

Formation of Long-Lived Silver Clusters in Aqueous Solution by Anodic Dispersion

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It was found that long-lived, subnanometer-sized silver clusters can be prepared by anodic dispersion of a silver electrode in aqueous NaOH solutions (pH 10.5–12), free of stabilizing polymers. The method, described by Nouhuys in 1938, is based upon the application of a dc voltage (10–65 V) between two silver electrodes and yields a range of different clusters, colloids, and oxides. The large colloids and oxides can be removed by centrifugation leaving small colloids and clusters in the sols as revealed by the strong absorption of light at wavelengths between 210 and 400 nm. Absorption spectra of the sols remain fairly unchanged for weeks, implying the stabilization of the clusters by hydroxyl ions. Significant formation of the clusters is only observed between pH \sim 10.5 and 12 and is explained by Joule heat generated in the Ag₂O surface layer at the anode. At pH above 12, a passivating AgO layer forms, preventing the dispersion of clusters while no significant amounts of clusters form either at pH below 10.5 due to the absence of Ag₂O at the surface.

Introduction

Subnanometer-sized silver particles or clusters are considered thermodynamically unstable in water, and considerable effort has been put into generating the clusters in pure and stable form in aqueous media.^{1,2} The present article describes the preparation of long-lived silver clusters in aqueous alkaline solutions (pH 10.5–12) by anodic dispersion. No stabilizing polymers or other organic additives have to be added.

The preparation of metal particles in aqueous media by electrical methods was first reported by Ritter in 1808.³ Black clouds were seen to evolve from a tellurium cathode and no trace of “Davy’schem Produkt” or tellurium oxide was observed. It was Magnus, in 1829, who referred to the particles formed as metallic.⁴ Later, in 1898, Bredig’s method was established, in which an electric arc is struck between two metal electrodes in water.⁵ The method is considered an intermediate one between dispersion and condensation procedures, although formation of the Bredig sol has still remained a matter of dispute.⁶ Some have compared it with particles formed by laser ablation methods explained by cooling of a plasma formed at the metal surface, others have explained it as an “explosion” of the wire.^{6,7} The preparation of the Bredig sol now attracts little interest as it usually contains polydisperse particles and undesired oxides.⁸ However, a few aspects are still worthy of investigation. First, Nouhuys found that dispersion of silver is greatly facilitated in alkaline solutions. Second, sols prepared in alkaline solutions often obtained their characteristic colloidal yellow color a few days after their preparation.⁸

Today, physicists try to blaze the trail from atom to metal and interest has focused on the preparation of silver clusters.^{1,9–12}

The clusters absorb light at wavelengths between 210 nm and about 380 nm, slightly shorter than colloids do, with the metallic surface plasmon band at approximately 390 nm arising at only 15 atoms.^{1,2,11–13} As absorption spectra of silver clusters and colloids are not hampered by interference between interband transitions and surface plasmon bands, a good indication is obtained of the particle sizes and shapes present in solution.¹ The high quantum yield of photon electron emission of the clusters (>0.1) relative to colloids (<0.007) makes them attractive for various applications and accounts for the interest in both practical and fundamental studies.¹⁴ Size effects nevertheless limit the lifetime of the clusters in aqueous solution as reflected by the coalescence, disproportionation, or oxidation of the clusters.^{1,15} The use of stabilizing polymers considerably prolongs the lifetime, but the preparation of long-lived silver clusters in aqueous solutions, free of stabilizing polymers, has remained a challenge.^{1,2,11}

In attempting to prepare colloidal silver sols in alkaline aqueous solutions (pH \sim 10.5–12), it was found that long-lived silver clusters can be prepared by anodic dispersion of a polarized silver electrode. Absorption spectra of the sols show strong light absorption in the ultraviolet light range which remains practically unchanged for days, indicating the presence of pure, long-lived silver clusters. Various parameters affecting the origin and character of the sols were studied, and the results are presented, together with a characterization of the sols by both microscopical and spectroscopical techniques. A subsequent paper will address the stability, identity, and properties of the clusters.

Experimental Section

Preparation of Sol, Standard Procedure. Two silver electrodes (length 5 cm, thickness 2 mm, purity 99.99%, Goodfellow, England) were cleaned by scouring the wires with silicon carbide emery paper (grit 4000) followed by immersion in concentrated nitric acid and rinsing with water. Next, the

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TABLE 1: Survey of the Experimental Conditions in the Preparation of the Various Dispersions

sol ^a	voltage (V)	distance electrodes (mm)	nitrogen flow ^b	concentration NaOH (10 ⁻³ M)	centrifugal field/time (10 ³ g/min)	T (°C)
1	65	6	++	0.5	1.11/6	20
2	65	6	++	1	1.11/6	20
3	65	6	++	5	1.11/6	20
4	65	1	++	0.1	1.11/6	20
5	65	1	++	0.0	1.11/6	20
6	65	6	+	0.5	1.11/6	20
7	65	6	+++	0.5	1.11/6	20
8	65	6	++	0.5	1.34 × 10 ² /15	20
9	50	6	++	0.5	1.11/6	20
10	35	6	++	0.5	1.11/6	20
11	20	6	++	0.5	1.11/6	20
12	65	6	++	0.5	1.11/6	70

^a All conditions concern silver sols polarized for 9 min. ^b + Moderate (less than 1 bubble s⁻¹); ++ medium (~5 bubbles s⁻¹); +++ strong (more than 10 bubbles s⁻¹).

electrodes were mounted at an angle of 60° relative to each other in a glass beaker with the tips at a distance of 6 mm apart, and held 1.5 cm under the surface of a 125 mL aqueous solution containing 0.5×10^{-3} M NaOH. A dc voltage of 65 V (BRA-EA 565/40 power supply) was applied for 9 min. Nitrogen was bubbled (~5 bubbles per second) through the solution to remove the brown "particle cloud" from the anode as quickly as possible (see below), and as the beaker was exposed to air, solutions were not entirely free of oxygen during the experiments. Typical current values observed ranged between 160 and 250 mA. The suspensions obtained after polarization were centrifuged in 10 mL tubes at $(1.1 \times 10^3)g$ for 6 min, and the supernatant was poured into glass cups and measured by UV-vis absorption spectroscopy within 7 min. All suspensions obtained after polarization were exposed to air, both during centrifugation and during storage.

Other Procedures. The standard procedure was modified by changing the voltage applied, the distance between the electrodes, the *g*-value and time of centrifugation, and the NaOH concentration as well as the nitrogen stream applied. Table 1 lists the experimental conditions, with the standard procedure denoted as sol 1. In addition, the influence of various additives was studied for sols prepared according to the standard procedure.

It is emphasized that the various sols were prepared by anodic dissolution or dispersion rather than by arc-induced sputtering of the tips of the electrodes (as is characteristic of the Bredig sol). To observe the electric arc, the distance between the tips of the electrodes had to be 1 mm, but the distance was set at 6 mm to avoid interference of anodic dispersion and arc-induced sputtering. One sol was prepared in water according to the Bredig method,⁵ and the distance between the tips of the electrodes was set at 1 mm (see Table 1, procedure 5). Attempts were made to prepare gold sols by sputtering and by dispersion in various solutions, but erosion of the gold wire (gold wires: 99.9% Goodfellow, England, shaped identically to the silver ones) was not observed.

To compare sols prepared by dispersion with sols obtained by nonelectrical methods, two silver sols were prepared by chemical reduction¹¹ and γ -irradiation.¹² The sol prepared by chemical reduction was obtained by adding 3 mL of an ice-cooled aqueous solution of 0.2 M NaBH₄ dropwise to a 50 mL aqueous solution containing 10^{-3} M (NaPO₃)_n and 2×10^{-4} M AgClO₄. The molarity of the stabilizing polymer, (NaPO₃)_n, referred to the formula NaPO₃, Nitrogen gas was bubbled through the solution. The sol prepared by γ -irradiation was

obtained by irradiating (⁶⁰Co source at a dose rate of 1.2×10^3 Gy h⁻¹) an aqueous solution containing 1×10^{-4} M AgClO₄ and 0.1 M CH₃OH for 45 min.

Characterization of Sols. Transmission electron microscopy (TEM) and energy-dispersive X-ray analysis (EDX) were performed on a Philips CM30ST/FEG high-resolution transmission electron microscope operating at 300 kV. Samples were prepared by placing a few droplets of the sol onto a copper grid covered by a carbon polymer microgrid and drying at ambient conditions. A precipitate obtained from a supersaturated Bredig sol (sol 5, Table 1) was dried for one night at 80 °C, disc-pressed at 1000 kg cm⁻² for 1 min, and analyzed by X-ray photon electron spectroscopy (XPS). The composition of the disk (1 cm diameter, 2 mm thickness) was investigated by sputtering off the silver layers with argon ions. Measurements were performed on a PMI 5400 ESCA (Perkin-Elmer) provided with a dual anode magnesium X-ray source, a spherical capacitor analyzer, and a 5 kV ion gun (PMI 04-303). The X-ray source was operated at 400 W, and the 3.5 keV ionic argon beam was scanned over an area of 2 mm².

Absorption spectra of the sols were measured with an Uvikon 940 spectrophotometer. Photon correlation spectroscopy (PCS) was performed to assess the size distribution of the sols using a helium neon laser (633 nm). Scattered radiation was transmitted using 45°, 90°, and 135° geometry, detected by a Hamamatsu photomultiplier tube and correlated using a Brookhaven BI 8000 correlator. Particle size distributions were obtained using the Contin program.¹⁶ The ratio of metallic silver to ionic silver and clusters in the sols was estimated by flame atomic absorption spectroscopy (AAS; Perkin-Elmer 1100). First, the total amount of silver in the sols was measured, after which sols were ultracentrifuged at $(1.11 \times 10^5)g$ for 15 min and measured again.

Results and Discussion

General Observations. A black oxide formed at the anode during formation of the sols in alkaline aqueous solutions through which a yellow-brown "cloud" evolved into solution. Slight deposition of metallic silver at the cathode occurred, accompanied by the evolution of hydrogen. Disintegration of the black oxide layer at the anode was observed, and the black fragments, identified as AgO by powder X-ray diffraction, were removed from the solution by centrifugation as the solubility of AgO is low under the conditions examined ($\sim 10^{-6}$ M).¹⁷ Exchange of the silver cathode for a platinum or gold one did not affect the formation of the sols as similar absorption spectra were obtained. The pH of the solution remained constant, in contrast to the current and temperature, which both increased (see below). Dispersion of the silver anode already was observed at 2.0 V, but solutions obtained at this voltage did not significantly absorb light between 230 and 700 nm. No stable sols were obtained at dispersion times longer than 25 min.

The sols obtained in alkaline aqueous solutions showed Tyndall effect and ranged in color from colorless, if prepared in 0.5×10^{-3} M NaOH, to brown, if prepared in 5×10^{-3} M NaOH. The yellow color, typical for colloidal silver sols, appeared within days for sols prepared in 0.5×10^{-3} M NaOH, while no transition was seen for sols prepared in 5×10^{-3} M NaOH within months. Sols stored in the dark were generally seen to develop a less intense yellow color than their equivalents stored in light, though no detailed studies were made. The stability of the sols had a maximum at pH around 11.5 and was seen to depend on the centrifugal field. Large particles, initially present in the sols, as revealed by the strong absorption at extended wavelengths (>500 nm), had to be removed in order to increase the stability of the sols.

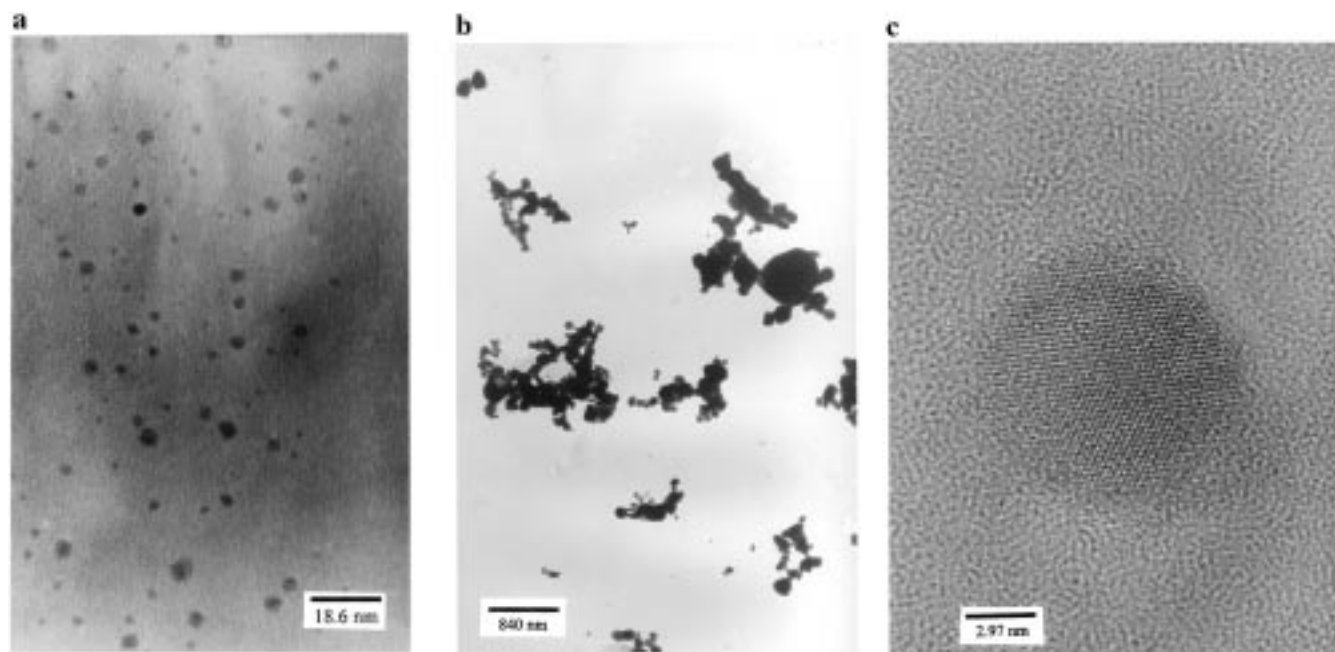


Figure 1. TEM micrograph of sols prepared in 0.5×10^{-3} M NaOH by polarization of two silver electrodes at 65 V: (a) electron micrograph showing the presence of very small metallic particles; (b) noncentrifuged, freshly prepared sample showing coalescence within hours; (c) ~ 3 nm particle showing twinning and stacking faults consistent with an fcc silver particle imaged in the [100] direction.

A freshly prepared, representative sol (standard procedure, sol 1, Table 1) contained 11.2 mg L^{-1} silver as determined by AAS. Ultracentrifugation at $(1.11 \times 10^5)g$ for 20 min followed by ultrafiltration over a 25 nm pore diameter filter yielded 5.8 mg L^{-1} . The reduction in mass was reflected accordingly by the absorbance in the spectra as the entire area between 240 and 800 nm decreased by the same ratio, the area at extended wavelengths thereby decreasing more rapidly than the area in the UV light range. It confirms the presence of small particles and suggests that only small amounts of Ag^+ ions may be present in the sols, as these do not absorb light at the wavelengths examined.

Composition and Size of the Particles. A TEM micrograph of a freshly prepared sol obtained in 0.5×10^{-3} M NaOH (sol 1, Table 1) is shown in Figure 1a. Particles with sizes between 0.8 and 100 nm were observed, the upper size being dependent on the centrifugal field. Noncentrifuged sols prepared at this pH contained larger particles which dragged along the small ones, explaining the enhanced stability of the sol upon centrifugation (Figure 1b). Both single-crystalline and polycrystalline particles were observed, the lattice spacings of the various particles being consistent with metallic silver (Figure 1c). The metallic character was further confirmed by EDX analysis and electron diffraction (parts a and b of Figure 2). Attempts were made to detect clusters in the sols with either a distinct peak at 265 nm (see below) or a broad band in the entire UV light range, but attempts were unsuccessful. The clusters may have been unstable toward the high energetic electrons of the microscope or toward the increase in pH upon drying the sample. PCS of the ultracentrifuged sols (sol 8, Table 1) suggested most of the particles were smaller than 2 nm as shown in Figure 3 (the corresponding UV-vis spectrum is shown in Figure 6b, spectrum 3). Considering the polydisperse character of the sols and the fact that larger particles scatter the helium light much more strongly than the smaller ones,¹⁶ particles may have been even smaller than suggested in Figure 3.

Sols prepared in 5×10^{-3} M NaOH (sol 3, Table 1) were highly polydisperse and contained a few larger amorphous particles (Figure 4a) tentatively identified as amorphous Ag_2O .

The brown Ag_2O phase is in line with the observation of a brown cloud evolving at the anode during formation of the various particles and is expected from the Pourbaix diagram, but its solubility is low at pH 11 ($\sim 10^{-6}$ M).¹⁷ Many particles showed stacking faults and twinning (Figure 4b). The origin of these defects may arise from the intense conditions during dispersion or from the rather nonideal coalescence of clusters formed at the anode.

The XPS spectrum and depth profile of the disk pressed from a supersaturated Bredig sol (sol 5, Table 1) is shown in parts a and b of Figure 5. Clearly, silver, oxygen, carbon, and nitrogen are present at the surface of the disk. Enhanced surface signals from oxygen, nitrogen, and carbon at the surface is an ordinary phenomenon in XPS studies¹⁸ and obviously metallic silver was formed during arc-induced sputtering of the silver poles.

Spectrochemical Properties. A representative spectrum of a sample prepared by the standard procedure is shown in Figure 6a. A broad band between 220 nm and ~ 400 nm is seen with a small shoulder at 265 nm. Depending on the height of the initial absorbance between 220 nm and about 400 nm in the spectra, the absorbance in the ultraviolet light range either disappeared within weeks to yield a colloidal peak (Figure 6a) or gradually sharpened to yield two peaks, a cluster peak at 265 nm and a colloidal peak at 415 nm (Figure 6b). The latter sol then remained virtually unchanged for months. Various bands in the ultraviolet light range have been reported in the literature, all ascribed to positively charged and neutral silver clusters.^{1,2} Consequently, it is proposed that anodic dispersion of silver yields a range of these subnanosized silver clusters. The peak at about 265 nm has been observed before and has been ascribed to the Ag_4^{2+} cluster.¹

From the observations it is clear that particles are formed at the anode which may yield either stable Ag_4^{2+} clusters or metallic colloids. The exact identity of the particles formed initially is unclear. Prior to dispersion, the silver anode was not oxidized, but we do not rule out the involvement of Ag_2O in the formation of Ag_4^{2+} . A subsequent paper is aimed at examining the matter in detail. Interestingly, ultracentrifugation of the sol with the peak at 265 nm at $(1.11 \times 10^5)g$ for 15 min

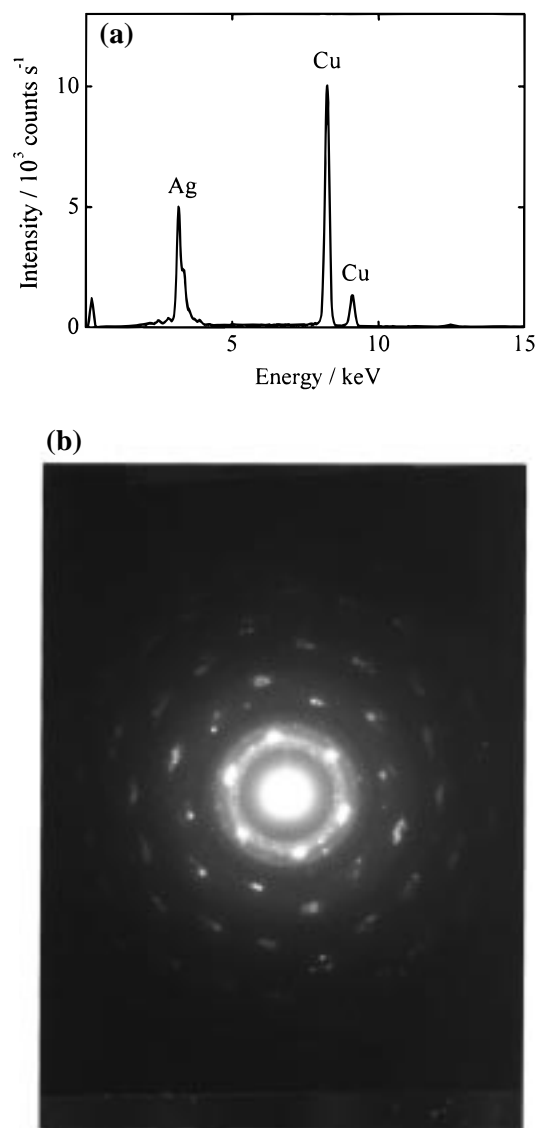


Figure 2. (a) EDX spectrum of a particle obtained in 0.5×10^{-3} M NaOH showing the presence of silver; the copper signal results from the grid. (b) Diffraction pattern of an area containing silver particles. The d spacings obtained from this pattern corresponded to metallic silver.

yielded a colorless solution with the peak at 265 nm still present, implying solely Ag_4^{2+} clusters were present in solution. The colloidal peak had disappeared after ultracentrifugation but reappeared upon aging accompanied by the reduction of the peak at 265 nm (Figure 6b). It reflects the disproportionation of Ag_4^{2+} clusters into colloidal particles.¹ Heating sols with a broad band between 220 and 400 nm induced the formation of the Ag_4^{2+} cluster peak at 40 °C which then coalesced into the colloidal peak at ~ 80 °C. The results are discussed in detail in a subsequent paper.

Both the position of the colloidal maximum at about 415 nm and the full width at half-maximum (fwhm) of about 125 nm of the sols obtained by dispersion are larger than the corresponding maxima and widths observed for sols prepared by chemical reduction and γ -irradiation. The latter show maxima between ~ 385 nm and ~ 405 nm and a fwhm between ~ 50 nm and ~ 80 nm (Figure 7a,b). The light absorption spectrum by metallic particles in aqueous systems is described by the Mie theory and was calculated by Creighton and Eadon for spherical, monodisperse silver particles.^{1,19} Calculations performed for 10 nm particles yielded a peak maximum at ~ 380 nm and a fwhm

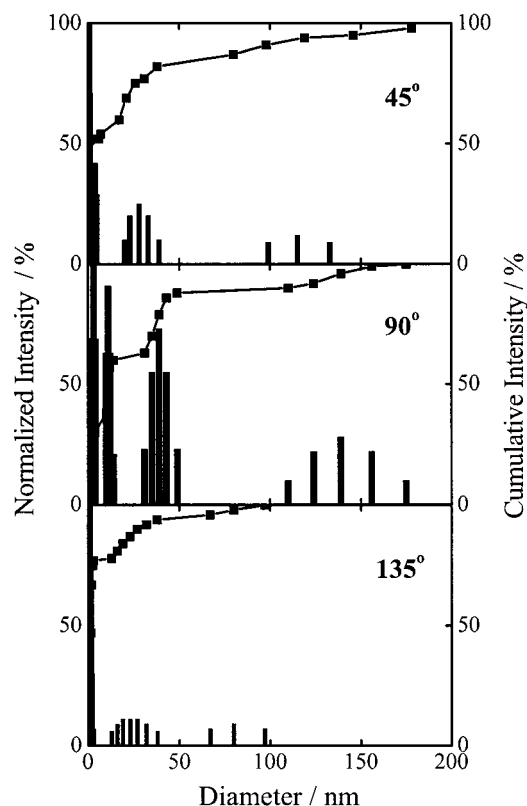


Figure 3. Particle size distribution obtained by photon correlation spectroscopy for light transmitted using different geometries. The corresponding absorption spectrum is shown in Figure 6b (spectrum 3).

of ~ 40 nm.¹⁹ Generally, the maximum in absorbance shifts to longer wavelengths when particles coagulate, when nonspherical particles are involved, and when particles form with a low density of states.^{1,20} As spherical particles were observed in the TEM micrographs, the maximum at 415 nm observed for sols obtained by dispersion is explained by coagulation of the particles as well as by the presence of particles with a low density of states. The latter may arise as a result of the strongly oxidizing conditions during expulsion.

Broadening of the spectra relative to the calculated one occurs when nucleophilic anions adsorb at the surface of the particles as well as when very small ($< \sim 3$ nm), polydisperse particles are present.^{1,11,13,19,20} The adsorption of hydroxyl ions at the surface may be expected in the alkaline medium examined, and the polydisperse character of particles obtained by dispersion was confirmed by TEM micrographs (Figure 1a,b). The polydisperse character of the particles prepared by dispersion is usually undesired in studies of silver colloids, although both the low content of contaminating chemical agents as well as the presence of clusters and nanometer-sized particles is particularly interesting. We hope to further raise the yield of clusters and very small particles in the future.

The influence of the NaOH concentrations on the formation of the sols is reflected by the spectra shown in Figure 8a (sol 1–4, Table 1). No clear peaks are seen, but a hump at 265 nm can be observed. Clearly, a higher NaOH concentration results in an increased dispersion of particles. Dispersion nevertheless ceased at concentrations above 1×10^{-2} M NaOH as a black AgO layer formed at the silver anode.^{21,22} The spectra of sols obtained in 5.0×10^{-3} M NaOH remained fairly constant for weeks, as shown in Figure 8b. It points toward a stabilizing role of OH^- ions in the stability of the clusters. True metallic colloidal sols generally show a slow red shift as their redox

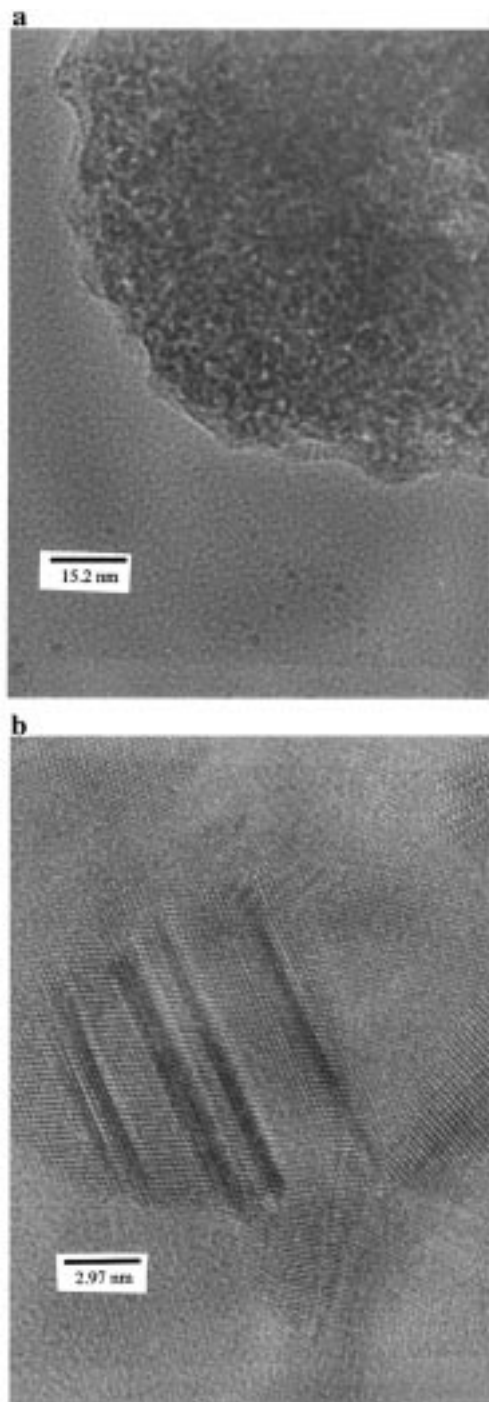


Figure 4. TEM micrograph of sols prepared in 5.0×10^{-3} M NaOH: (a) large amorphous particles were seen, tentatively ascribed to Ag_2O ; (b) edge dislocations and lattice imperfections (stacking faults, twinning) were seen to be explained by the intense conditions during expulsion of the particles.

potential drifts toward open circuit values but no significant red shift was observed in the spectra. No clear colloidal peaks were present in the spectra, and no oxygen was observed in the metallic particles by EDX analysis. The absence of a red shift is therefore explained by the presence of small amounts of metallic particles and large amounts of clusters in the suspensions measured. As mentioned, the not yet identified clusters yield Ag_4^{2+} clusters upon heating and may be oxidized.

The influence of the voltage applied on the sols (sol 1, 9–11, Table 1) formed is reflected in Figure 9a. Clearly, a higher voltage results in an increased formation of clusters. Increase

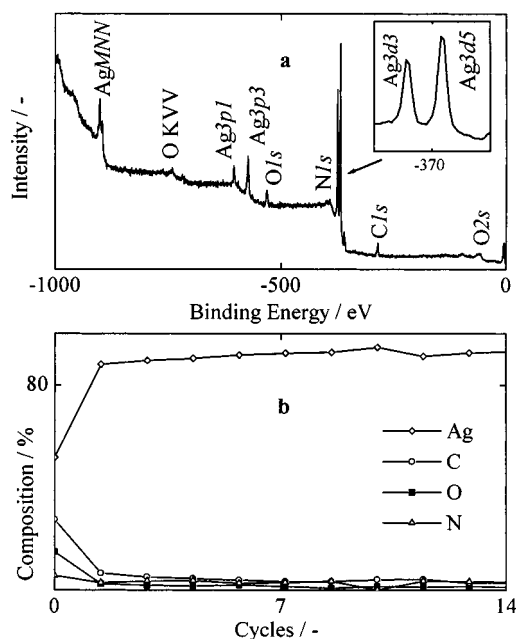


Figure 5. (a) XPS spectrum of the precipitate obtained from supersaturated suspensions prepared in water by the Bredig method (sol 4, Table 1). (b) The corresponding depth profile pointed toward the metallic silver phase.

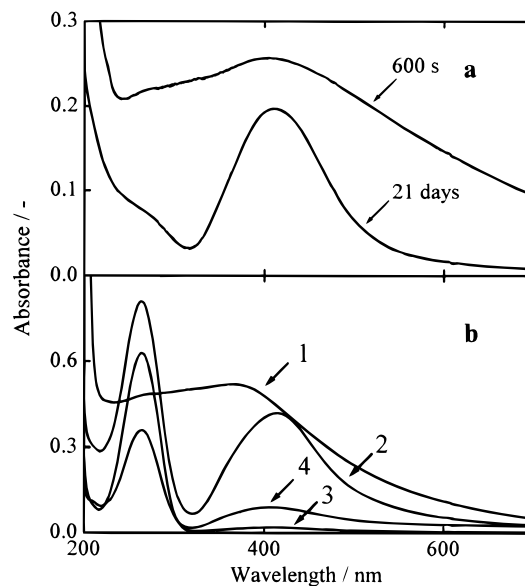


Figure 6. (a) Absorption spectra of a representative sol prepared in 0.5×10^{-3} M NaOH according to the standard procedure (sol 1 in Table 1), at 600 s and 21 days after preparation. (b) A distinct band at 265 nm appeared from the initial spectrum after 7 days (spectra 1 and 2). The larger colloids could be removed by ultracentrifugation (spectrum 3) but gradually reappeared upon aging of the sol (spectrum 4).

in the temperature of the solution (sol 12, Table 1) yielded an unstable brown-black sol with many large particles as confirmed by the eye and by the strong absorption at extended wavelengths (Figure 9b). The yield of clusters could be increased by applying a stronger gas flow to the space between the electrodes (sols 6 and 7, Table 1, spectra are shown in Figure 9b). This is explained by a slower coalescence and disproportionation of clusters at the anode as the gas flow blows away the clusters more rapidly. Increased amounts of clusters were also obtained upon adding stabilizing sodium polyphosphate to the solution

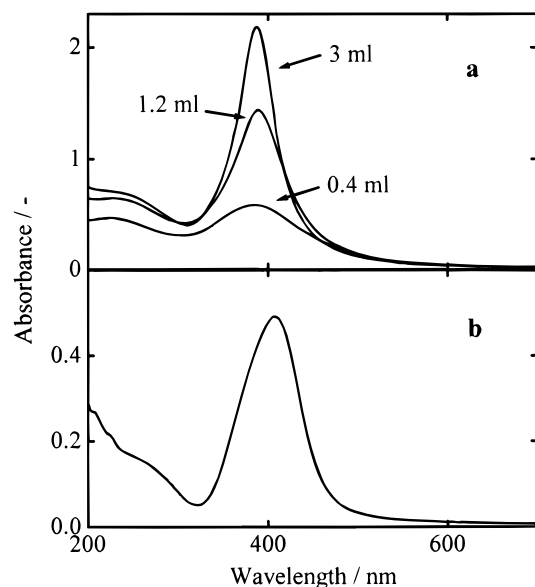


Figure 7. Absorption spectrum of a sol prepared by (a) chemical reduction with different aliquots of a solution containing 0.2 M NaBH_4 to 50 mL 10^{-4} M AgClO_4 and (b) γ -irradiation (see Experimental Section for detailed procedures).

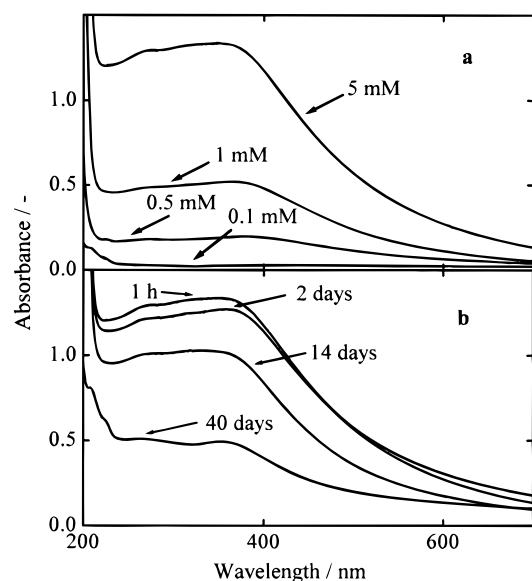


Figure 8. (a) Absorption spectra of a silver sol prepared in solutions at different concentrations of NaOH (sols 1–4, Table 1). (b) Sols prepared in 5×10^{-3} M NaOH were particularly stable.

(10^{-4} M). The much higher absorbance seen from the ordinate confirms the stabilization of clusters by polyphosphate (Figure 9c).

Mechanism of Sol Formation. The dispersion of metal into clusters, colloids, and oxides anodically is unexpected from an electrochemical point of view, as either dissolution of ions or oxidation of the anode is expected.^{17,21,22} Dispersion requires energy, which may come from dissipated Joule heat generated in the most resistive phases of the circuit. It therefore appeared useful to measure the temperature and current transients during polarization of the silver and gold electrodes in 5.0×10^{-3} M NaOH (Figure 10a,b). The temperature profiles obtained for both metals resemble each other, contrary to the currents, which were larger for silver than for gold, in particular at 65 V. The lower current for gold than for silver is explained by roughening of the silver anode relative to the gold one upon polarization.

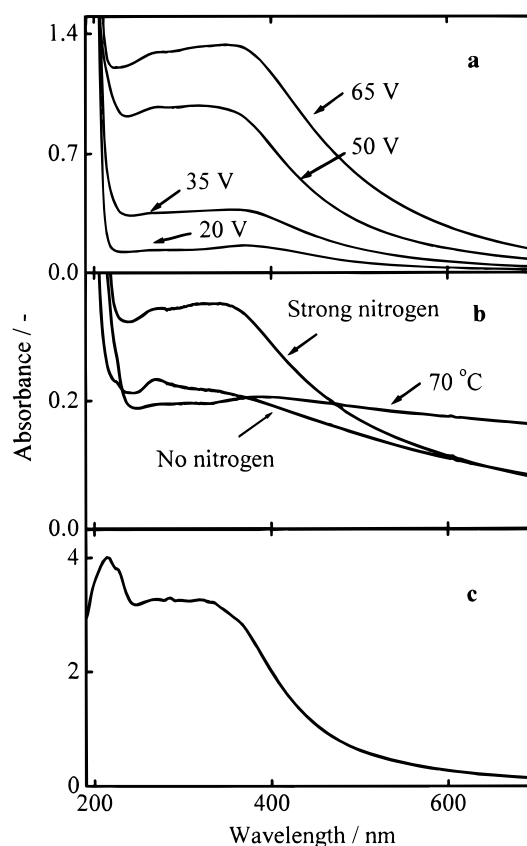


Figure 9. (a) Absorption spectra of sols prepared at different voltages. (b) Absorption spectra obtained for sols with different nitrogen streams and prepared at 70 °C (sols 6, 7, 9, Table 1). (c) The addition of sodium polyphosphate ($6.25 \text{ g L}^{-1} \text{ Na(PO}_3)_6$) stabilized the clusters initially formed and higher yields were obtained.

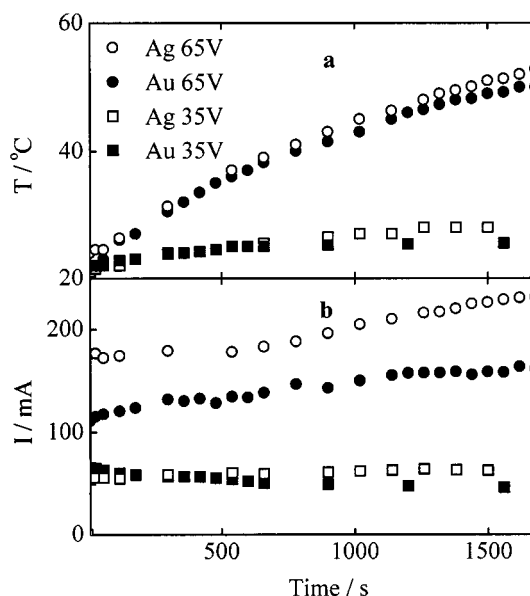


Figure 10. Temperature (a) and current (b) transients for gold and silver at different voltages.

Electrocatalytic considerations should not be taken into account in an explanation of the current difference between the gold circuit and silver circuit. Both currents are governed by diffusion of the reacting solution species rather than by the electrocatalytic kinetics of surface reactions at these high overpotentials.^{21,22}

The total Joule heat is proportional to R^2 and more heat is expected to develop in the silver circuit as the latter passes a

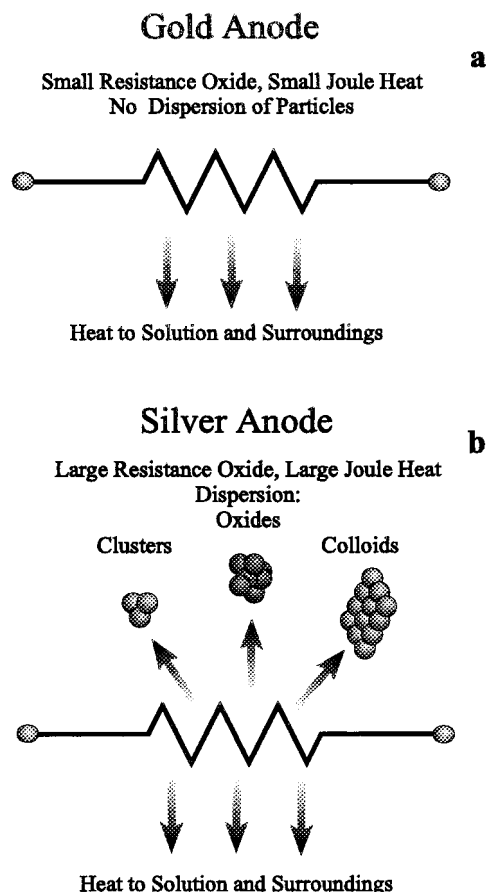


Figure 11. Qualitative model explaining the dispersion of clusters for silver. Contrary to the silver anode, no highly resistant oxide forms at the gold anode and consequently no large local Joule heat is generated, thus no particle dispersion occurs.

higher current (the voltage applied was equal for both circuits). However, as no significantly higher temperatures were seen in the solution of the silver circuit, it therefore seems reasonable to assume that a considerable amount of heat liberated in the silver circuit is consumed in endothermic processes. These processes may be the endothermic evaporation of Ag_2O or the evaporation of metal. The Joule heat generated most likely originates from the highly resistant Ag_2O layer ($\sim 10^8 \Omega\text{cm}$, see ref 22) and may be consumed in the endothermic disproportionation of Ag_2O into metallic silver and oxygen followed by the successive evaporation of metallic silver and expulsion of clusters. Assuming equal amounts of heat dissipated to the solution and surroundings by the silver circuit and gold circuit and bearing in mind that the gold circuit does not comprise highly resistant oxides,^{23,24} the energy for the possible consumption in endothermic processes may be calculated.²⁵ It is easily calculated that this energy is sufficient to explain the expulsion of the particles.²⁶

At pH above 12, a passivating AgO film forms, preventing the dispersion of clusters. Besides, less Ag_2O forms under these conditions^{21,22} and less heat is dissipated at the surface. At pH below ~ 10.5 , no significant amounts of Ag_2O form at the anode to yield clusters. Besides, the conductivity of the solution may be too low to yield the Joule heat required to expel particles. Gold does not form highly resistant oxides under the conditions examined, and not enough heat is dissipated at the surface to disperse particles.^{23,24} Figure 11 illustrates the various considerations and observations.

Conclusion

Anodic polarization of silver results in the expulsion of silver oxides, metallic colloids, and subnanometer-sized clusters. The oxides and large metallic colloids can be removed by centrifugation, leaving mainly clusters and small colloids in the solution. Formation only occurs at pH values between 10.5 and 12. At lower pH, the current and associated Joule heat at the surface is too low to cause dispersion of clusters. At higher pH, a blocking AgO layer forms, preventing the dispersion of particles or ions. At pH ≈ 11.5 , the clusters live for weeks, implying the role of OH^- in the stability of the clusters.

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- (25) The power is calculated from $P = \Delta I \times V$. It yields 3.25 W taking 50 mA as the difference in current between the circuits at 65 V (see Figure 11b).
- (26) The heat, ΔG_f° , to disproportionate the Ag_2O into Ag and O_2 and to evaporate metallic silver amounts to $-256.6 \text{ kJ mol}^{-1}$ (see ref 27). To obtain the $\sim 200 \text{ mg}$ dispersed material before centrifugation in the case of a $5.0 \times 10^{-3} \text{ M}$ NaOH solution, 246.8 J heat is required assuming solely metallic silver to be dispersed. Nine minutes of dispersion yields 1755 J (see ref 25).
- (27) Reference 24, p D-84.