only a small fraction of Ag^+ ions is bound to the polymer. The latter conclusion is based on the observation that the UV absorption of the PEI−Ag^+ complex had not reached a saturation value when the Ag^+ concentration was further increased.

Illumination of a solution containing Ag^+, PEI, and 2-propanol without acetone did not lead to the reduction of silver, which shows that the process of eq 1 is necessary to initiate the reduction.

Effects of Carbon Tetrachloride and of Oxygen. Figure 6 shows absorption spectra obtained from the addition of carbon tetrachloride to a 4.0 × 10^{-4} M silver sol, before and at various times after the addition. The CCl_4 concentration was 2 × 10^{-3} M. Initially, the absorption maximum was at 377 nm, and the half-height width of the band was 25 nm. After the addition of CCl_4, the absorption band shifted to longer wavelengths with time. This shift was most pronounced at short times, and the band also became broader. After 30 min, a final spectrum was reached, with the band maximum at 395 nm and a half-height width of 47 nm. The respective maximum absorbancies were 2.16 before and 1.30 after the CCl_4 addition (after 30 min).

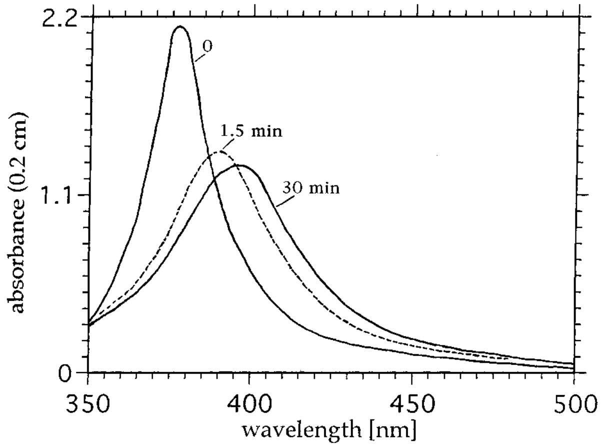

Figure 6. Absorption spectrum of a silver sol before and at various times after the addition of 2 × 10^{-3} M carbon tetrachloride. [Ag] 4.0 × 10^{-4} M; [PEI] 6.0 × 10^{-4} M; [acetone] 2.0 × 10^{-2} M; [2-propanol] 1 M.

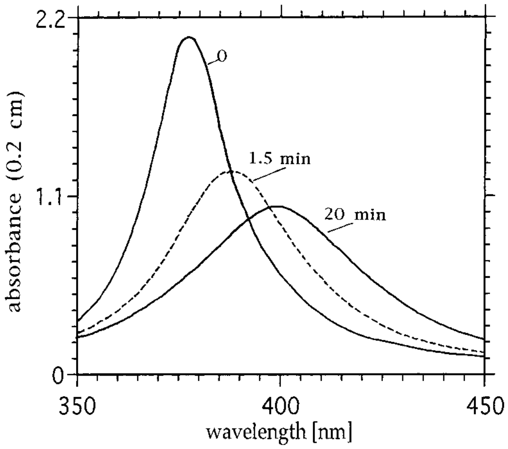

Figure 7. Absorption spectrum of a silver sol before and at various times after exposure to air. Concentrations as in Figure 6.

Figure 7 shows the absorption spectrum of a sol, composed as in Figure 6, before and after exposure to air. After an exposure time of 1.5 min (the time required to record the spectrum), a strong decrease and broadening of the absorption band is seen; this effect continued slowly, but no further changes took place after 20 min. The sol obviously is extremely sensitive to oxygen; the changes in the absorption spectrum are attributed to the oxidation of silver atoms. As Ag^+ ions are formed, the Fermi level in the silver particles moves toward a more positive potential until the oxidation ceases. It is noteworthy that the phenomena observed with O_2 and CCl_4 are qualitatively the same. Therefore, it seems plausible to postulate that carbon tetrachloride also acts as an oxidizing agent toward the colloidal silver particles as does oxygen. Quantitatively, the effect of

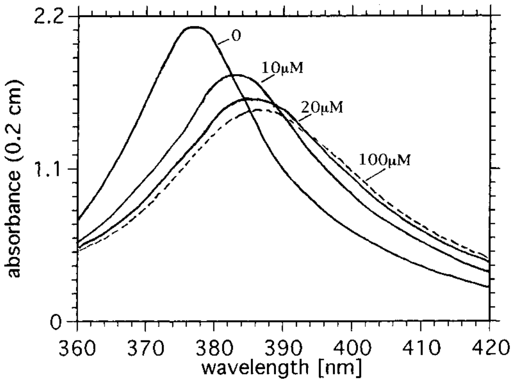

Figure 8. Absorption spectrum of a 4.0 × 10^{-4} M silver sol before and after addition of Ag^+ in different concentrations. Stabilizer: 6.0 × 10^{-4} M polyethyleneimine.

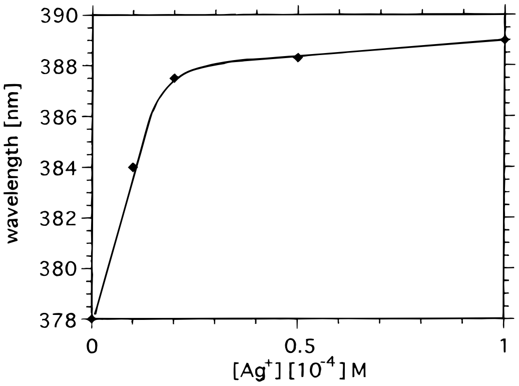

Figure 9. Wavelength of the absorption maximum as a function of the concentration of added Ag^+ ions. Silver colloid as in Figure 8.

oxygen is more pronounced, which is not surprising, as oxygen certainly is a stronger oxidant than carbon tetrachloride.

Effects of Metal Ions. As already mentioned, chemisorbed silver ions cause a red-shift of the plasmon absorption band as was previously found for a colloid that was stabilized by polyphosphate.[8] In the experiment of Figure 8, various amounts of $AgClO_4$ were added to a 4.0 × 10^{-4} M colloid, which was stabilized by polyethyleneimine, and the spectrum was recorded. It can be seen that the plasmon band is shifted to longer wavelengths and reaches a final position at about 1.0 × 10^{-4} M excess Ag^+ ions. Figure 9 is a plot of the wavelength of the band maximum as a function of the concentration of added Ag^+ ions. The shape of the curve is interpreted in terms of the saturation of the particle surface by chemisorbed silver ions. This saturation, corresponding to the formation of a monolayer, is reached at a concentration of excess silver ions of about 2.0 × 10^{-5} M. The slight absorption changes above this concentration are possibly due to the interaction of silver ions which are more loosely bound to the particles than those of the first layer.

In comparing the final spectra in Figures 7 and 8, one notes that the final absorbance in Figure 7 is lower than in Figure 8. This is explained by the fact that the concentration of reduced silver decreased in the experiment of Figure 7, whereas it remained constant in the experinent of Figure 8.

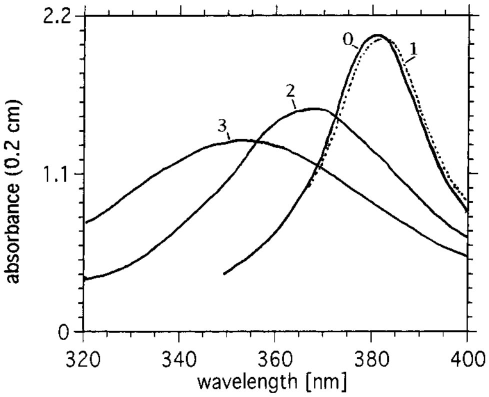

Figure 10. 0: Absorption spectrum of 4.0 × 10^{-4} M silver colloid. 1: after the addition of 3.3 × 10^{-4} M $Cd(ClO_4)_2$. 2: after 20 min UV illumination. 3: after 40 min UV illumination.

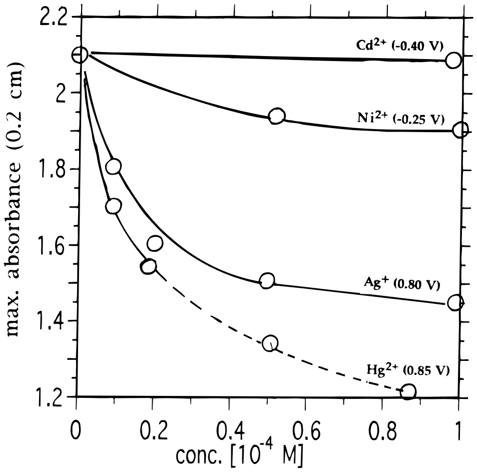

Figure 11. Absorbance in the maximum of the plasmon band of a 4.0 × 10^{-4} M silver sol as a function of the concentration of added metal perchlorates. The electrochemical potential of the metal is also indicated. The dashed part of the curve for Hg^{2+} indicates the region where the plasmon band undergoes a blue-shift. In all the other case, the decrease in absorbance is accompanied by a red-shift of the band.

Figure 10 shows the absorption spectrum of a 4.0 × 10^{-4} M silver sol before (0) and after (1) the addition of 3.3 × 10^{-4} M $Cd(ClO_4)_2$. The absorption band is almost unaffected, as it experiences only a tiny red-shift. When the dispersion was now illuminated, the absorption band shifted to shorter wavelengths (368 nm (2); 352 nm (3)) and became much wider, which is interpreted to be due to the deposition of metallic cadmium on the silver particles. When the solution was finally exposed to air, the absorption band almost instantaneously shifted to 390 nm, as the deposited cadmium metal was rapidly reoxidized by oxygen.

Experiments were also carried out with $Ni(ClO_4)_2$ added to a 4.0 × 10^{-4} M silver sol, which resulted in a shift of the absorption band to longer wavelengths of decreased intensity. The effect was more pronounced than by the addition of Cd^{2+} ions but less pronounced than for Ag^+ ions, as displayed in Figure 11, where the maximum absorption is plotted as a function of the concentration of added cations. UV illumination of a silver sol that contained 3.0 × 10^{-3} M Ni^{2+} ions did not produce any effect, indicating that Ni^{2+} was not reduced to the metal, contrary to what had been observed for Cd^{2+}.

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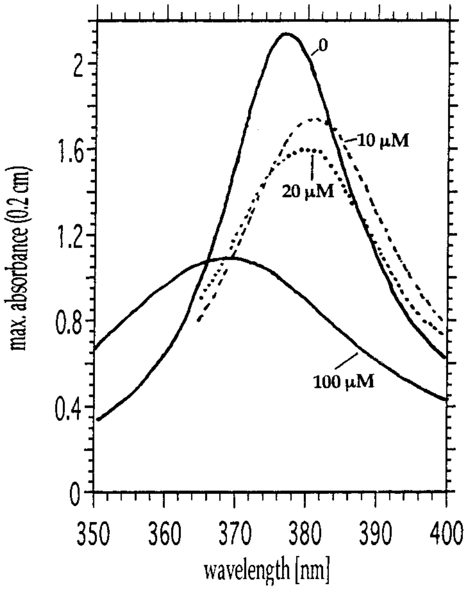

Figure 12. Absorption spectrum of a 4.0×10^{-4} M silver sol before and after addition of $Hg(ClO_4)_2$ in various concentrations.

The addition of $Hg(ClO_4)_2$ in small concentration leads to a red-shift and a decrease in the intensity of the plasmon band as in the case of the other ions. However, above about 2.0×10^{-5} M Hg^{2+}, the absorption band starts to shift to shorter wavelengths. This effect can be seen in Figure 12, where the absorption spectrum of a 4.0×10^{-4} M silver sol is shown before and after the addition of Hg^{2+} ions in various concentrations. The curve for Hg^{2+} in Figure 11 is dashed in the range, where the blue-shift occurs.

Discussion

Reduction of Ag^+. The reaction of the ketyl radical with the silver ion, eq 3, where Ag^0 is a free silver atom, is very slow. The reason lies in the fact that the electrochemical standard potential of the free silver atom

$$Ag^0 \rightarrow Ag^+ + e^- \qquad (4)$$

is as negative as −1.8 V.[9] Comparing the potentials of reactions 2 and 4, it seems that there is no driving force for reaction 3 to occur. However, the ketyl radical undergoes protolytic dissociation with $pK = 12.2$:[10]

$$(CH_3)_2\dot{C}OH \rightleftharpoons (CH_3)_2\dot{C}O^- + H^+ \qquad (5)$$

and the radical anion, which has a very high negative electrochemical potential of −1.9 V),[5] may be the true reductant:

$$(CH_3)_2\dot{C}O^- + Ag^+ \rightarrow (CH_3)_2CO + Ag^0 \qquad (6)$$

The specific rate of reaction 3 is not known, although an upper value of 10^6 M^{-1} s^{-1} can be derived from pulse radiolysis studies.[11] This rate is at least 3 orders of magnitude lower than that of a diffusion-controlled radical reaction.

The induction period of silver reduction is explained by the low rate of reaction 3. Once a small number of silver particles are formed, a second reduction process occurs, in which silver ions are reduced on the surface of the primary colloidal particles. This reduction occurs in two steps: in the first step, the ketyl radicals transfer an electron to colloidal silver particles.[12] As this reaction occurs diffusion controlled, it can efficiently compete with reaction 3, even when rather few nuclei are present. A silver particle is able to react with many radicals, i.e., to store many electrons:

$$Ag_n^{m-} + (CH_3)_2COH \rightarrow Ag_n^{(m+1)-} + (CH_3)_2CO + H^+ \qquad (7)$$

In the second step, silver ions are reduced by the stored electrons. It is this kind of silver reduction which makes the particles grow smoothly. Polyethyleneimine acts as a buffer, as it binds the H^+ ions formed.

As long as silver ions are still present during the photoreduction, the absorption band peaks at rather long wavelengths. This is explained by the chemisorption of Ag^+ ions on colloidal silver particles[8] (see also Figures 8 and 9). The effect is not pronounced when polyphosphate is used as stabilizer (Figure 2), since, in this case, the concentration of free Ag^+ ions in solution is low because most of them are bound to the polymer chains.[13]

Oxidation of Nanosilver by Oxygen and Carbon Tetrachloride. The silver−polyethyleneimine sol is extremely sensitive to air. It seems that previous authors who prepared silver sols by different methods have not encountered this effect, the reason probably being that they did not carry out the experiments under strict exclusion of air. Apparently, some residual silver ions were always present in their sols, which stabilized the Femi level in the particles at a rather positive potential. The Fermi level in the particles of Figure 1 must lie at a rather negative potential. Once no Ag^+ ions are present, a metal nanoelectrode with a well-defined Nernst potential cannot be established. The polyethyleneimine solution had a pH of 7.0. At this pH, the thermodynamic potential for H_2 formation from water is −0.41 V. Taking into account a small overpotential, one would expect that the Fermi level in silver particles is positioned no more negative than, say, −0.5 V.

The effects with O_2 and CCl_4 are explained as electron transfer from the silver particles to the solutes. Both solutes require less negative potential than −0.5 V for reduction. For example, the first polarographic wave of CCl_4, which is ascribed to the process

$$2e^- + CCl_4 + H_2O \rightarrow CHCl_3 + Cl^- + OH^- \qquad (8)$$

appears at −0.48 V (vs NHE).[14] This wave is kinetically hindered, as one calculates an even more positive potential of +0.32 V from the well-known thermody-

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namic data of the species in eq 8. Thus, it does not appear surprising that CCl_4 is readily reduced on the colloidal silver particles as long as there are no excess silver ions present. The reduction would occur even more readily, if the Cl^- ion formed remained adsorbed on the particle surface. The silver particles act toward CCl_4 in the absence of Ag+ ions almost as reducing as the particles of crude metals, such as Zn or Sn.[15]

Effect of Excess Ag^+ Ions. The decrease in the electron density in the colloidal particles upon the chemisorption of silver ions can be treated quantitatively, if it is assumed that each adsorbed Ag^+ ion becomes part of the particle, at least at low degrees of adsorption, i.e., below 2×10^{-5} M in Figure 9. The wavelength of the absorption maximum is proportional to the reciprocal square root of the density of free electrons in the metal, and for particles of a few nanometer, it is independent of size.[16,17] Each silver atom donates one electron to the electron gas. Thus, in a particle of agglomeration number n, the electron density changes by the factor $n/(n + m)$, when m Ag^+ ions are chemisorbed. Expressing the ratio $n/(n + m)$ by $[Ag]/([Ag] + [Ag^+])$, where [Ag] is the overall silver concentration in the colloid before Ag^+ addition, one derives readily the relation:

$$\lambda = \lambda_0(1 + [Ag^+]/[Ag])^{1/2} \tag{9}$$

where λ_0 and λ are the respective wavelengths of the absorption maximum before and after the addition of Ag^+ ions, assuming that all added Ag^+ ions are chemisorbed. This relation is now applied to data of Figure 9. At $[Ag^+] = 2 \times 10^{-5}$ M and using $[Ag] = 4 \times 10^{-4}$ M, and $\lambda_0 = 378$ nm, one calculates $\lambda = 387.5$ in agreement with the observed wavelength.

One may also get some indication regarding the area occupied by a chemisorbed silver ion. A simple geometrical consideration shows that the fraction, f, of surface atoms in a spherical particle is $6d/D$, where D is the diameter of the particle and d the diameter of an atom (provided that $D \gg d$). For silver particles in Figure 9, using $D = 7$ nm, and the size d of 0.25 nm of a silver atom (as calculated from the molar volume of silver: $d = (V_m/N_A)^{1/3}$), one obtains $f = 0.2$. Thus, the concentration of surface atoms is $4.0 \times 10^{-4} \times 0.2 = 8 \times 10^{-5}$ M. Each chemisorbed Ag^+ ion would thus "occupy" the area of $8 \times 10^{-5}/2.0 \times 10^{-5} = 4$ silver atoms.

The shift of the Fermi level to a more positive potential by the chemisorption of silver ions may also be calculated under the above assumptions. The Fermi energy, E_F, of a metal is proportinal to $N_e^{2/3}$, where N_e is the number of electrons in 1 cm^3. A small change, xN_e, where $x \ll 1.0$, would cause the Fermi level to shift by

$$\Delta E_F = {}^2\!/_3 E_F x \tag{10}$$

Using $E_F = 5.5$ eV for silver[18] and $x = 0.05$ (2×10^{-5} M in Figure 9), one calculates a shift of 0.18 eV. It is also noteworthy that the electrode potential of silver nanoparticles at very low Ag^+ concentrations is not determined by the concentration of the free silver ions in solution as it is the case for a normal Nernst electrode, but by the amount of chemisorbed Ag^+ ions.

These calculations should be regarded as approximate, since the assumption that the absorption changes are solely due changes in the electron density of the particles may not be exactly fulfilled. As electron transfer processes occur between the colloidal particles and the solutes, changes in the charges on the particles, which determine their stability, may also occur. Before the particles interact with solute molecules, they are well dispersed as concluded from the electron micrograph of Figure 5. However, they may be slightly aggregated after their interaction with a solute, which may also contribute to the absorption changes. It should be emphasized that the solutions were always clear before and after the addition of solutes and did not show any opalescence.

Effects of Chemisorbed Cd^{2+}, Ni^{2+}, and Hg^{2+}. The red-shift and decrease in intensity of the plasmon band upon the addition of these cations to the silver sol are interpreted as the donation of electron density from the silver particles to the cations. In fact, the effect is the stronger the more positive is the electrochemical potential of the added metal ion. It should also be emphasized that the charge on the cation is not important: the monovalent Ag^+ ion exhibits a strong effect on the absorption band, whereas a much lesser influence is observed with the divalent Cd^{2+} and Ni^{2+} ions (Figure 11). Thus, *ionic strength* effects by the added salts cannot be responsible for the observed changes; rather the *electronic* interaction of the solutes with the silver particles determines the changes.

The deposition of cadmium metal upon the illumination of a silver sol, which contains Cd^{2+} ions, is attributed to the cathodic charging of silver particles, eq 7, followed by the reduction of the ions directly on the surface of the colloids:

$$Ag_n{}^{(m+2)-} + Cd^{2+} \rightarrow (Ag_nCd)^{m-} \tag{11}$$

The Cd^{2+} ions are not reduced by organic radicals in the absence of silver particles. The blue-shift that accompanies the cadmium deposition is due to the change in the refractive index directly on the surface of the silver particles, which is understood in terms of extended Mie theory.[19,20] We restrain here from further discussion, as bimetallic colloids consisting of a silver core and cadmium shells of different thicknesses have already been prepared γ-radiolytically and their spectra discussed in detail.[21] However, it seems useful to offer here a general remark on the use of radiations in the preparation of bimetallic colloids: the use of γ-irradiation, i.e., free radical formation by these rays, has a great advantage because the reaction is uniformly

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initiated in the entire volume of the solution, regardless of the optical absorption of the system. In the case of UV illumination, the product particles often absorb in the 260 nm region, where acetone absorbs, which hampers further photochemical initiation. In fact, only thin layers of the second metal can be produced by UV illumination. Moreover, it has been observed that UV illumination of Ag−Cd colloids leads to partial reoxidation of the deposited Cd metal.[21]

Although the electrochemical potential of nickel is less negative than that of cadmium, Ni^{2+} ions are not reduced on the silver particles that carry excess electrons, whereas Cd^{2+} ions are reduced. Ni^{2+} is known to have a high overpotential of about −0.5 V for reduction,[22] which obviously is not attained in the cathodic charging of silver particles by ketyl radicals.

Mercury is slightly more electropositive than silver, which explains the strong interaction of Hg^{2+} with the silver particles. The interaction, however, is complex. At low Hg^{2+} concentrations (up to about 2×10^{-5} M), the silver plasmon band ungergoes a red-shift, indicating a decrease in electron density in the particles as the main effect. At higher Hg^{2+} concentrations, the silver absorption band shifts to shorter wavelengths, which is explained by the changes in the refractive index of the particles as amalgam formation is the dominant effect:

$$Ag_n + Hg^{2+} \rightleftharpoons Ag_{(n-2)}Hg + 2Ag^+ \qquad (12)$$

The formation of an amalgam by reducing Hg^{2+} ions on silver particles carrying excess electrons and by simultaneous reduction of Ag^+ and Hg^{2+} ions was described previously.[23,24]

To summarize the present findings: A readily accessible method for the preparation of silver nanoparticles that have a very narrow plasmon absorption band is described, and a few examples are given, which show that the interaction of solutes with the silver particles can be investigated by following the changes in the shape of the absorption band. This kind of experiments should be applicable for the study of many other adsorption phenomena in colloid dispersions.

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