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Development Kinetics of Bimetal Clusters in Solution

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Abstract

Pulse radiolysis of mixed solutions of two monovalent metal ions $KAg(CN)_2$ and $KAu(CN)_2$ has permitted to follow from nanosecond to second time-range the dynamics of the alloying process between gold and silver and of the reactions of the alloyed cluster. The pulse induces the simultaneous ion reduction into silver and gold atoms. Then, through coalescence and association with excess ions, homolog or different, these coexisting atoms give rise to transient bimetallic alloyed clusters. However, in the interval 2-20 sec the clusters are enriched in silver to the expenses of gold, the process being assigned to a slow intermetal electron transfer form gold atoms (less noble in the presence of CN^-) to silver ions adsorbed on clusters.

In the presence of the electron acceptor/donor couple MV^{2+}/MV^+, gold atoms generated in monometallic $KAu(CN)_2$ solutions act as an electron relay and transfer readily electrons to MV^{2+} while they are oxidized. In contrast, when silver and gold atoms are generated simultaneously, the transient bimetallic clusters that they form behave as catalytic electron acceptor towards MV^+ acting as a developer beyond a critical nuclearity as for pure silver clusters. The clusters grow as large alloyed particles. From the analysis of kinetics signals, it is concluded that even in low proportion the silver increases the redox potential of mixed clusters relative to pure gold clusters in the presence of cyanide. Consequences for gold-sensitization of photograpic emulsions are discussed.

Introduction

In the field of photographic processes, the role of gold as a catalytic sensitizer for the development of silver clusters in exposed emulsions has been demonstrated for long. The dynamics of metal ion reduction, of the growth and of the reactivity of silver clusters in solution have been studied already by the pulse radiolysis technique for different ligands.[1-4] The aim of this work is to extent this type of investigation to the couple of silver and gold ions in order to follow by time-resolved techniques for the first time the progressive building and the developability of bimetallic clusters and to examine whether the metals are intimately alloyed in the cluster or successively reduced so that the metals are segregated in a core-shell structure.[4]

The system selected for the study is the couple $Ag(CN)_2^-/Au(CN)_2^-$ where both metal cations are monovalent and are complexed with the same ligand. First, the growth of mono and bimetallic clusters formed in the radiation-induced reduction of $Ag(CN)_2^-$ or $Au(CN)_2^-$ together or separately will be examined. Then, the perturbation introduced by the presence of the developer on the growth dynamics of pure or alloyed clusters will be studied.

Experimental

All reagents were pure chemical: gold and silver salts, $KAu(CN)_2$ and $KAg(CN)_2$ were from Comptoir Lyon Alemand Louyot, 2-propanol and acetone from Prolabo, methyl-viologen chloride $MVCl_2$ from Aldrich. Mixed solutions of gold and silver cyanide were stable for hours without change of the UV spectrum with the specific bands of the complex $Au(CN)_2^-$ at 232 and 242 nm. Solutions were thoroughly deaerated by flushing nitrogen gas or under vacuum and stored in the dark.

Pulse radiolysis equipment (0.15-1.2 kGy per 3ns-pulse) and γ-irradiation facilities (dose-rate 10-30 kGy h^{-1}) were already described.[1] The Ag^I and Au^I ions are reduced by hydrated electrons, and $OH^\bullet$ and $H^\bullet$ radicals are scavenged by 2-propanol or and replaced by $(CH_3)_2C^\bullet OH$ radicals with strong reducing properties. The developer $MV^{+\bullet}$ is formed during the pulse.

Results

Cluster Formation in Mixed $Ag(CN)_2^-/Au(CN)_2^-$ Solutions

The mixed solutions to be irradiated contain $KAg(CN)_2$ and $KAu(CN)_2$ in the 50/50 ratio. To follow the optical absorption evolution we selected the same wavelengths as in previous studies on monometallic solutions of $Ag(CN)_2^-$ and $Au(CN)_2^-$ to facilitate the comparisons, that is at 400 and 520 nm, which correspond to the maximum of the surface plasmon bands of silver and gold clusters, respectively (Figure 1). The early steps of the mechanism are the Ag^I and Au^I reductions by solvated electrons with the rate constants 1.5×10^9 [5] and $(9.5 \pm 1.5) \times 10^9$ 1 mol^{-1} s^{-1} [6,7] respectively.

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In an equimolar solution of precursors, complexed gold and silver atoms are thus generated quite readily. Then, within microseconds, the association of these atoms with excess ions may involve the same or different metal species, according to the statistics of the encounters:

$$Au^{\circ}_{CN^-} + Au^{+}_{CN^-} \rightarrow (Au_2)^{+}_{CN^-} \quad (1)$$
$$Ag^{\circ}_{CN^-} + Ag^{+}_{CN^-} \rightarrow (Ag_2)^{+}_{CN^-} \quad (2)$$
$$Ag^{\circ}_{CN^-} + Au^{+}_{CN^-} \rightarrow (AgAu)^{+}_{CN^-} \quad (3)$$
$$Au^{\circ}_{CN^-} + Ag^{+}_{CN^-} \rightarrow (AgAu)^{+}_{CN^-} \quad (4)$$

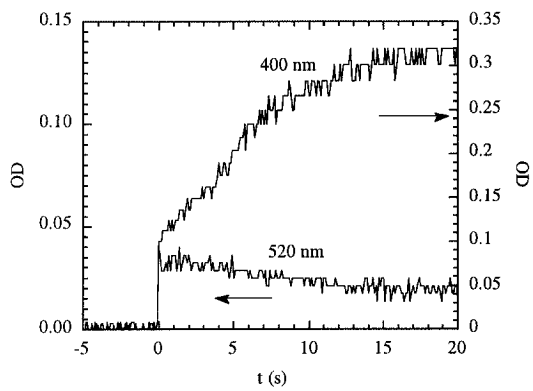

Figure 1: Correlated signals at 400 and 520 nm with a single pulse.5 x 10^{-4} mol.l $^{-1}$ KAg(CN)$_2$ and KAu(CN)$_2$

The products are identical in reactions (3) and (4). These reactions constitute the early binding between the two metals within the same entity. Further coalescence of the species formed in (3) and (4) would yield alloyed clusters of increasing nuclearity, $(Ag_iAu_j)_{CN^-}$, and thus causes the increase of the extinction coefficient per atom, which accounts for OD increases at 400 and 520 nm at least up to 2 s (Figure 1). Despite the competitive scavenging by Ag^+, the absorbance at 520 nm during 2 s is almost the same as in pure gold solutions under same dose conditions (instead of being twice less if the metal atoms of gold and of silver would coalesce separately) whereas the 400 nm absorbance is half of that in pure Ag^+ solutions. These features suggest an interaction between both metal atoms, at least during 2 s, yielding alloyed species.

The absorbance increase at 520 nm is followed beyond 2 s by a decrease while OD_{400} continues to increase correlatively. Then the absorbances at 520 nm and 400 nm reach a plateau at 20 s, the latter being nearly the same as for pure silver solutions, as if the reduction equivalents of gold atoms had been all transferred to silver: silver ions displace the gold atoms from the alloyed clusters and gold ions are slowly released.

The progressive replacement of gold atoms by silver atoms in the cluster implies that the redox potential at a given nuclearity is more positive for silver than for gold, which is less noble in the presence of cyanide. Note that the electrode potential of silver cyanide is also more positive (-0.4 V_{NHE}) than that of gold cyanide (- 0.6 V_{NHE})

Development of Silver Clusters in Cyanide Solutions

The redox potential of metal clusters in solution is known to increase with their nuclearity. Therefore, in the presence of a redox probe S/S^- two cases are possible.[1] First the aggregates of silver may behave as an electron donor, for small n and $E^{\circ}(Ag^+_{n,CN^-}/Ag_{n,CN^-}) < E^{\circ}(S/S^-)$ (the positive charge of the clusters will symbolize its oxidized form although excess CN^- are adsorbed):

$$Ag_{n,CN^-} + S \xrightarrow{k_{corr}} Ag^+_{n,CN^-} + S^- \quad (5)$$

Second, the aggregates may behave as an electron acceptor for supercritical values of n and $E^{\circ}(Ag^+_{n,CN^-}/Ag_{n,CN^-}) > E^{\circ}(S/S)$:

$$Ag^+_{n,CN^-} + S^- \xrightarrow{k_{corr}} Ag_{n,CN^-} + S \quad (6)$$

Successively, both processes have to compete with the concomitant evolution of silver cluster coalescence. The critical aggregate Ag_{n_c,CN^-} corresponds to the thermodynamic threshold beyond which the electron transfer is reversed from reaction (5) to reaction (6). It corresponds to a critical size to which a redox potential $E^{\circ}(Ag^+_{n,CN^-}/Ag_{n,CN^-})$ close to $E^{\circ}(S/S^-)$ may therefore be assigned. The monoelectronic redox couple $MV^{2+}/MV^{\bullet+}$ was chosen because of the intense optical absorption band around 600 nm of $MV^{+\bullet}$ which behaves as the reference donor. The hydrated electrons are scavenged partly by MV^{2+} and partly by $Ag(CN)_2^-$ in the range of 500 ns. The 2-propanol radicals are all scavenged by MV^{2+}.

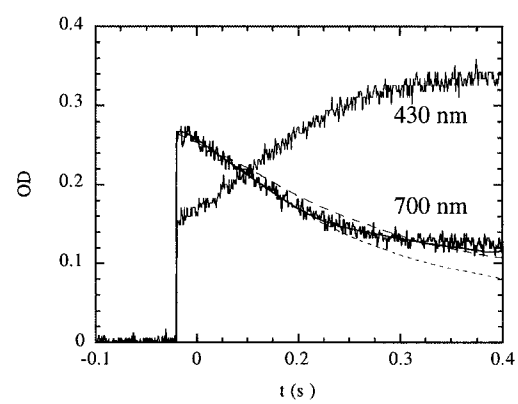

Figure 2: Single pulse correlated signals at 700 and 430 nm in a deaerated solution of 5 × 10^{-4} mol.l $^{-1}$ KAg (CN)$_2$ and MV^{2+}. Simulation of the decay at 700 nm with:
k_{corr} = 0 (....), 10^4 (----), 1.1 10^2 *mol.l* $^{-1}$.s^{-1}(—).

Figure 2 presents the typical profiles of the time evolution of the absorbance at two wavelengths, λ = 700 nm and λ = 430 nm, obtained after the same pulse. $MV^{+\bullet}$ is observed at 700 nm where the spectrum is quite intense (ε_{700} ($MV^{+\bullet}$) = 3460 l mol^{-1} cm^{-1}). In this time range the silver aggregates are small and hence do not exhibit any absorbance at this wavelength. At 430 nm, the $MV^{+\bullet}$ extinction coefficient is much smaller (ε_{430} ($MV^{+\bullet}$) = 1000 l mol^{-1} cm^{-1}) than that of Ag_n. It appears that $MV^{+\bullet}$ (signal at 700 nm) is stable for ~ 15 ms under the conditions of Figure

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2 before starting to decay. Correlatively, the 430 nm absorbance is first constant during the same period but then increases. As expected, the delay is induced by the time required for the clusters to grow enough such that their redox potential becomes higher than that of the reference donor, which imposes a threshold (reaction [6]). The time delay t_c, is a reciprocal function of the dose. After the induction time, the $MV^{+\bullet}$ decay lasts for 1.5 s under the conditions of Figure 2 with a marked change in the slope at 0.2 s. The fast decay up to 0.2 s is due to reaction.[6] The absorbance increase after 1.5 s is due to large aggregates that are absent at shorter times. Their absorption spectrum, shifted towards higher wavelengths than for small clusters, is increasing, particularly beyond l0s.

The slower decay after 0.2 s, which appears as a shoulder in the signal of Figure 2, is assigned to supplementary formation of $MV^{+\bullet}$ through the reversible reduction reaction of MV^{2+} by the subcritical silver clusters still present, which are thus corroded (reactions [5]).

In order to determine the values of n_c k_{corr} and k_t, a numerical simulation model[8] taking into account the value of the coalescence rate, k_d and the cascades of successive coalescence, electron transfer and corrosion reactions was carried out. The experimental signal of the absorbance at 700 nm in Figure 2 is compared with the kinetics calculated using the values adjusted for the experimental signals obtained under different dose-perpulse conditions:

n_c = 5 or 6; $k_d = (6 \pm 2) \times 10^6$ 1.mol^{-1} s^{-1}; $k_{t=} (5.3 \pm 0.1) \times 10^6$ 1 mol^{-1} s^{-1}; $k_{corr} = (1.0 \pm 0.2) \times 10^2$ 1.mol^{-1} s^{-1}.

The value of the critical size n_c = 5-6 corresponds to the redox potential of the cluster containing one more silver cation *i.e* . of the couple E°(Ag_{6-7}^{+}, $_{CN^-}$/Ag_{6-7}, $_{CN^-}$) = - 0 4 V_{NHE}

In the case of monometallic $Au(CN)_2^-$solution, the signal (Figure3a) corresponding to MV^+ does increase at 700 nm instead of decaying as in the MV^+ /silver system. In fact, at long times after γ-irradiation of an identical solution under vacuum, the characteristic MV^+ spectrum is obtained alone: the very first Au_n clusters formed have been oxidized by MV^{2+}, similarly to reaction [5] for $Ag(CN)_2^-$and hence no supercritical cluster may be produced and developed.

Development of Bimetallic Gold-Silver Clusters

Signals obtained with a mixed solution of Ag^I and Au^I in the presence of the $MV^{2+}/MV^{+\bullet}$ probe will be compared with signals in monometallic solutions of silver with the same redox couple. Initial equimolar solutions of metal ions ($[KAu(CN)_2]$ = $[KAg(CN)_2]$ = 2.5×10^{-4} mol l^{-1}) also contained $[MV^{2+}] = 5 \times 10^4$ mol.l^{-1}.

After the pulse, the respective initial amounts of metal atoms and of $MV^{+\bullet}$ ions result from the competition between the reduction reactions induced by radiolytic species. If the cluster formed reaches the critical size, it will act as a nucleus that initiates a catalyzed growth fed alternatively by the electron donor and the adsorption of excess metal ions. Otherwise, a subcritical cluster is unable to accept an electron from $MV^{+\bullet}$. Moreover the reverse transfer[5] will occur from these clusters to MV^{2+} (faster for gold than for silver).

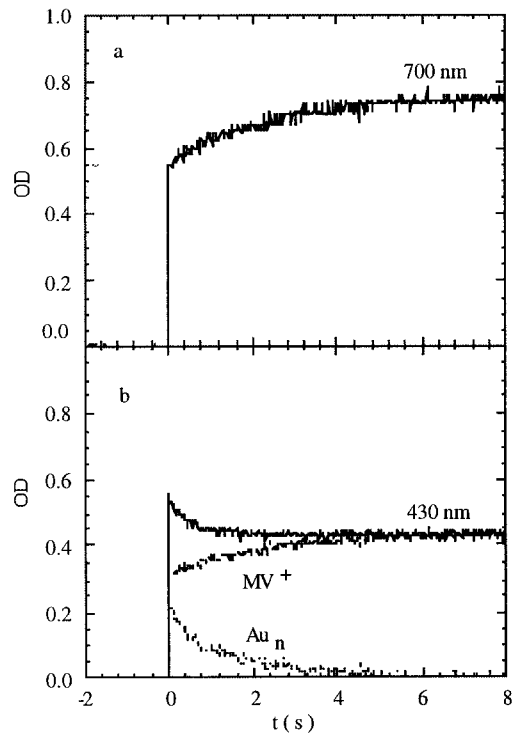

Figure 3: Correlated signals with a single pulse. 5×10^{-4} mol.l^{-1} $KAu(CN)_2$]and MV^{2+}.

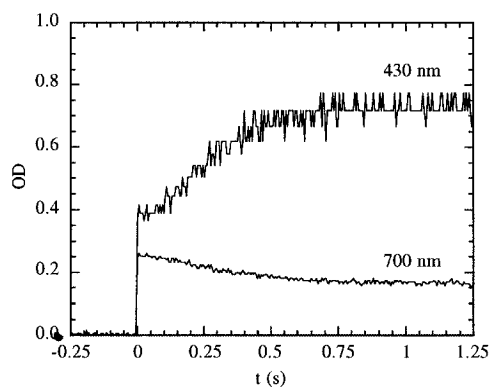

Figure 4: Correlated signals with a single pulse 2.5×10^{-4} mol.l^{-1} $KAu(CN)_2$ and $KAg(CN)_2[MV^{2+}] = 5 \times 10^{-4}$ mol.l^{-1}.

After a single pulse, the evolution of $MV^{+\bullet}$ is observed at 700 nm and the cluster absorbance at 430 nm (Figure 4). The general scheme of $MV^{+\bullet}$ decay now presents the same decreasing features as in the silver case, as if gold in the alloyed cluster exhibited the same properties as silver. We exclude the explanation that gold atoms have already been replaced by silver atoms since the displacement mechanism in gold-silver solutions appeared to be much slower (t > 2 s) than the process here observed within 20 ms. The critical time under various conditions is not affected by the presence of gold ions replacing part of the silver ions in the mixed solution.

We observe that after t_c the absorbance OD_{700} decays while OD_{430} increases, strictly as in silver solutions up to

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1.5 s (Figure 5) (the reverse occurs in pure gold solutions). That means that the donor $MV^{+\bullet}$ is consumed catalytically and that subsequent growth of supercritical alloyed clusters occurs.

For $i + j > n_c$:

$$(Ag_iAu_j)^+_{F\ CN^-} + MV^+ \rightarrow (Ag_iAu_j)_{CN^-} + MV^{2+} \qquad (7)$$

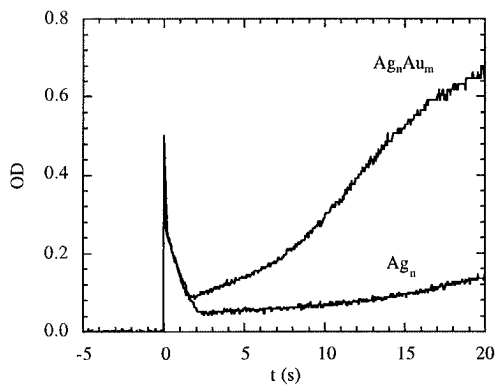

Figure 5: Comparison of signals at 700 nm in silver cyanide solution and a mixed solution of Ag^I/Au^I (0.50/0.50) having the same total concentration 5×10^{-4} mol.l $^{-1}$

After 2 s the absorbance at 700 nm increases drastically (Figure 5). This absorbance is no longer due to $MV^{+\bullet}$ already consumed, but to the red component of large clusters, which developed from a small concentration of nuclei[1]. The comparison of this signal with that obtained in the case of silver under the same conditions[4] indicates that, when we replace part of the silver ions by gold ions in the solution, the increase of OD_{700}, and therefore that of ε with *n,* is much stronger (twice at 2 s and 5 times at 20 s) for the mixed than for the silver solution (Figure 5) (it was zero for the gold solution). Therefore, a clear synergy is observed in the mixed system, which supports the conclusion of a strong binding between gold and silver atoms and on the bimetallic character of the clusters after the end of the reduction by MV^+.

It is noteworthy that, except for the cluster absorbance at long time, the signals are only slightly affected by substitution of an increasing amount of silver ions by gold ions in the initial solution[9]. We conclude that the critical nuclearity for alloyed gold-silver clusters to reach the reference redox potential E° = - 0.4 V_{NHE} would seemingly be that of pure silver clusters n_c = 5-6 in the presence of CN^-, instead of $n_c = 4$[1] for SO_4^{2-}. When included in alloyed clusters even at a low ratio, silver which is a more noble metal than gold in CN^- environment seems to impose its properties (coalescence rate, redox potential) on the silver-gold clusters.

Discussion

It is known for long that a small amount of gold is quite efficient to enhance the sensitivity of the AgBr emulsions. Observations on the catalytic efficiency of mass-selected mixed clusters $(Ag_mAu_n)^+$ $(m+n = 5)$ for the development of photographic emulsions have been already published[10]: when $n > m$, no development is observed, in contrast with the case of $n < m$ where the development efficiency is dominated by the silver atom content.

The kinetics results of the present work were obtained in solutions and in the presence of CN^-. With this ligandation, gold is less noble than silver, and the latter, even in small proportion, imposes the critical nuclearity. Considering now AgBr emulsion, added with gold chloride as sensitizer, the nuclearity dependence of the redox potential presents the same trend as in solution[1]. However, gold is now more noble than silver and the respective roles observed in cyanide solution should be reversed.

Therefore, for a given nuclearity of an alloyed cluster, substitution of a silver atom by a gold atom must confer on this cluster a more noble character. That is to say as well that with a given developer, the critical size for the development is lowered by alloying silver with gold.

In conclusion, time-resolved observations of the development of an alloyed gold-silver cluster have demonstrated the role of a more noble metal in controlling the critical nuclearity for the electron transfer from the developer.

Aknowledgments

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