Complexed Metal Clusters in Organically Modified Oxide Matrices

T. Gacoin,* F. Chaput, and J. P. Boilot

Groupe de Chimie du Solide, Laboratoire de Physique de la Matière Condensée, CNRS URA 1254 D, Ecole Polytechnique, 91128 Palaiseau, France

G. Jaskierowicz

CEA/DTA/CEREM/DTM, Laboratoire des Solides Irradiés, Ecole Polytechnique, 91128 Palaiseau, France

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A two-step procedure was developed to prepare composite materials containing nanometer-sized metal particles (Ag, Au) homogeneously dispersed in sol–gel matrices. In the first step, irradiation with γ-rays from a ^{60}Co source was used to initiate the growth of metal particles in a solution containing both metal ions and stabilizing multifunctional silanes $\mathcal{F}(CH_2)_3Si(OR)_3$ ($\mathcal{F}$ = H_2N–, N≡CS–, ...). In the second step, transparent and closed porosity xerogels with metal clusters grafted on the oxide network were prepared via hydrolysis–condensation of alkoxides. The nanocrystallites were characterized by transmission electron microscopy and optical spectroscopy.

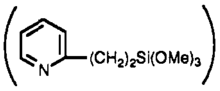
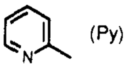
Introduction

Composites containing uniform nanometer-sized metal particles homogeneously dispersed in ceramic matrices are of potential interest as catalysts and possibly also for optical and electronic applications.[1,2]

In the past years, metal/SiO_2 and metal/Al_2O_3 composites have been prepared by sol–gel processing.[3–6] A metal salt was dispersed in a gel matrix and metal particles were obtained by reduction at high temperature. The major problems associated with this method are the control of the metal size distribution and the metal cluster dispersion.

Recently, the use of amine functionalized alkoxides has been proposed to obtain highly dispersed metal-containing gels.[7–9] In this technique, the functionalized silicon monomers were reacted with a metal salt leading to the formation of metal complex containing gels. However, the preparation of composites with nanometer-sized metal particles required subsequent thermal treatments: oxidization in air at high temperature to remove all organic components and reduction of metal oxide particles to obtain metal/oxide composites.

Table I. Functionalized Silicon Alkoxides ($\mathcal{F}(CH_2)_3Si(OR)_3$) and Complexing Groups ($\mathcal{F}$)

$\mathcal{F}(CH_2)_3Si(OR)_3$	$\mathcal{F}$
(3-aminopropyl)triethoxysilane ($H_2N(CH_2)_3Si(OEt)_3$)	H_2N–
[*N*-(2-aminoethyl)-3-aminopropyl]trimethoxysilane ($H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3$)	$H_2N(CH_2)_2NH$–
[(trimethoxysilyl)propyl]diethylenetriamine $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_3Si(OMe)_3$	$H_2N(CH_2)_2NH$-$(CH_2)_2NH$–
[2-(trimethoxysilyl)ethyl]pyridine 	 (Py)
(3-thiocyanatopropyl)triethoxysilane (N≡CS$(CH_2)_3Si(OEt)_3$)	N≡CS–

We report here a two-step procedure to prepare optically clear and metal-doped xerogels at room temperature, in which silver or gold metallic clusters (2–10 nm in diameter) are homogeneously dispersed. In a first step, the synthesis of the colloid is achieved by using γ-irradiation of an alcoholic solution of the metal salt. As previously shown,[1,10–12] the interactions between the γ-rays and the solution lead to the decomposition of the alcohol molecules:

$$RHOH \rightarrow e^-_s, RHOH_2^+, H^\bullet, R^\bullet OH...$$

The reducing agents produced are solvated electrons (e^-_s) and alcohol radicals ($R^\bullet OH$). $H^\bullet$ is an oxidant but reacts with alcohol to give $R^\bullet OH$ and H_2. Reduction of the metal cations occurs between the metal ions and the reductive species which are randomly produced within the solution. It has been shown,[13–14] in the early steps of the growth of silver particles, that the metal atoms are rapidly stabilized by complexation with surrounding metal ions and that

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* To whom correspondence should be addressed.

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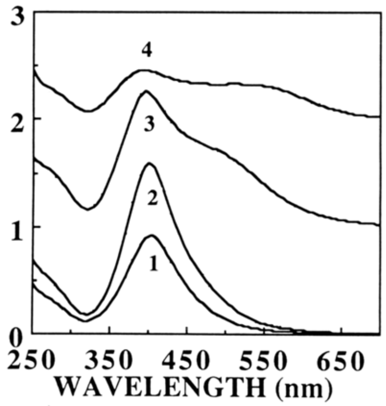

Figure 1. Absorption spectra of silver particles produced by γ-radiolysis of deaerated ethanolic solutions of $H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3$ containing 10^{-3} M Ag^+. The alkoxide/Ag^+ molar ratio is 10. Curves 1–4 correspond to doses of 200, 400, 600, and 800 krad. The origin of absorbance is shifted for clarity. Optical path length of 2 mm.

the metal clusters are produced from the aggregation of small units composed of reduced metal atoms complexed with unreduced ions. Consequently, assuming that the metal clusters are superficially charged and described by the general formula M_n^{p+}, one can expect a complexation of the surface of the metal particles by electronic donor agents. This would limit the growth of the particles and stabilize the colloid, avoiding cluster fusion. In fact, our choice of the complexing agent is governed by the need to incorporate, in a second step, the aggregates in gel matrices prepared by inorganic polymerization of silicon alkoxides. Consequently, functionalized silicon alkoxides with the general formula $\mathcal{F}\mathcal{S}\mathrm{Si(OR)_3}$ were tested as complexing agents. The functional group ($\mathcal{F} = H_2N{-}, N{\equiv}CS{-}, ...$) is connected to the alkoxy group via an inert spacer ($\mathcal{S} = (CH_2)_3, ...$). Different parameters have been taken into account as they seem to have a great influence on the average size, the size distribution, and the morphology of the final silver or gold nanoaggregates: the irradiation dose, the nature and the concentration of the complexing agent, and the presence of other transition metal ions. Finally, the gel matrix is synthesized at room temperature using the slow hydrolysis of different alkoxide mixtures in a wet atmosphere.[15] We show that this technique leads to gels with a closed porosity allowing the protection of the metal aggregates against corrosion.

Experimental Section

Radiolytic Synthesis of the Colloids. Alcoholic solutions of the metal salt are prepared by dissolution of $AgNO_3$ or $HAuCl_4$ in ethanol. In the case of silver, the influence of the addition of $Ni(NO_3)_2$ is studied. The functionalized silicon alkoxides which are added to these solutions are taken from those listed in the Table I. The final concentration of metallic ions (Ag^+, Au^{3+}, Ni^{2+}) is 10^{-3} M while the concentration of the functionalized silicon alkoxide may be varied in the 10^{-4}–10^{-1} M range. After preparation, air is removed from the solutions by bubbling with nitrogen. Irradiations are then carried out for 16 h at different distances from a ^{60}Co source so that the total dose received by the samples varies from 100 to 1200 krad.

Incorporation in the Sol–Gel Matrix. Sol–gel matrices are prepared at room temperature by polymerization of alkoxides using the slow hydrolysis technique:[15] an alcoholic solution of alkoxide is placed in a covered Petri dish so that a very low exchange with the outside wet atmosphere is possible. The slow hydrolysis of the alkoxide and the progressive evaporation of the alcohol leads to gelatinization after about 1 week under our experimental conditions. The drying of the gels is carried out in an inert atmosphere for 3 more weeks. In fact, this technique requires the use of a mixture of, at least, two alkoxides: the first is a metallic alkoxide, such as a zirconium one, which is rapidly hydrolyzed leading to self-polymerizing oxo clusters. These hydrolyzed species are then able to initiate the polymerization of a second network forming alkoxide, which is a silicon one and exhibits a very low reactivity to the moisture. This method for the synthesis of the oxide matrix was chosen essentially because of oxidation which occurs in the case of silver particles when incorporated into usual sol–gel matrices prepared by adding acidic water in excess to an ethanolic solution of silicon alkoxide. By contrast, in the case of the slow

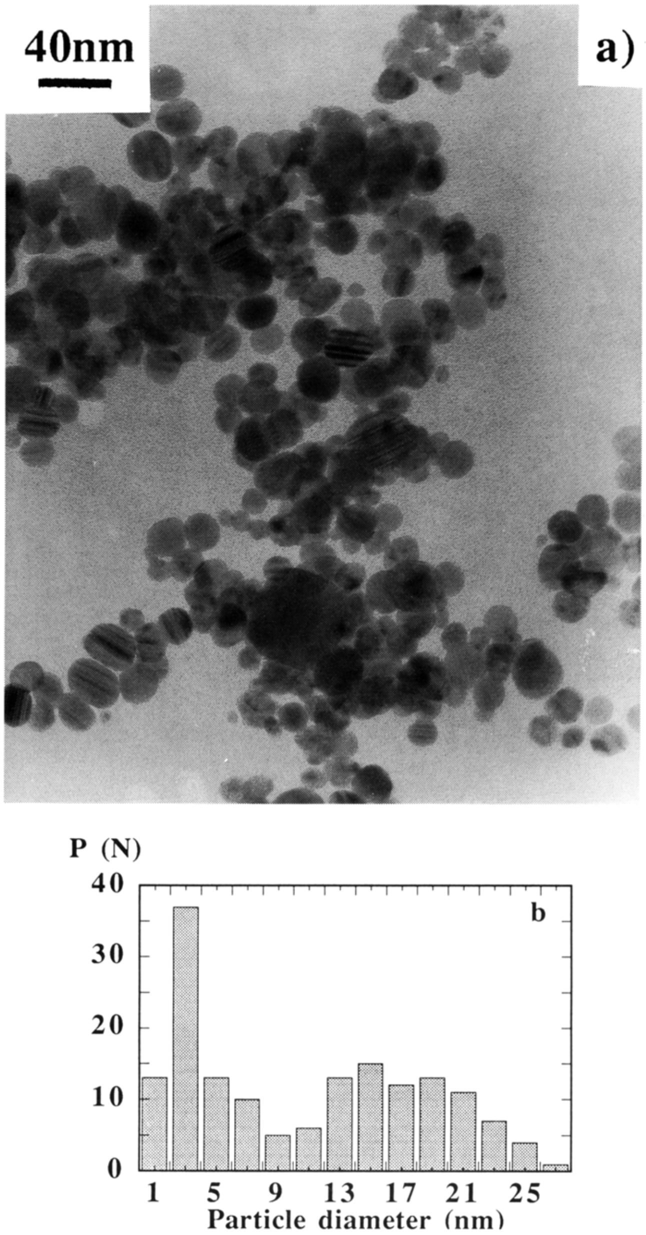

Figure 2. Structural characterization of the sample corresponding to curve 4 in Figure 1. (a) Electron micrograph; (b) histogram of the size distribution.

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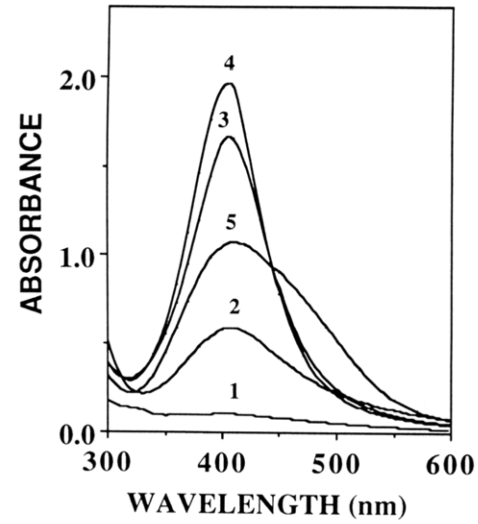

Figure 3. Absorption spectra of silver particles produced by γ-radiolysis of deaerated functionalized alkoxide ethanolic solutions containing 10^{-3} M Ag^+. The radiation dose is 300 krad and the alkoxide/Ag^+ molar ratio is 100. Curves 1–5 corresponding to $N{\equiv}CS$–, Py, $H_2N(CH_2)_2NH(CH_2)_2NH$–, $H_2N(CH_2)_2NH$–, and H_2N– groups. Optical path length of 2 mm.

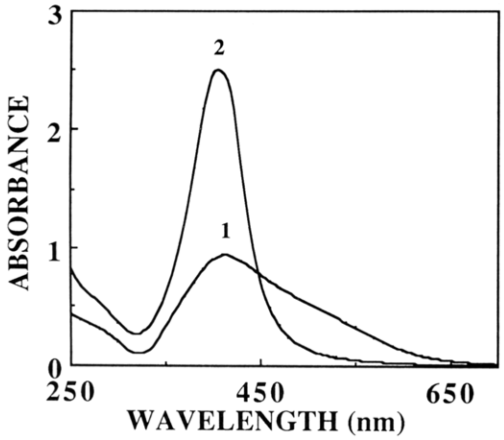

Figure 4. Absorption spectra of silver particles produced by γ-radiolysis of deaerated ethanolic solutions of $H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3$ containing 10^{-3} M Ag^+. The radiation dose is 600 krad. Curves 1 and 2 correspond to alkoxide/Ag^+ molar ratios of 10 and 100, respectively.

hydrolysis technique, no acid is required and only water from a H_2O-saturated outside inert atmosphere is allowed to diffuse in the gel.

In our experiments, sol–gel matrices are obtained from an ethanolic mixture of the zirconium butoxide and of a silicon ethoxide. The Si/Zr molar ratio is 4. The matrix prepared from $Si(OEt)_4$ is hereafter noted TEOS. In other preparations, $Si(OEt)_4$ is replaced in the initial solution by the same concentration (1.55 M) of a silicon ethoxide having one permanent organic function, such as the vinyl, methyl, or amyl triethoxysilane. The resulting matrices are then respectively noted VTEOS, MTEOS, and ATEOS. In this case, compared to TEOS matrices, it seems that the drying is easier, probably resulting from the hydrophobous character of the permanent organic group, and larger pieces of gels are obtained.

The density of the matrices are measured by the Archimedes' method, both in Hg and He media, in order to deduce the pore volume fraction. In fact, the same values are found in the two experiments: 2.00 and 1.49 g/cm^3 for TEOS and MTEOS matrices, respectively.

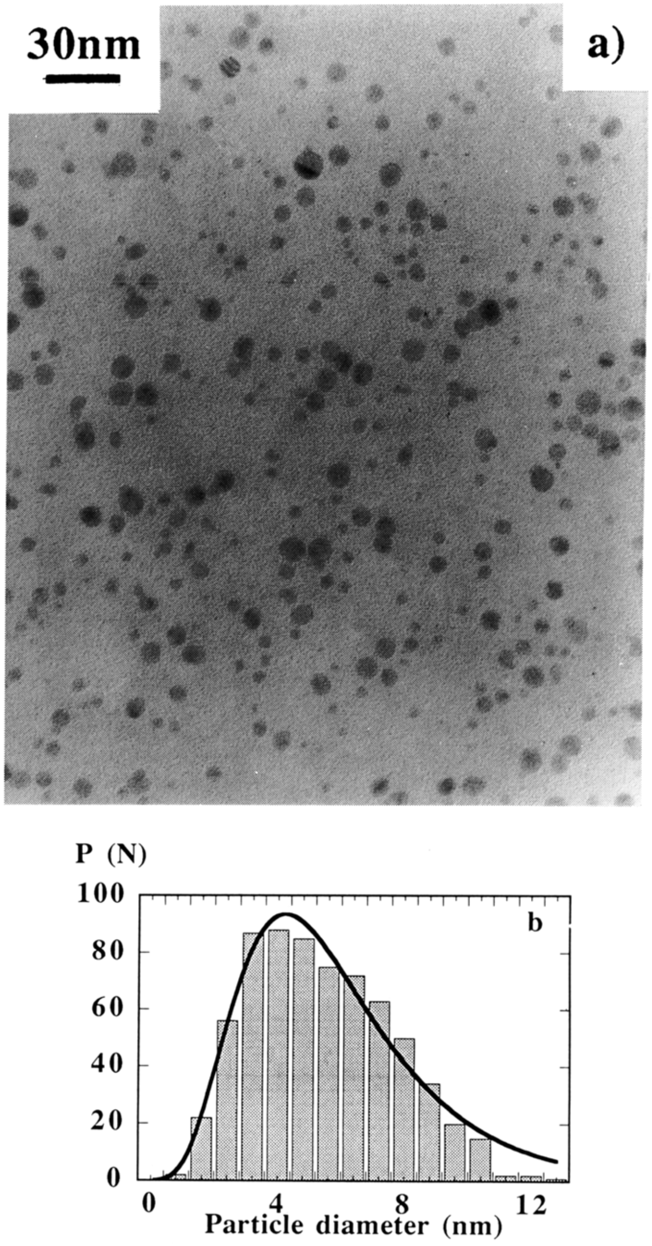

Figure 5. Ag sample corresponding to curve 2 in Figure 4: (a) electron micrograph; (b) histogram of the size distribution. The full line corresponds to a best fit of a log-normal distribution $P(D)$ (D_0 = 41 Å, σ = 0.5).

Moreover, TGA measurements performed on the TEOS matrix indicate a weight loss of 20% between 300 and 500 °C due to the combustion of the remaining organic groups. Consequently, it is clear that the slow hydrolysis technique leads to closed porosity matrices with trapped organic groups resulting from the incomplete hydrolysis of alkoxides. Once again, this contrasts with the characteristics of the TEOS gel samples prepared under the usual conditions (complete hydrolysis with acidic water in excess): low density (1.4–1.6 g/cm^3) and open porosity with a pore volume fraction of 10–20%. Finally, it can be expected that the closed porosity matrices are able to protect for a long time the metal aggregates against corrosion.

The incorporation of the aggregates into the gel is achieved by adding the solution containing the metal clusters stabilized with functionalized alkoxide into the solution of matrix precursor alkoxide. Typically, in order to prepare doped TEOS matrices, 13.5 mL of the alcoholic

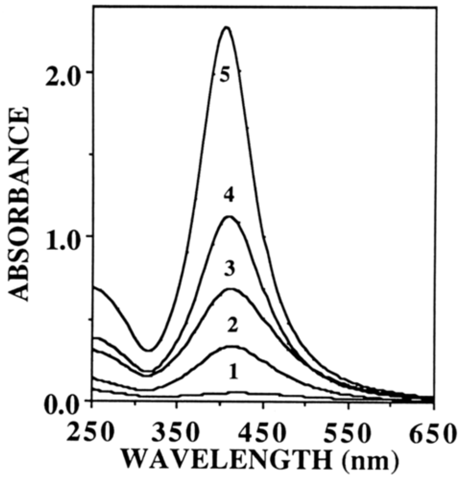

Figure 6. Absorption spectra of silver particles produced by γ-radiolysis of deaerated ethanolic solutions of $H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3$ containing 10^{-3} M Ag^+ and 10^{-3} M Ni^{2+}. The alkoxide/Ag^+ molar ratio is 10. Curves 1–5 correspond to doses of 300, 400, 500, 600, and 800 krad. Optical path length of 2 mm.

solution of the metal aggregates is added to 9.3 mL of $Si(OEt)_4$ (42 mmol) and 4.2 mL of $Zr(OBu)_4$ (10.5 mmol). Aging of the solution is then carried out as described above. Depending on the volumic contraction of the gel during the drying, the final concentration of metal in the oxide matrices is typically in the range 0.01–0.1 wt %. All the gels exhibit the characteristic colors of the corresponding metal nanoaggregates: yellow and violet for silver and gold respectively.

Characterization of Metal Particles. It is well-known that, in the case of silver and gold, the metallic state is easily recognized by the presence of a band (Ag, 400 nm; Au, 540 nm) in the absorption spectrum which is caused by surface plasmon absorption of the electron gas.[1] In previous studies, Kreibig et al.[16] and Smithard[17] have established correlation curves between the measured width of the optical absorption and the particle diameter measured by electron microscopy for small spherical silver particles (1–10 nm) in a glass matrix. Concerning silver particles, it seems that small distortions from a spherical shape affect the optical absorption much more than the changes in size. For small prolate spheroids of silver, depending on the average axial ratios, a shift of the main absorption peak (near 400 nm) to shorter wavelengths and a shift of a secondary peak to longer wavelengths have been found with an increase of the elongation of particles.[18] In this study, the characterization of metal particles is performed both on solutions and on oxide xerogels by recording absorption spectra on UV–visible spectrophotometer (Shimadzu UV 160A). Moreover, in all the experiments, the aggregates produced by radiolysis exhibit the electron diffraction pattern characteristic of the silver or gold metal structure. Size and shape determinations of metal particles in functionalized alkoxide solutions are also obtained from observations by transmission electron microscopy (Philips CM 30).

Results

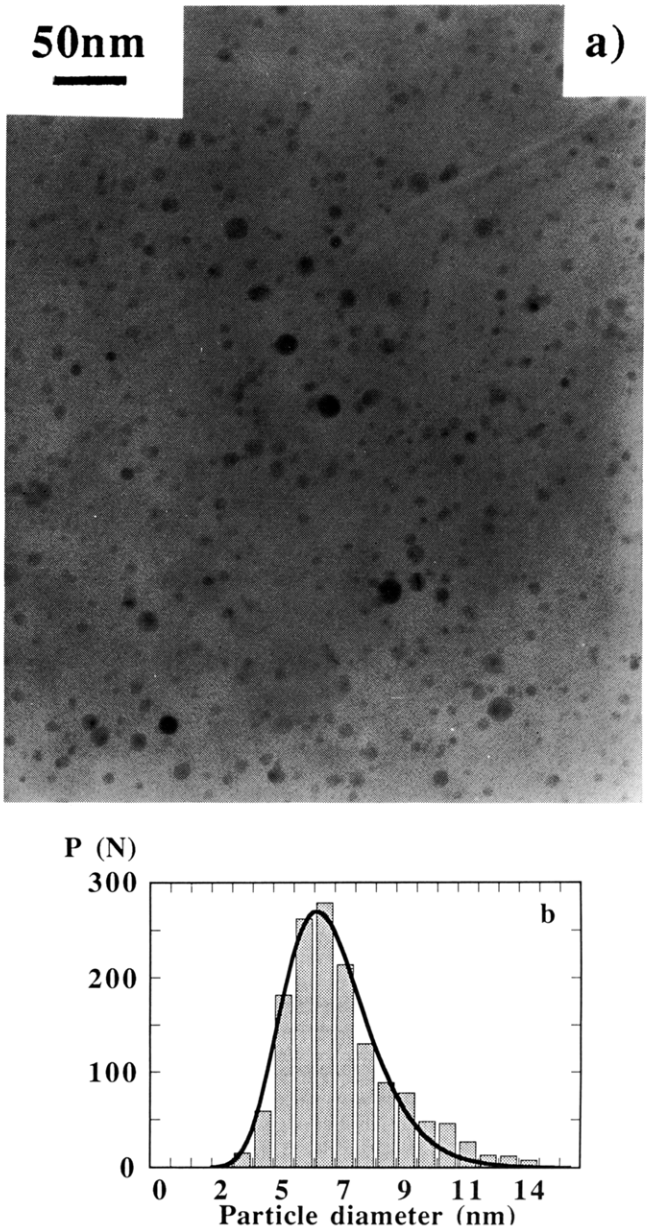

Figure 7. Ag sample corresponding to curve 5 in Figure 6: (a) electron micrograph; (b) histogram of the size distribution deduced from electron microscopy observations. The full line corresponds to a best fit of a log-normal distribution $P(D)$ (D_0 = 57 Å, σ = 0.26).

Production of Silver Particles in the Functionalized Alkoxide Solution. (*a*) *Influence of the Radiation Dose.* Figure 1 shows absorption spectra for solutions of $H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3$ ([$\mathcal{F}(CH_2)_3Si(OR)_3$]/[Ag ions] molar ratio of 10) irradiated with different doses (from 200 to 800 krad). As the dose increases, from 0 to 400 krad, the peak at about λ_m = 400 nm is sharpened and its intensity is increased. This corresponds to a growth of the silver particles due to a progressive release of reduced silver atoms. The mechanism which has been previously proposed[13] consists in a complexation of the reduced atom by surrounding metal ions and subsequently agglomeration of the complex to larger particles. Metal aggregates in solution can then be viewed as being charged at their surface by the presence of adsorbed unreduced ions. In the absence of any stabilizing agents, such colloids are not stable and precipitate. In our experiments, colloids obtained for irradiation doses less than 400 krad are stable for days, indicating a stabilizing effect of the added functionalized alkoxide. This stabilization effect can be attributed to the formation of a surface complex

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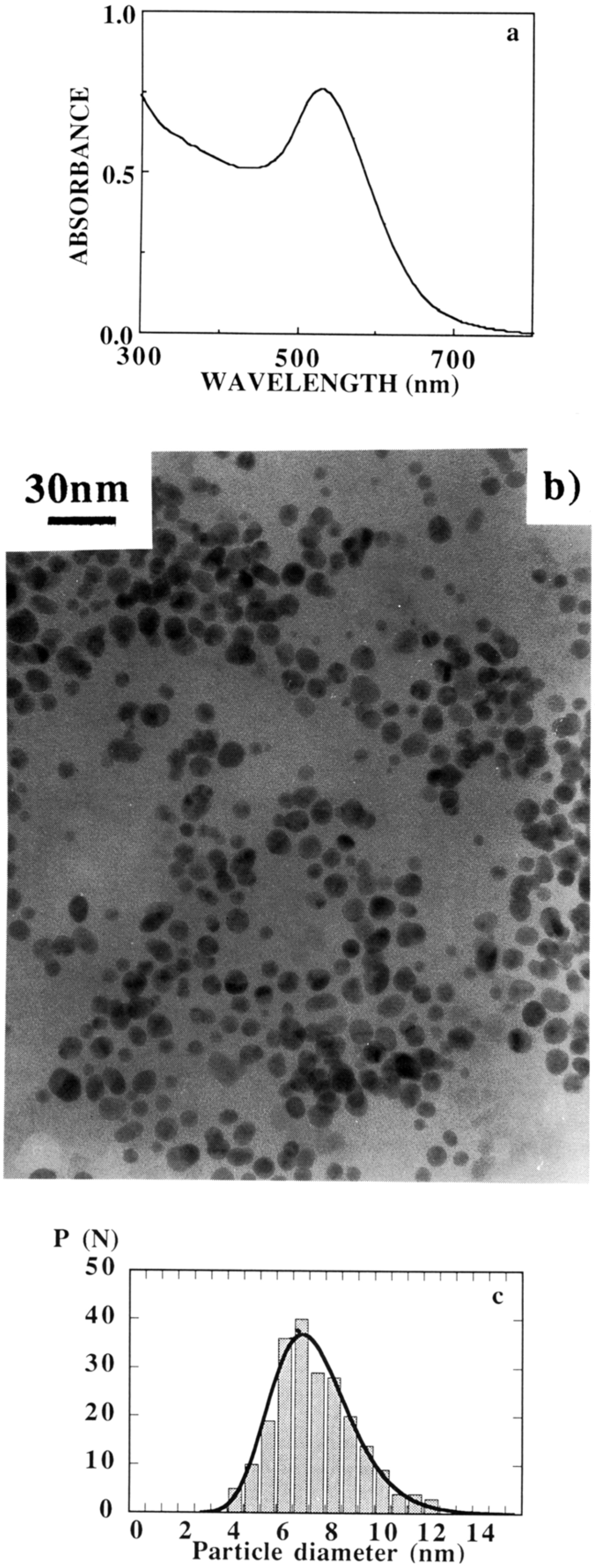

Figure 8. Gold particles produced by γ-radiolysis of deaerated ethanolic solution of $H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3$ containing 10^{-3} M $HAuCl_4$. The alkoxide/Au molar ratio is 10. The radiation dose is 1000 krad: (a) Absorption spectrum. Optical path length of 2 mm. (b) Electron micrograph. (c) Histogram of the size distribution from electron microscopy. The full line corresponds to a best fit of a log-normal distribution $P(D)$ (D_0 = 62 Å, σ = 0.20).

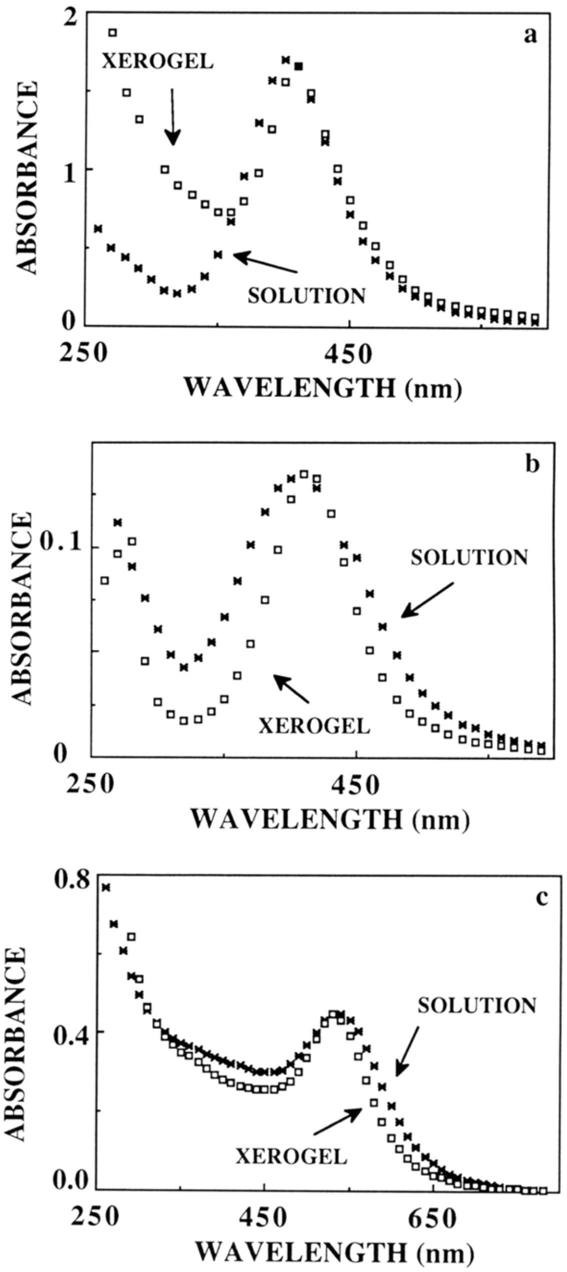

Figure 9. Comparison of the absorption spectra of metal particles in a functionalized alkoxide ethanolic solution ($H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3$) containing 10^{-3} M metal ions and xerogel matrices prepared by the slow hydrolysis technique: (a) silver particles in a solution and in TEOS matrices; (b) silver particles in a solution and in ATEOS matrices; (c) gold particles in a solution and in VTEOS matrices. Absorbances are normalized to the one of the xerogel (optical path length of 0.5 mm).

$M_n{}^{p+}\cdots\mathcal{F}\mathcal{S}Si(OR)_3$ between the adsorbed unreduced ions and the complexing function of the alkoxide.

Above 400 krad, the appearance of a secondary peak is clearly observed in the spectrum with a shift to longer wavelengths when the dose increases. As shown on the electron micrographs (Figure 2a) this peak corresponds to the growth of the metal particles and small departures from the spherical shape. For the sample irradiated at 800 krad, the secondary peak is observed at 550 nm and the average axial ratio deduced from electron micrograph is about 0.8. As suggested by the size distribution from 160 grains (Figure 2b), the changes of the spectra are due to the aggregation between silver clusters. This can be explained by considering the decrease of the proportion of unreduced ions as the irradiation goes on. There are less and less unreduced ions at the surface of the particles and consequently the number of stabilizing molecules becomes too small to prevent the aggregation between metal clusters. This leads to the observed dramatic polydispersity of the metal particles.

(*b*) *Influence of the Chemical Nature of the $\mathcal{F}$ Group.* Silver particles are produced in ethanolic solutions of the different alkoxides shown in Table I with a constant radiation dose (300 krad) and the same concentration of functionalized alkoxide ($[\mathcal{F}(CH_2)_3Si(OR)_3]/[\text{Ag ions}]$ molar ratio of 100). As shown by the absorption spectra (Figure 3), the size of the particles and the radiolytic efficiency are drastically influenced by the nature of the ligand. In fact, the influence of the chemical nature of the functionalized silicon alkoxide is thought to arise essentially from the difference of stability constants of the complex formed with metal ions. Taking into account the previously reported data,[19] one can expect an increase of the stability constant in the following order: Py < H_2N– < $H_2N(CH_2)_2NH$– < $H_2N(CH_2)_2NH(CH_2)_2NH$– < N≡CS–.

Using the Py and H_2N– groups, a partial precipitation of the silver particles is observed and the absorption spectrum of the filtered solutions spreads over a large wavelength domain (from 300 to 600 nm). This indicates a very low efficiency of the surface complexation using these complexing groups.

Using the N≡CS– group, it appears that only a very small quantity of silver is reduced compared to the other alkoxides. It seems then that the very strong complexing property of this group prevents the easy reduction of the complexed silver.

The best results were obtained using the $H_2N(CH_2)_2NH$– and $H_2N(CH_2)_2NH(CH_2)_2NH$– ligands for which the absorption spectra of the solutions suggest the formation of nearly spherical particles. We therefore may conclude that the complexing agent has to be efficient enough so that surface stabilization can occur, but not too much because this leads to a drastic decrease of the reduction yield.

(*c*) *Influence of the Concentration of the Complexing Agent.* Different ethanolic solutions of Ag^+ ions complexed by the $H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3$ functionalized alkoxide are irradiated with a dose of 600 krad. In these solutions, the $[\mathcal{F}(CH_2)_3Si(OR)_3]/[\text{Ag ions}]$ molar ratio was made to vary from 0.1 to 100. Precipitation occurs in the 0.1–1 range. For a molar ratio of 10, the main absorption peak is still broadened, indicating incomplete surface complexation. It is only for a molar ratio of 100 that the profile of the main peak at about $\lambda_m = 400$ nm appears as being symmetric, corresponding to the formation of quasi-spheroic particles (Figure 4). For this last sample, an histogram of the size distribution is deduced from electron micrographs (Figure 5a) using 650 grains with two pictures (Figure 5b). The best fit made by a least-squares refinement is obtained for a log-normal distribution $P(D)$:

$$P(D)/P(D_0) = \exp\left[-\frac{1}{2\sigma^2}\ln^2\left(\frac{D}{D_0}\right)\right]$$

in which D_0, the most probable value of the particle diameter D and σ, the standard deviation, are respectively equal to 4.1 nm and 0.5.

As expected for an equilibrium between complexed and uncomplexed particles, these results show that the proportion of stabilized particles increases with the concentration of donor ligands. However, using a high concentration of ligands, the colloids obtained in this way are still far from being monodisperse.

(*d*) *Influence of the Addition of Nickel Ions.* To improve the complexation of silver particles, Ni^{2+} ions (10^{-3} M) are added into initial solutions of $H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3/Ag^+$ (alkoxide/Ag^+ molar ratio of 10). Nickel ions are not radiolytically reduced in our experimental conditions and are well known to give amino complexes more stable than silver ions.[19] Therefore, after reduction of silver ions, one can expect the adsorption of Ni^{2+} at the surface of Ag particles and then, the formation of strong stabilizing Ni^{2+}–amino complexes which reduce the cluster aggregation. Figure 6 shows absorption spectra after irradiation with different doses (from 300 to 800 krad). As expected, the absorption peaks exhibit Gaussian profiles corresponding to the formation of spherical particles. As the dose increases, the peak becomes sharpened and its intensity is increased. The size distribution analysis was performed on the sample irradiated at 800 krad. A histogram was realized using 1500 grains with four pictures (Figure 7). The best fit is obtained for a log-normal distribution with a mean diameter $D_0 = 57$ Å and a standard deviation $\sigma = 0.26$. These results clearly demonstrate the efficiency of the addition of Ni^{2+} ions which leads to a significant reduction of the size dispersion in comparison with the sample illustrated in Figure 5.

Production of Gold Particles in the Functionalized Alkoxide Solution. The radiolytic route is achieved in the ethanolic solution of $H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3$ using an irradiation dose of 1000 krad and an alkoxide/Au molar ratio of 10. The absorption spectrum (Figure 8a) presents the expected main peak at $\lambda_m = 540$ nm. The characterization of the irradiated solution is also performed from electron micrographs. They show that the particles are roughly spherical (Figure 8b). A histogram of the size distribution using 250 grains is presented in Figure 8c. The best fit is obtained for a log-normal distribution with a mean diameter $D_0 = 62$ Å and a standard deviation $\sigma = 0.20$. These results clearly show that the stabilization of the gold particles with the $H_2N(CH_2)_2NH$– groups is much more efficient than in the case of silver under the same experimental conditions.

Characterization of Nanoaggregate Doped Gels. Figure 9 shows absorption spectra for silver and gold particles complexed by $H_2N(CH_2)_2NH$– groups both in the alkoxide solution and in the xerogel matrices. Surprisingly, the gel spectra, when compared to the solution, shows a slight shift of the absorption peak and a significant reduction of its half height width. The last effect is enhanced for xerogel matrices having a permanent group (VTEOS, MTEOS, and ATEOS). For instance, in comparison with the solution, the reduction of the half-height width is 40 nm for Ag particles in ATEOS matrices instead of less than 10 nm in the TEOS matrix. According to the classical theory for small metal particles,[20] this could be explained by the change of the dielectric constant of the medium in which the metal particles are dispersed and

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probably also by a coupling effect between metal particles and the gel network.

As expected, the absorption spectra do not significantly vary after aging of the doped xerogels for three months in air, showing that metal particles are well protected against corrosion in the closed porosity matrices.

Conclusion

The first part of this work consisted of testing a method to stabilize silver and gold colloids produced in ethanol by the radiolytic technique. It seems that the presence of unreduced ions at the surface of the colloid permits the surface complexation of the aggregates by functionalized silicon alkoxide, thus allowing their stabilization. Different complexing functions have been tested, the best results are obtained with the $H_2NCH_2CH_2NH_2-$ ligand which appears as the best compromise between the efficiency of surface complexation and the ability to reduce free complexed metal ions. In the case of silver, the size dispersity of the colloids was found to be significantly improved by addition of nickel ions in the solution prior to irradiation. This effect is interpreted by the adsorption of nickel ions at the surface of the particles and formation of a strong stabilizing surface complex. The presence of such an additive in the case of gold is not necessary since the surface complex between adsorbed unreduced gold ions and the stabilizing function seems to be strong enough to obtain colloids with a relatively narrow size distribution. Nevertheless, in all cases, the asymetrical behavior of the distribution is typical of a log-normal distribution.

The second part of our work involved the incorporation of the colloids in sol–gel silica based matrices. As the incorporation of the silver aggregates in the usual silica sol–gel matrix (i.e., obtained by hydrolysis of the alkoxide with excess acidic water) leads to their oxidation, we used a slow hydrolysis technique for the synthesis of the matrix. This method produces closed porosity gels in which stable metal aggregates are homogeneously dispersed.