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ORIGINAL CONTRIBUTION

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Corrosion of Au particles in air-exposed NaI-treated Au colloidal suspensions

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Abstract This study examines the influence of the treatment of citrate-capped Au colloidal particles with NaI under exposure to air. Whereas in the NaI-treated centrifugate of the Au colloidal suspension the iodide-induced formation of triiodide runs spontaneously, its accumulation is found to be strongly decelerated in the Au colloidal suspension under the same conditions. In accordance with the experimental findings from electron absorption spectroscopy and transmission electron microscopy, a mechanism is proposed which describes the oxidation of the Au particles by oxygen under intermediate participation of triiodide.

Keywords Corrosion · Au colloids · Iodide · Triiodide · Electron absorption spectroscopy

Introduction

The electronic properties of small metal particles are strongly influenced by chemisorption [1, 2, 3]. The surface atoms of the metal core, which are attacked by Lewis bases, are slightly positively charged. Since simultaneously the excess electron density is donated into the metal core such chemisorption processes are supposed to induce a shift of the Fermi level to a more negative value, which could lead to a drastically increased sensitivity of the particle towards oxidation [3].

Concerning this idea there is a certain amount of experimental evidence. The corrosion of differently capped Ag particles was described accurately [3, 4, 5] and in principle one should expect that owing to size effects [6] Au particles could also be oxidized by air if the Fermi level of these particles is lowered sufficiently.

For a suspension of citrate-capped colloidal Au particles Westerhausen et al. [7] observed a slight red-shift of the surface plasmon resonance (SPR) band in the absorption spectrum after the suspension had been exposed to air for 13 h. This shift was attributed to the formation of gold ions or gold oxide at the surface of the metal core.

Here, we present some evidence for the corrosion of colloidal Au particles treated with NaI. The colloidal suspension was characterized time-dependently by electron absorption spectroscopy (EAS) and samples from such suspensions were observed by transmission electron microscopy (TEM) in order to study the effects of the NaI treatment on these particles exposed to air.

Experimental

Colloid formation

The aqueous colloidal suspension, consisting of approximately 15-nm-diameter Au particles, was prepared similarly to the method of Turkevich et al. [8]. Chloroauric acid (5 mg, 2.3×10^{-5} mol, 99.99%, Alfa Aesar) was solved in 95 ml distilled water and heated. With vigorous stirring 5 ml (2.3×10^{-4} mol) aqueous 0.9%-solution of citric acid (Merck) was added rapidly to the boiling solution. After about 15 s, the liquor turned from colourless to purple. The Na-Hal-treated Au colloidal suspensions (Hal = Cl, Br, I) were prepared by dissolving the anhydrous salts in the original Au colloidal suspension.

Electron absorption spectroscopy

UV–vis spectra were obtained using a Varian CARY 5E UV–vis–near IR spectrophotometer (resolution 1 nm) and 1.5-ml quartz cuvettes (diameter 5 mm).

Transmission electron microscopy

TEM was carried out with a Philips CM200 FEG/ST electron microscope at an electron energy of 200 keV. The samples for TEM investigation were prepared by dropping the colloidal suspensions through holey films of amorphous carbon (thickness about 10 nm) mounted on copper grids, which were placed on absorbent material.

Results and discussion

The treatment of the Au colloidal suspension with NaHal, $c(\mathrm{NaHal}) = 7\times10^{-2}$ M, resulted in all cases in an instantaneous change in colour from purple to blue or lavender. The electron absorption spectra of the visible range for freshly prepared samples are shown in Fig. 1a. In comparison with the spectrum of the original Au colloidal suspension, these spectra are characterized by broad agglomeration bands in the typical range (above 600 nm) as well as by specific redshifts of the SPR band. These shifts indicate the changes in the electronic situation of the affected particles. The extent of the redshift may be correlated with the electron-withdrawing effect of the capping anionic species and therefore in most cases with its electronegativity [9]. The SPR absorption maximum of the original colloidal suspension is located at 523 nm, whereas the suspensions treated with NaHal, $c(\mathrm{NaHal}) = 7\times10^{-2}$ M, show maxima at 538, 530 and 538 nm, respectively (Fig. 1a). Since the electronegativity of the halogens decreases with their molecular weight, the given EAS data can not be correlated with the electronegativity directly.

More details of the NaI-treated Au colloidal system can be taken from Fig. 1b. The redshift of the SPR band depends on the concentration of NaI. At $c(\mathrm{NaI}) = 3.5\times10^{-2}$ M a redshift of just 2 nm is observed [$\lambda_{\max}(\mathrm{SPR}) = 525$ nm] and no typical agglomeration band arises. This indicates that only some of the citrate anions, capping the Au core originally, were substituted by the stronger Lewis basic iodide. Since iodide is referred to as a typical "soft" Lewis donor, whereas the carboxylate oxygen atoms of the citrate anions are regarded as "hard", the "soft" Lewis acid Au atoms should prefer iodide by far [10]. So one should conclude that a concentration of $c(\mathrm{NaI}) = 3.5\times10^{-2}$ M is just too low to substitute all the citrate anions. Anyhow, there seems to be also a kinetic effect. When the spectrum of the same solution is detected after a delay of 15 min once more, a further damping of the SPR band as well as an additional redshift of 3 nm [$\lambda_{\max}(\mathrm{SPR}) = 528$ nm] are observed. Taking into account the relatively bulky iodide anion as well as the stabilizing chelate effect concerning the capping citrate anions, which preferentially act as polydentate ligands towards the Au surface [11], a kinetic hindrance of the exchange reaction seems to be plausible.

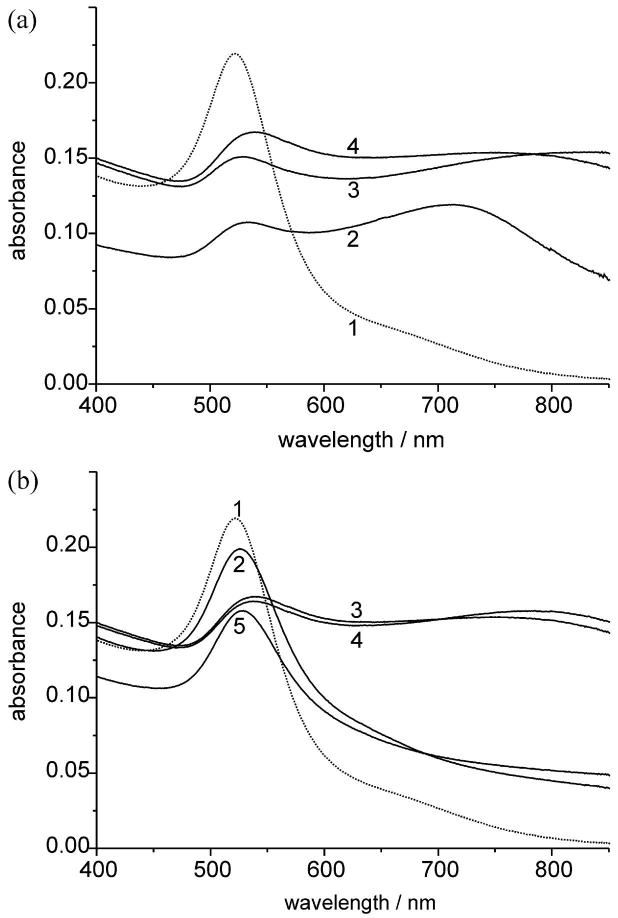


Fig. 1a,b Electron absorption spectroscopy (*EAS*) spectra of samples of Au colloidal suspensions in part treated with NaHal. **a** Untreated suspension (*1*), $c(\mathrm{NaCl}) = 7\times10^{-2}$ M (*2*), $c(\mathrm{NaBr}) = 7\times10^{-2}$ M (*3*), $c(\mathrm{NaI}) = 7\times10^{-2}$ M (*4*). **b** Untreated suspension (*1*), $c(\mathrm{NaI}) = 3.5\times10^{-2}$ M (*2*), $c(\mathrm{NaI}) = 7\times10^{-2}$ M (*3*), $c(\mathrm{NaI}) = 1.4\times10^{-1}$ M (*4*), $c(\mathrm{NaI}) = 3.5\times10^{-2}$ M after a delay of 15 min (*5*)

In contrast, at a concentration of $c(\mathrm{NaI}) = 1.4\times10^{-1}$ M only slight differences occur in the EAS spectrum compared with the situation at $c(\mathrm{NaI}) = 7\times10^{-2}$ M. The SPR absorption maximum remains at 538 nm; the agglomeration band becomes somewhat more intense and its maximum shifts to lower energy. The unchanged SPR maximum indicates that the surface of the gold cores is capped by iodide to the same extent at these two concentrations. Thus one could conclude that the substitution of citrate by iodide is almost complete at $c(\mathrm{NaI}) = 7\times10^{-2}$ M.

But can we be sure that the active iodine species is iodide? Owing to the excess of citric acid (see the preparation), the pH of our colloidal suspension is around 3. Moreover, our experiments were not carried out under the exclusion of air. In such systems

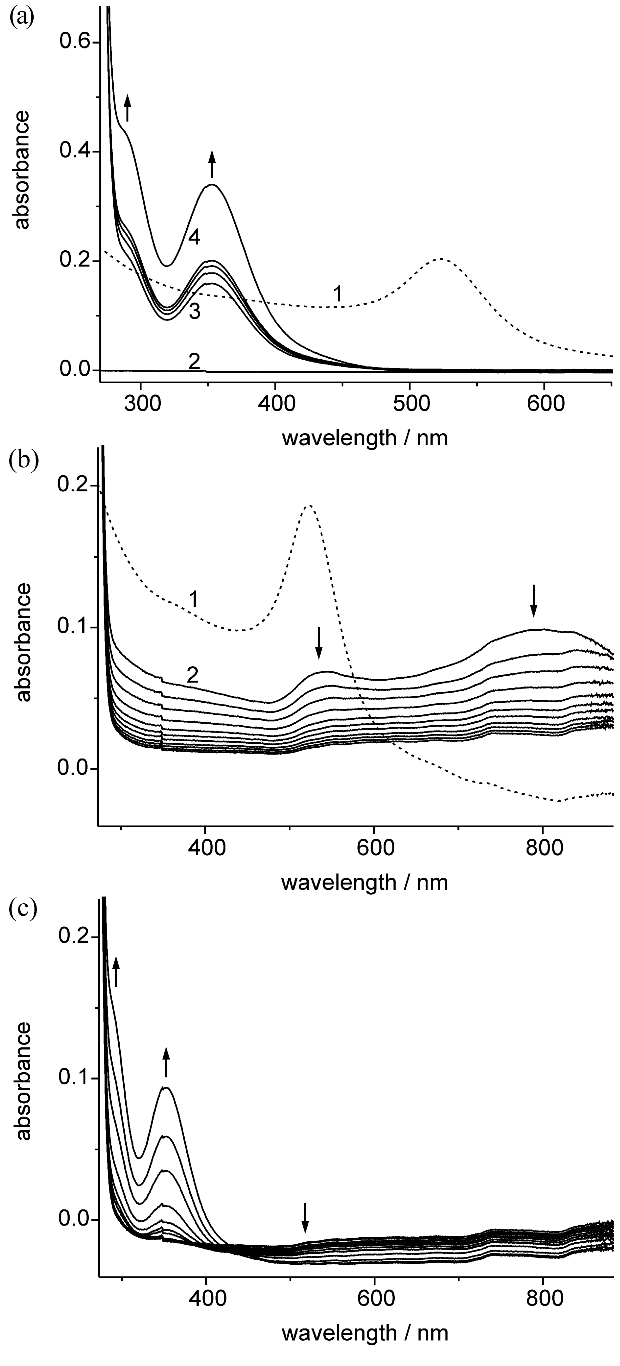
$$I^- + H^+ \rightleftharpoons HI \tag{1}$$

$$4HI + O_2 \rightleftharpoons 2I_2 + 2H_2O \tag{2}$$

$$I_2 + I^- \rightleftharpoons I_3^- \tag{3}$$

should take place to a significant extent. So at least the anionic triiodide could also play a role as a capping agent towards the Au core. In order to get a picture of the extent of the triiodide formation in our system, 20 ml of the original Au colloidal suspension was centrifugated at 17,000 rpm for 10 min. Anhydrous NaI (337 mg) was solved in 1.5 ml of the resulting colourless centrifugate, $c(\mathrm{NaI}) = 1.5$ M. Some spectra from this sample together with the spectrum of the original Au colloidal suspension are shown in Fig. 2a. As expected, the SPR band of the latter is completely missing in the other spectra, meaning that all the Au particles were removed by centrifugation. The bands at 352 and 289 nm indicate the formation of triiodide [12]. At higher energy a very intensive band starts to appear, which is attributed to the charge transfer to solvent (CTTS) transition of iodide ($\lambda_{\max} = 229$ nm) [5]. The first spectrum of the centrifugate [with $c(\mathrm{NaI}) = 1.5$ M] was recorded 2 min after its preparation. The following three measurements were performed after periods of 2.5 min each. A continuous, slightly decreasing increment in intensity resulted. After the fourth measurement, the solution ($V = 1.5$ ml) was poured into an open box of polystyrene, whereby the surface of the solution increased from 0.5 to 8 cm^2. After 2.5 min the solution was again added to the cuvette and measured once more. The recorded spectrum showed a significant further increase in the intensities of the triiodide bands. In summary, the formation of triiodide in the 1.5 M NaI solution of the centrifugate has to be regarded as relatively fast as well as strongly sensitive to the extent of contact to the air.

A similar experiment was then performed using the Au colloidal suspension instead of its centrifugate. The spectrum of the original Au colloidal suspension as well as a time-dependently recorded series of its 1.5 M NaI solution are shown in Fig. 2b. Starting from 2 min after its preparation, the following measurements were performed after 10 min each. The bands can be correlated to the bands of the NaI-treated suspension in Fig. 1. Curve analysis of the SPR band in the spectrum, recorded after 2 min, resulted in $\lambda_{\max}(\mathrm{SPR}) = 538$ nm. Although a 20-fold higher concentration of NaI was present in this experiment than in the experiment of Fig. 1a, no significant deviation in the SPR band

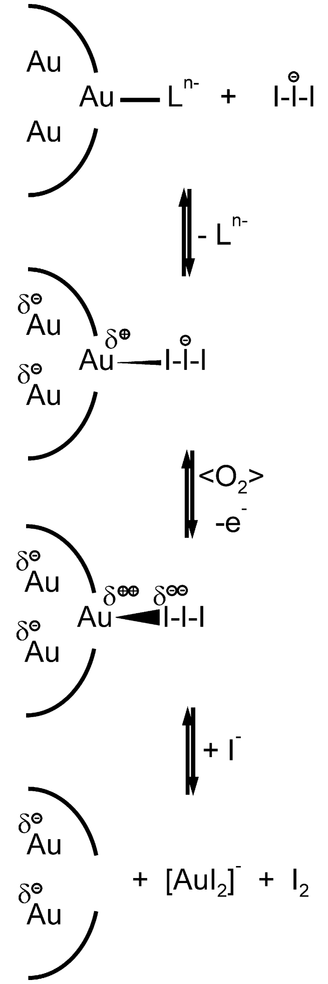


▶

Fig. 2 EAS spectra of **a** the untreated Au colloidal suspension (*1*), the centrifugate (10 min at 17,000 rpm) of the Au colloidal suspension (*2*), the NaI-treated centrifugate, $c(\mathrm{NaI}) = 1.5$ M, a series of four scans ($\Delta t = 2.5$ min each) starting 2 min after preparation of the sample (*3*), the NaI-treated centrifugate, $c(\mathrm{NaI}) = 1.5$ M, after reinforced exposure to the air; for details see text (*4*), **b** the untreated Au colloidal suspension (*1*), the NaI-treated Au colloidal suspension, $c(\mathrm{NaI}) = 1.5$ M, a series of 11 scans ($\Delta t = 10$ min each) starting 2 min after preparation of the sample (*2*), and **c** the NaI-treated Au colloidal suspension, $c(\mathrm{NaI}) = 1.5$ M, after reinforced exposure to the air (for details see text), a series of 13 scans ($\Delta t = 2.5$ min each) starting 102 min after preparation of the sample absorption maximum is observed. A damping of the bands is found, which is attenuated in the next run. As expected, the strong CTTS band of iodide is present continuously, but even after more than 100 min no triiodide absorptions are found. After 102 min this solution was more intensively exposed to air as described for the centrifugate.The spectra as they were recorded after the solution had been kept for successive periods of 2.5 min in the open polystyrene box are shown in Fig. 2c. The more the remaining intensity of the SPR and the agglomeration band is reduced, the more the intensities of the triiodide bands increase. After 13 of these periods the intensities of the triiodide bands have increased close to the magnitude of those which were recorded from the NaI-treated centrifugate 2 min after its preparation (Fig. 2a, c).

From the experiment, using the centrifugate of the colloidal suspension (Fig. 2a), we conclude that the reactions in Eqs. (1), (2) and (3) should also rapidly occur in the NaI-treated Au colloidal suspension. Nevertheless, the accumulation of triiodide is dramatically decelerated in this system, although a large excess of iodide is present. In order to obtain comparably intensive triiodide bands, it is necessary to expose the NaI-treated Au colloidal suspension to a much larger extent to the air. In our opinion a mechanism like that given in Scheme 1 could explain the specific findings.

Owing to the fact that triiodide is to be regarded as the ‘‘softest’’ anionic species in the system, it should play a significant role as a capping ligand towards the gold core, which could explain the lack of the triiodide absorptions in Fig. 2b. Moreover, it seems to be reasonable to associate the strong redshift of the SPR band, obvious from Fig. 1a, with the adsorption of an iodine species, which is able to stabilize additional negative charge to considerable extent. Thus the capability of charge delocalization in the triiodide anion seems to match such a strong redshift. It should result in a strongly polarized metal-to-ligand bond and therefore in enhanced ionic contributions concerning this bond. If one assumes that oxygen could take away electron density from the Au–I_3^- system, the extent of polarization concerning the Au–I bond clearly could be increased up to the point that it becomes comparable to the situation in the system using the strongly electron-withdrawing chloride anion as a capping ligand (Fig. 1a). After an oxidation like this, the reaction of iodide with the oxidized Au–I_3^- system could lead to the formation of $[AuI_2]^-$, I_2 and a negatively charged metal core fragment (Scheme 1). Such fragments were discussed by Henglein et al. [4] in the case of the corrosion of Ag colloidal particles by oxygen. In a further run of the reaction the accumulated negative charge, which increasingly inhibits the attack of Lewis basic anions, is supposed to be picked up by oxygen and so the corrosion could go on. Thus we believe that the remarkable need for ‘‘air’’, which is necessary for the formation of a detectable amount of triiodide in our NaI-treated Au colloidal suspension (Fig. 2b, c), is caused by a similar mechanism of corrosion in our system.



Scheme 1 Mechanism proposed for the corrosion of Au particles in acidic air-exposed NaI-treated Au colloidal suspensions

Iodine, which is formed in the last step of the proposed mechanism, surely plays its role in the equilibria illustrated in Eqs. (2) and (3). But what happens to $[AuI_2]^-$? There are several reasons for the finding that it is not possible to record absorption data of this species from our samples. The absorption maximum of $[AuI_2]^-$ is reported to be located around 290 nm ($\epsilon = 90$ M^{-1} cm^{-1} in acetonitrile) [13]. Since the simultaneously produced I_2 (Scheme 1) induces the formation of I_3^-, which absorbs much more strongly ($\epsilon > 30{,}000$ M^{-1}cm^{-1}) around a similar wavelength (289 nm) [12], conspicuous hints concerning the formation of $[AuI_2]^-$ cannot be expected from EAS. Moreover $[AuI_2]^-$ is known to be quite unstable in aqueous solution [14]. Principally, there is a high tendency for Au(I) compounds to dissociate [6, 13]; thus,

$$3[\mathrm{AuI}_2]^- \rightleftharpoons [\mathrm{AuI}_4]^- + 2\mathrm{Au}(0)\downarrow + 2\mathrm{I}^- \tag{4}$$

should take place to a considerable extent. The supposedly formed $[\mathrm{AuI}_4]^-$ is used up by the equilibrium [15]

$$[\mathrm{AuI}_4]^- \rightleftharpoons [\mathrm{AuI}_2]^- + \mathrm{I}_2, \tag{5}$$

since this equilibrium is displaced to the right, owing to Eq. (3), as long as there is an excess of iodide. Moreover, the solubility of AuI(s), whose formation from $[\mathrm{AuI}_2]^-$ competes against the formation of Au(0) described in Eq. (4), was found to be proportional to the iodide concentration [16]:

$$[\mathrm{AuI}_2]^- \rightleftharpoons \mathrm{AuI(s)} + \mathrm{I}^- \tag{6}$$

Since in our system a large excess of iodide is present continuously, Eq. (6) is displaced to the left. Thus one should expect that under the conditions given all the intermediately formed $[\mathrm{AuI}_2]^-$ is finally reduced to Au(0). This means that the NaI treatment of the colloidal suspension induces a corrosive decomposition of the original particles as well as the formation of new Au centres or the growth of particles owing to the dissociation of $[\mathrm{AuI}_2]^-$ on the surface of Au nucleation centres. In any case, the NaI treatment of the Au colloidal suspension should affect the size distribution of the Au particles considerably.

A TEM micrograph of a sample of Au colloids which was prepared immediately after NaI had been dissolved and the colour had changed from purple to greyish-blue, indicating the formation of agglomerates, is shown in Fig. 3a. In fact, particles from such samples are characterized by a considerable extent of agglomeration, which may be explained by decreased Coulomb-repelling forces owing to the lower charge of the capping after the exchange of citrate anions [17, 18]. Anyhow, no observable effects concerning the size distribution of the particles can be deduced from micrographs like Fig. 3a in comparison with micrographs from the original Au colloidal suspension. In contrast, Fig. 3b shows considerable deviations concerning the size distribution as well as the particle shape. The situation shown in this micrograph can be regarded as typical for a sample from an Au colloidal suspension which was treated with a large excess of NaI after its yellow colour had indicated the formation of triiodide. In such samples particle diameters around 15 nm no longer dominate. Small particles (here typically around 7 nm in diameter) of partly irregular shape are quite common and also particles larger than 30 nm in diameter occur, which were not present in the original Au colloidal suspension. Concerning the small as well as the large particles, Au was the only element found by the energy-dispersive X-ray detector. Thus, we suppose that the small particles have to be regarded either as fragments of original Au colloidal particles, which were attacked by corrosion, or as particles growing from new nucleation centres according to Eq. (4). The presence of larger particles can be regarded as a consequence of the particle growth, which was inhibited at the end of the particle synthesis owing to a lack of oxidized Au species. Thus the formation of $[\mathrm{AuI}_2]^-$ (Scheme 1) and its dissociation (Eq. 4) clearly could induce particle growth.

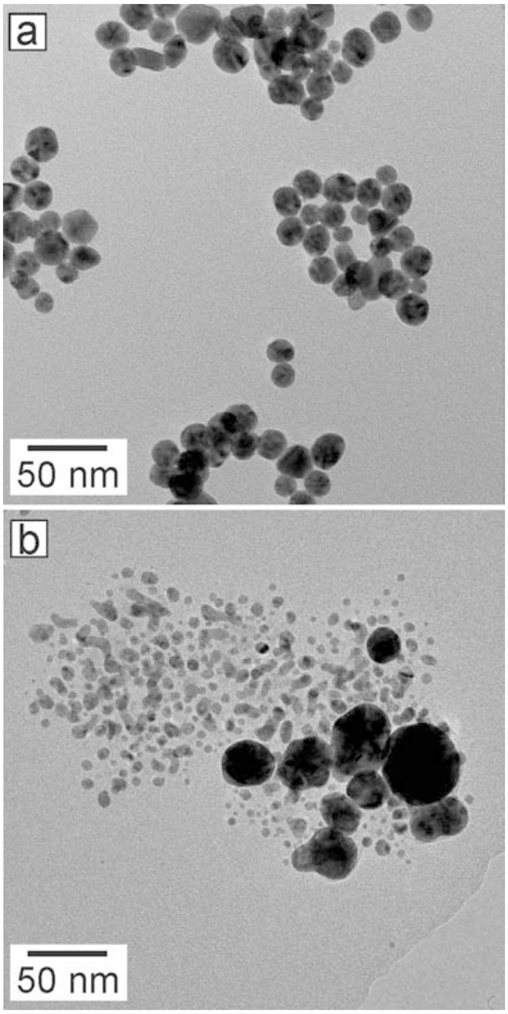


Fig. 3a,b Transmission electron microscopy (*TEM*) micrographs of particles from the Au colloidal suspension using amorphous carbon film as a substrate. **a** Au particles as received from a NaI-treated Au colloidal suspension immediately after its colour had changed to greyish-blue. **b** Au particles as received from an air-exposed NaI-treated Au colloidal suspension after its colour had changed to yellow

A closer look at the particles gives some further evidence for the substitution of citrate anions located at the surface of the original Au colloidal particles by iodine species. A typical citrate-capped Au colloidal particle approximately 15 nm in diameter is shown in Fig. 4a. It is located at the edge of the carbon substrate film and

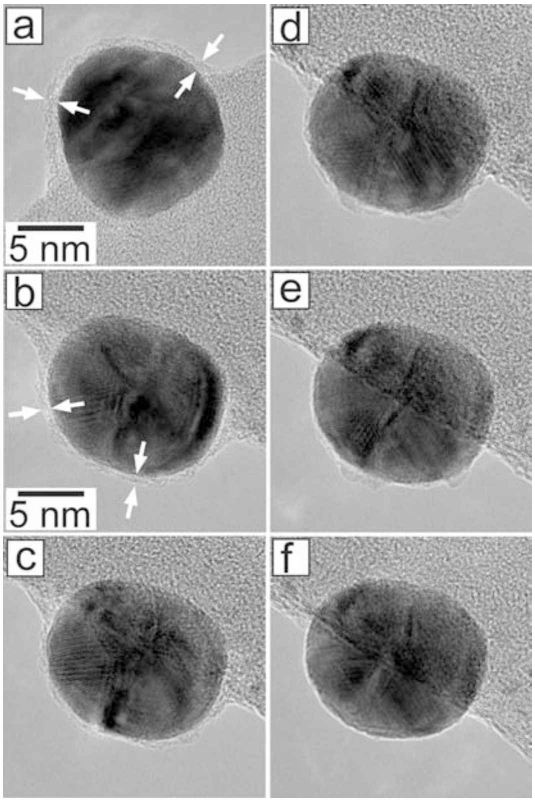


Fig. 4a–f TEM micrographs of particles from the Au colloidal suspension using amorphous carbon film as a substrate; the capping is indicated by the *arrows*. **a** One particle from the original Au colloidal suspension; the capping is stable for at least 15 min under the influence of the electron beam. **b**–**f** One particle from a NaI-treated Au colloidal suspension; a series showing the disappearance of the capping under the influence of the electron beam ($\Delta t = 1.5$ min each)

thus the capping is discernible around this half of the particle, which is located over a vacuum (see arrows). The thicknesses of such cappings are observed to be in the range between 1 and 3 nm. Even after prolonged exposure to the electron beam, this citrate-capping seems to be completely persistent. In contrast, the time-dependent observation of the capping around one of the few "single" particles from a NaI-treated suspension indicates the significantly diminished persistence of this capping, which was also observed in the case of the agglomerated particles. Figure 4b–f was taken after delays of approximately 1.5 min each and shows that under the influence of the electron beam the capping disappears continuously until nothing from it seems to be left (Fig. 4f). The disappearance of the capping under the influence of the electron beam was also observed in the case of NaCl-treated Au colloidal particles [19]. Two aspects can be taken into account in order to explain this finding. Firstly, the halogenide anions surely act as monodentate ligands towards the Au surface, whereas citrate is known to be a polydentate ligand in this case [11]. Thus the cleavage of one bond induced by the electron beam does not necessarily "liberate" the ligand molecule in the case of the capping consisting of polydentate citrate anions (chelate effect). Secondly, one could expect the formation of halogene radicals, if a capping of halogenide anions is exposed to the electron beam. To a certain extent these radicals surely combine to form Hal_2, which is highly volatile in any case under the conditions inside the microscope ($p < 10^{-4}$ Pa). The complete disappearance of the capping under the influence of the electron beam may therefore be regarded as a typical accompaniment of the substitution of capping citrate anions by halogenide species.

Conclusion

The treatment of citrate-capped Au colloidal suspensions with NaI results in a strong redshift of the SPR band in the EAS spectrum. This indicates a pronounced electron-withdrawing effect of the capping species towards the Au surface atoms. Owing to the relatively low electronegativity of iodine, iodide seems not to be able to affect the electronic situation of the Au particles to such an extent. Since, on the one hand, the spontaneous formation of triiodide in an air-exposed NaI-treated centrifugate of the Au colloidal suspension can be demonstrated by EAS and, on the other hand, polyhalogenide anions like triiodide are known to stabilize additional electron density much better than their corresponding monohalogenides, triiodide is supposed to play a major role as a citrate-exchanging anion in our system. The accumulation of free triiodide anions in air-exposed NaI-treated Au colloidal suspensions is strongly decelerated and occurs accompanied by substantial changes concerning the size distribution of the Au particles. A mechanism is introduced which may explain why these two findings coincide with each other and which describes the corrosion of triiodide-capped Au particles.

When Au particles from a NaI-treated suspension are exposed to the electron beam inside the microscope, the progressive disappearance of the capping can be observed. This finding indicates that the citrate anions which originally capped the Au particles were substituted by iodine species at least to a considerable extent, since from the latter the electron beam induced the formation of iodine radicals and finally iodine, which leaves the Au surface into the vacuum.

In summary, the experimental findings given in this work may be regarded as a more detailed [6, 7] description of the phenomenon of corrosion with respect to small Au particles.

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