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Preparation of Gold Nanoparticles in a Layer of Gelatin Film Using Photographic Materials. VII. Acceleration of Gold Deposition by Using Ascorbic Acid

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The preparation of gold nanoparticles using silver-salt photographic materials and a method of gold-deposition development are investigated. Although gold rapidly precipitated in the gold-deposition developer when ascorbic acid was added, gold atoms were deposited only on the exposed areas of the photographic plate when the plate was immersed in the solution. While the deposition proceeds slowly via the disproportionation reaction of gold(I) ions in the absence of ascorbic acid, the addition of ascorbic acid accelerates the deposition rate significantly and increases the photosensitivity of the photographic plate. The gold deposition is catalyzed by photolytic silver specks, called latent image specks, on silver halide grains. Absorption spectra and TEM observations suggest a broadening of the particle size distribution, and this indicates that the difference in the catalytic activities of the photolytic silver specks between the two reactions is due to the difference in the critical size of the silver specks for triggering the deposition. Because the catalysts were prepared using light, light-based control of the catalytic properties may be possible.

Reports on a method for preparing gold nanoparticles by exploiting the photosensitivity of silver-salt photographic materials date back many years.[1–3] We have also studied this method,[4–11] which involves the formation of gold nanoparticles from dithiocyanatoaurate(I) $[Au^{I}(SCN)_2]^-$ ions via the catalytic action of latent image specks, which are silver specks produced by the photolysis of silver halide grains in the photographic materials. Because the particles form only on the exposed areas of the materials, it is possible to prepare images or patterns with gold nanoparticles. Thus, this process is referred to as gold-deposition development.[8–11]

Gold-deposition development is nearly the same as gold latensification, which is a process of immersing photographic materials in a solution of $[Au^{I}(SCN)_2]^-$ ions,[12,13] except that the treatment period is much longer. The latent image specks remaining after gold latensification contain gold atoms and have a higher activity for triggering the development. Gold latensification is an important process for increasing photographic sensitivity, thus its mechanism was analyzed in detail to determine whether it proceeded through the replacement of silver with gold or the plating of gold on silver. Finally, Spencer and co-workers concluded that it proceeded via the plating process.[13] This explains the formation of gold particles of several tens of nanometers on much smaller silver specks. Normally, latent image specks consist of silver specks that are no more than several nanometers;[14] the critical size for triggering development corresponds to four silver atoms.[15]

In the normal photographic development process, photolytic silver specks, which are called latent image specks, act as catalysts to reduce the silver halide grains containing the specks. This is a primary process in the production of images in silver-salt photography. Because gold nanoparticles are deposited only on the exposed area, the photolytic silver specks seem to act in a manner identical to that in the gold-deposition development.

Since the starting material in this process is a $[Au^{I}(SCN)_2]^-$ ion and there are no reductants, the reaction has been considered to proceed via the following disproportionation reaction of gold(I) ions:[5,16]

$$3[Au^{I}(SCN)_2]^- \rightarrow 2Au(0) + [Au^{III}(SCN)_4]^- + 2SCN^- \quad (1)$$

In initial studies of this process, the rate of this process was found to be low, and several hours to several days were required for the completion of the process.[4–10] Therefore, techniques to accelerate the rate were necessary, and we have searched for such techniques. The $[Au^{I}(SCN)_2]^-$ ions are prepared from $NaAuCl_4$ and KSCN. We found that the ratio of these species is important[11] and that although the rate can be increased by varying this ratio, the obtained increase is not sufficient.

The preparation of gold nanoparticles via the reduction of gold(I) ions with reductants is also possible. One such study involved the addition of phenol in this process.[3] However, we could not confirm the effectiveness of phenol. On the other hand, we found that the use of ascorbic acid in this process increased the rate of the process considerably. Herein, we report the results.

Results

When exposed photographic plates were immersed in solutions of a gold-deposition developer both with and without ascorbic acid, images with colors in the red-purple range were

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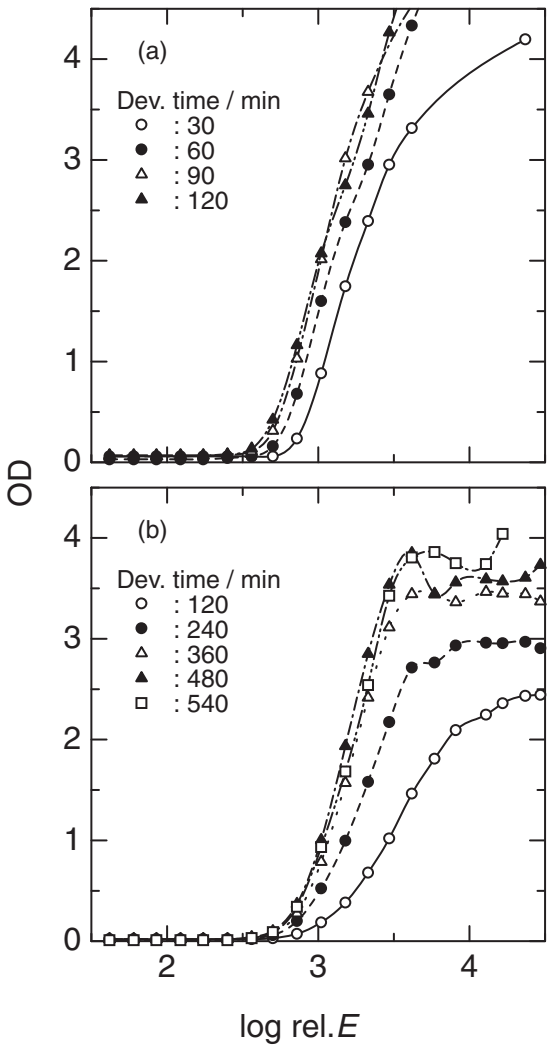

Figure 1. Photographic characteristic curves obtained by gold-deposition development on HRP-SN2 plates, for each development time. (a): Ascorbic acid added to developer; (b): ascorbic acid not added to developer. Exposure time = 60 s, and development temperature = 25 °C.

obtained. Gold nanoparticles were deposited on the exposed area, forming the image. The gold-deposition developer solution without ascorbic acid remained clear for several days. However, when ascorbic acid was added to the developer, a red-brown gold precipitate was formed. This precipitate appeared a little over ten minutes after the addition of the acid. On the other hand, when an exposed photographic plate was immersed in the developer just after the addition of ascorbic acid, no precipitate appeared until the plate was extracted from the solution.

Photographic characteristic curves, which indicate the relationship between the optical density (OD) and the exposure value, are shown in Figure 1 for HRP-SN2 plates for different development times. The exposure time was 60 s, and the exposure values are represented as relative values ($\log \mathrm{rel}.E$); these values were calculated from the optical density of each step on a step wedge in the sensitometer. Figures 1a and 1b show the results obtained with and without ascorbic acid, respectively. These figures show a drastic increase in the

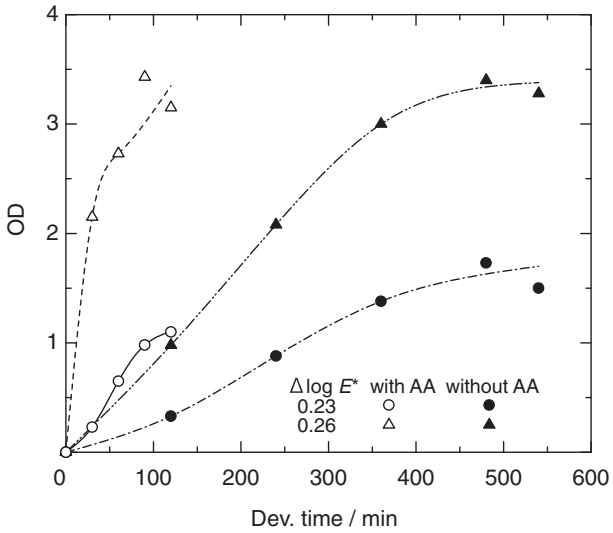

Figure 2. Development rates in the presence and absence of ascorbic acid (AA), measured at exposure values ($\Delta \log E^*$) that are equidistance from the inertia point, as determined from Figure 1.

development rate, which can be seen from the difference between the development times in the figures. The increase in the OD saturates at long development times of 90–120 min when ascorbic acid is used and at development times of 480–540 min when ascorbic acid is not used. The points at which the characteristic curves in Figure 1a rise steeply are shifted left relative to the corresponding points in Figure 1b. This indicates an increase in the light sensitivity upon the addition of ascorbic acid. Moreover, the points at which the characteristic curves in Figure 1a (for the case in which ascorbic acid was used) rise steeply shift to the left with increasing development time; the corresponding points in Figure 1b (the case in which ascorbic acid was not used) are at nearly the same positions. These results indicate different formation processes of gold nanoparticles in the presence and absence of ascorbic acid.

The development rates were assessed from the results in Figure 1. As the light sensitivities in the presence and absence of ascorbic acid differ, a comparison of the rates at identical exposure values is not appropriate. Therefore, the rates were compared at the exposure value equidistant from each photographic inertia point ($\log E^*$). The inertia point is the intersection point between the abscissa and the extension of the linear portion of the characteristic curve at the saturation level of the OD.[17] These points correspond to $\log \mathrm{rel}.E = 2.67$ for the curves obtained with ascorbic acid and $\log \mathrm{rel}.E = 2.85$ for those obtained without ascorbic acid. As the γ values (curve gradients) obtained when ascorbic acid was used are similar to those obtained when ascorbic acid was not used, a comparison of these values at the point equidistant from the inertia points ($\Delta \log E^*$) is appropriate. The development rates in the presence and absence of ascorbic acid are shown in Figure 2 for two $\Delta \log E^*$ values. This figure also shows the increase in the development rate with the addition of ascorbic acid.

The relationship between sensitivity and development time in the presence and absence of ascorbic acid is shown in Figure 3. The sensitivity in the presence of ascorbic acid is

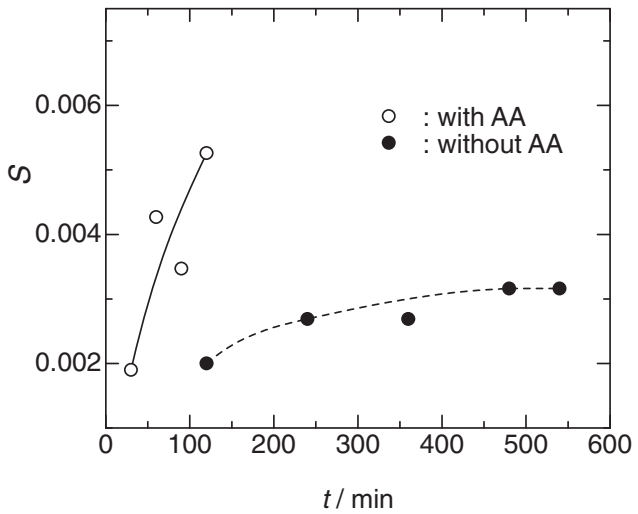

Figure 3. Relationships between sensitivity (*S*) and development time in the presence and absence of ascorbic acid (AA), as determined from Figure 1. Sensitivity is defined as a reciprocal of the exposure value that gives the optical density of 0.01 above the fog density. Open circles with a solid line depict the case with ascorbic acid; closed circles with a dashed line depict the case without ascorbic acid.

greater than that in the absence of ascorbic acid. Furthermore, the sensitivity in the presence of ascorbic acid increases considerably with the development time, while that in the absence of ascorbic acid increases only slightly.

Absorption spectra of the layer of gold nanoparticles on the P5600 plates are shown in Figure 4 for each development time. The plates were exposed for 30 s and developed with the same process. Curves obtained with and without ascorbic acid indicate that the absorbance appears to saturate as the development time is increased; this behavior is similar to that observed in Figure 1. The spectra obtained when ascorbic acid was not used show a peak around 550 nm; this peak is due to the surface-plasmon absorption of the gold nanoparticles. The spectra obtained when ascorbic acid was used also show a peak at a similar wavelength for a shorter development time of 30 min, but this peak is broader than that obtained without ascorbic acid. The absorption at longer wavelengths increases significantly with the development time. This results in the broadening of the peak to the right side, and thus, the plate color changes from magenta to purple-blue.

Electron micrographs of the gold nanoparticles obtained from the same samples as those used for the plot in Figure 4 are shown in Figure 5. Gold nanoparticles with sizes of several tens of nanometers are present, and the sizes of these particles increase with the development time. The particles with ascorbic acid grow faster than those without, which is apparent from the difference in the scale between the two figures. Moreover, the size distribution obtained when ascorbic acid was used appears to be broader than that obtained when ascorbic acid was not used.

Figure 6 also shows that the mean diameter of the gold nanoparticles increases with the development time. The particle growth rate in the presence of ascorbic acid is significantly larger, which also indicates the acceleration effect of ascorbic

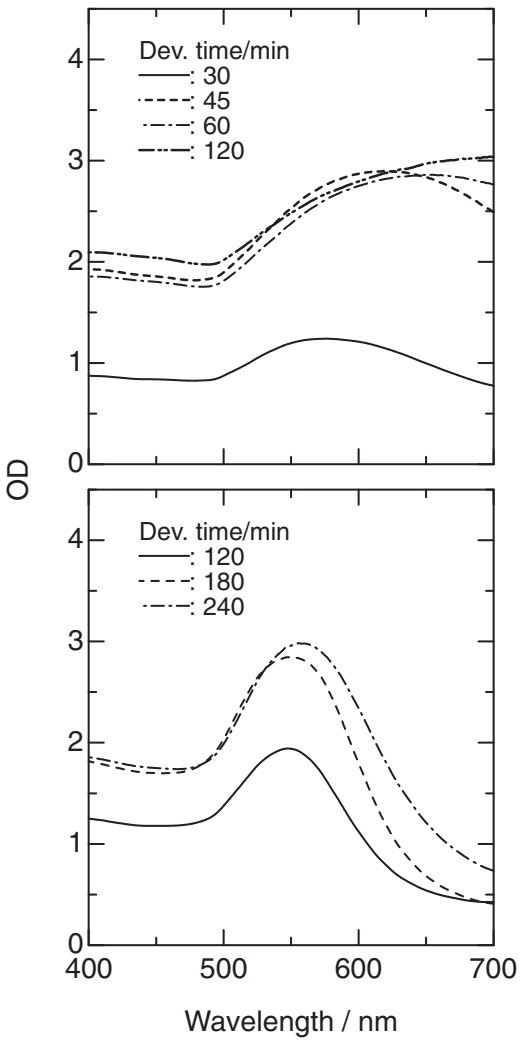

Figure 4. Absorption spectra of the layer with gold nanoparticles formed on P5600 plates for each development time. Top figure: ascorbic acid added to developer; bottom figure: ascorbic acid not added to developer.

acid. In the presence of ascorbic acid, the particle diameter increases continuously with development time to exceed 80 nm, while in the absence of ascorbic acid, it appears to saturate at roughly 30–40 nm. The standard deviation of the particle diameter, indicated by bars on the plotted points, increases in the presence of ascorbic acid. This also indicates that gold nanoparticles prepared with ascorbic acid have a broader size distribution.

Discussion

The use of ascorbic acid in the gold-deposition development process had several effects: (1) a drastic increase in the development rate, as shown by measurements of plate absorbance and particle size; (2) an increase in photosensitivity; (3) a broadening of the peak in the absorption spectra; and (4) a broadening of the particle size distribution. These results suggest that the formation mechanism of gold nanoparticles in the presence of ascorbic acid differs from that in the absence of ascorbic acid. The formation of gold nanoparticles in the absence of ascorbic acid is thought to proceed via the

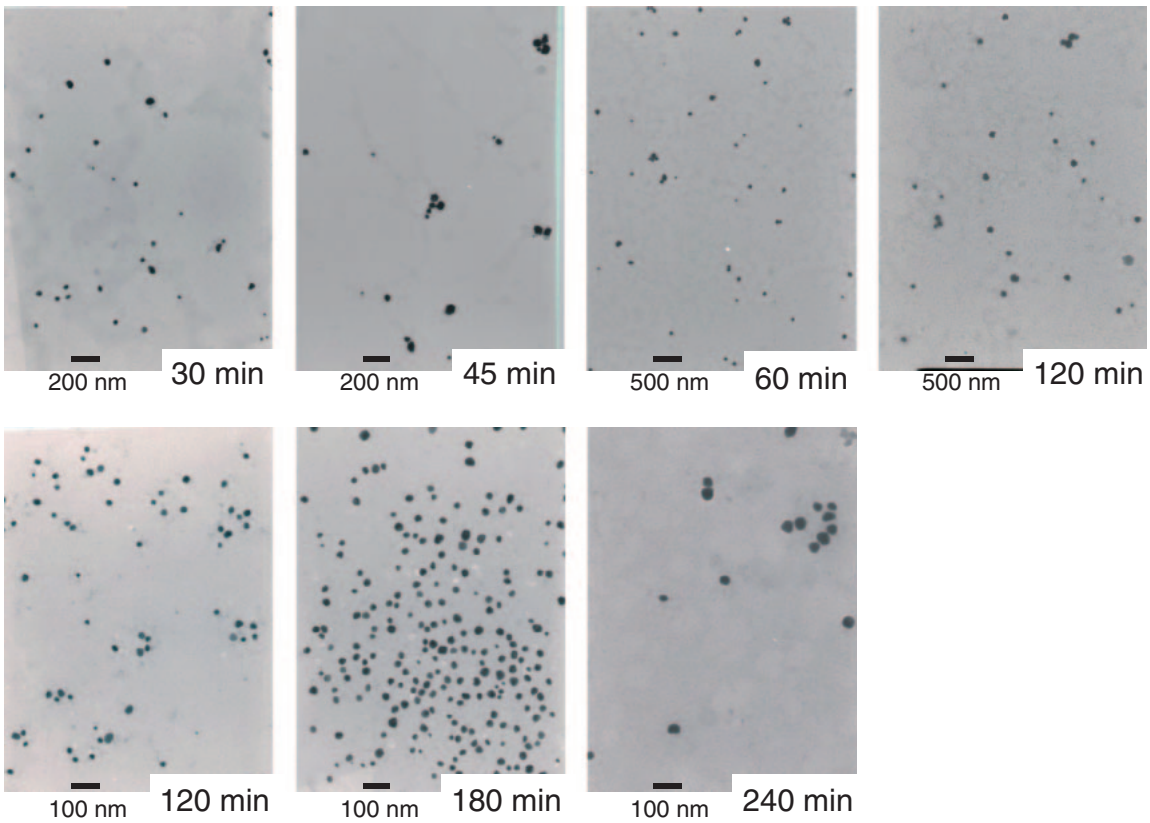

Figure 5. Electron micrographs of gold nanoparticles obtained from the same samples as those used to obtain the spectra in Figure 4. Top figures: ascorbic acid added to developer; bottom figures: ascorbic acid not added to developer. The times at the lower right side of each figure indicate the development time.

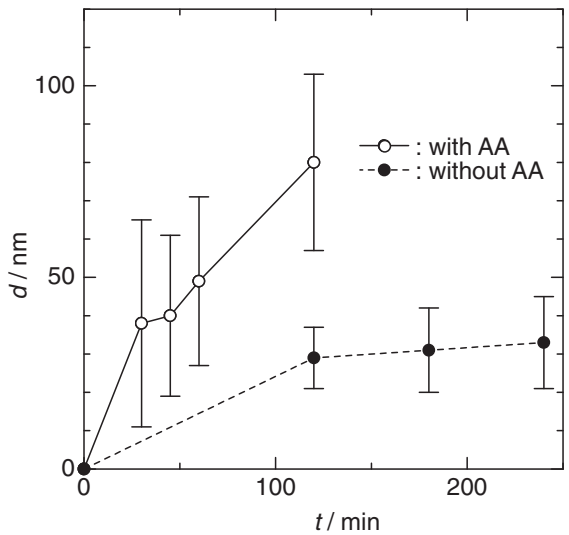

Figure 6. Growth rates of the average diameter (d) of the gold nanoparticles, as determined from Figure 5. Open circles with a solid line depict the case with ascorbic acid; closed circles with a dashed line depict the case without ascorbic acid. The bars on the circles represent standard deviations of the particle diameter.

disproportionation reaction of gold(I) ions, as shown in eq 1. On the other hand, when ascorbic acid is used as a reductant, it can reduce gold(I) ions and thus facilitate the formation of gold nanoparticles. This mechanism is supported by the precipitation of gold in the developer when ascorbic acid was added but no photographic plates were immersed. The reduction reaction proceeds more readily than the disproportionation reaction, and thus, the development rate in the presence of ascorbic acid is greater than that in the absence of ascorbic acid.

When an exposed photographic plate was immersed into the developer just after the addition of ascorbic acid, no precipitate appeared until the plate was extracted from the solution. This suggests that gold(I) ions are reduced to gold nanoparticles preferentially on the silver specks and that these specks thus serve as effective reduction sites for gold(I) ions and inhibit the precipitation of gold in the solution.

Because the photosensitivity differs between the reaction involving reduction by ascorbic acid and the disproportionation reaction occurring in the absence of ascorbic acid, the catalytic activity of the silver specks may differ between these two reactions. The light sensitivity in the presence of ascorbic acid was higher than that in the absence of ascorbic acid, which suggests that when ascorbic acid is used, gold nanoparticles are formed at a lower exposure value. Therefore, effective catalysis of the reduction of gold(I) ions by ascorbic acid can also occur at lower exposure values.

There is a critical size of the silver specks for triggering the reduction of silver halide grains in the normal development process.[15] For low-intensity exposures, such as the one employed here, the number of silver specks formed on each silver halide grain becomes one or less, according to the

concentration principle.[18,19] An increase in the exposure results in an increase in the speck size rather than an increase in the number of specks per grain, with lower exposure values resulting in the formation of photolytic silver specks of a smaller size. The high sensitivity attained indicates that the smaller silver specks still possess sufficient catalytic activity. Therefore, the critical speck size for reduction by ascorbic acid is less than that for the disproportionation reaction occurring in the absence of ascorbic acid.

The probability of triggering reduction in the normal development process depends on the size of the photolytic silver specks. The reduction reactions catalyzed by each of the silver halide grains do not proceed simultaneously at the beginning of development, rather they proceed in a random probabilistic fashion as the development time increases. Consequently, the development has an induction period, and the development rate is characterized by an S-shaped curve.[20,21] It has been suggested that statistical fluctuations cause large variations in induction periods when the size of the silver specks is equal to the critical size.[22] The induction period decreases with increasing exposure values for a low-intensity exposure.

The probability that gold deposition is triggered on a silver speck also depends on the speck size, and gold-deposition development will also have an induction period. The development rates at high exposure values, plotted in Figure 2, do not follow S-shaped curves. However, this may be due to the large development rate, which masks the induction period.

The increase in sensitivity with the development time is because of the successive appearance of new gold nanoparticles in the low-exposure region. The gold deposition is not triggered simultaneously on all silver specks at the beginning of development, and this leads to an increase in the OD and the shift of characteristic curves to the left as the development time increases. This is because the sizes of silver specks formed in the low-exposure region are close to or equal to the critical size, and the specks trigger the gold deposition randomly after some induction period. It is also probable that the process of reduction of gold(I) ions by ascorbic acid has a broader distribution of the induction period. These considerations explain the broadening of the size distribution of gold nanoparticles. Experimental results on the broadening of the absorption spectra and the broadening of the size distribution of gold nanoparticles also support this hypothesis.

The gold-deposition process proceeds as the development time increases. The absorbance indicated by the absorption spectra increased with the development time and became saturated both in the presence and absence of ascorbic acid. However, in the presence of ascorbic acid, the size of the gold nanoparticles increased continuously with a significant growth rate, while in the absence of ascorbic acid, the increase reduced and approached saturation.

In the disproportionation reaction occurring in the absence of ascorbic acid, one-third of the initial gold(I) ions are converted to gold(III) ions and are not deposited on the plates.[5] The reaction rate decreases rapidly with a decrease in the concentration of gold(I) ions, since the reaction proceeds via the participation of three gold ions, as shown in eq 1. On the other hand, since the reduction reaction occurring in the presence of ascorbic acid proceeds via collisions between gold(I) ions and ascorbic acid, the dependence of the reaction rate on the concentration of gold(I) ions decreases. The reaction proceeds even when the amount of gold(I) ions decreases, and thus, the size of the gold nanoparticles increases continuously.

As the size of the particles increases, the absorption of the particles changes from plasmon absorption to bulk absorption. This results in a red shift of the peak and increased absorption in the red region, but the absorbance at the peak wavelength does not increase. The total absorbance does not increase at the same rate as the size. The increase in the number of deposited gold atoms causes an increase in the particle size, but this does not directly result in an increase in absorbance because of the particle-dispersed system.

Gold nanoparticles were prepared by both disproportionation and reduction reactions of $[Au^{I}(SCN)_2]^-$. Both reactions were catalyzed by silver specks formed by the photolysis of silver halide, and the reduction of silver halide in the normal photographic development process was also catalyzed by these silver specks. This indicates that the photolytic silver specks on silver halide grains act as efficient catalysts for several reactions.

The most important property of this silver-speck catalyst is that the catalysis is mediated by light. As a result, optical control of the catalytic properties is possible. The amount or concentration of the catalyst can be precisely controlled by varying the amount of exposure. Moreover, as the resolution of this system is very high (e.g., 4000 lines/mm, where the line width is shorter than the wavelength of visible light[8]), the preparation of catalysts arranged in fine structures is possible. As gold nanoparticles can be used as catalysts, similar systems employing them are also possible. These systems can be used in microreactors etc.

Experimental

We used HRP-SN2 (Konica-Minolta) photographic glass plates for fabricating photomasks and P5600 (Konica-Minolta) plates for recording holograms. Both types have photographic emulsions with ultrafine silver halide grains and have properties that make them suitable for preparing fine gold nanoparticles.[7] The light source used for the exposures was a tungsten lamp in a JIS III photographic sensitometer, and the exposure was provided through an optical step wedge for 30–60 s.

Plates were developed via gold-deposition development. The composition of the developer is given in Table 1. This formula is similar to that of the developer used in a previous study,[11] except that in the present study, a solution of ascorbic acid was added to the developer just before the development was started. The reagents were added in the order in which they are listed in Table 1, and an exposed plate was immersed in the developer

Table 1. Formula for Gold Deposition Development

Reagent	Concentration/mol L^{-1}
KSCN	4.0×10^{-3}
$NaAuCl_4 \cdot 2H_2O$	1.0×10^{-3}
KBr	8.0×10^{-3}
Ascorbic acid	2.0×10^{-3}

Table 2. Procedure for Gold Deposition Development

Procedure	Processing solution	Time/min
Development	Developer shown in Table 1	30–540
Stop	Distilled water	5
Removal of antihalation dye layer	$NaHCO_3$ 15 g L^{-1}	5
Wash	Distilled water	1
Fix	F-5	4
Wash	Running water	30

immediately after the addition of ascorbic acid. The development procedure is presented in Table 2. The development temperature was 25 °C, and the development time was varied between 30 and 540 min. Because a layer of antihalation dye was coated on the reverse surface of the plates, an alkaline bath with sodium hydrogen carbonate was used to remove this layer.

Since the layer with gold nanoparticles formed by this method had a magenta color because of surface plasmon absorption, we measured the OD for green light with an optical densitometer. We then obtained photographic characteristic curves, which indicate the relationship between the OD and the exposure value, for each development time. The sensitivity was measured as the reciprocal of the exposure value that gave an OD of 0.01 above the fog density. Development rates were obtained from the relationship between the OD for the given exposure values on a characteristic curve and the development time. This rate indicates the rate of preparation of gold nanoparticles.

Absorption spectra of the plates with gold nanoparticles were measured with a double-beam spectrometer (Shimadzu, UV-2600). Gold nanoparticles on these plates were observed with a transmission electron microscope (JEOL, 1200 EX) to obtain the size distribution. The gold nanoparticles, located in a gelatin layer on the plate, were removed from the plate by scratching it and mounted on grids for observation; a previously reported procedure was used.[11]

References

1 T. H. James, *J. Colloid Sci.* **1948**, *3*, 447.
2 D. C. Birch, G. C. Farnell, R. B. Flint, *J. Photogr. Sci.* **1975**, *23*, 249.
3 S. Jablonka, C. Mora, P. M. Nowak, A. Zaleski, *J. Inf. Rec.* **1996**, *23*, 249.
4 K. Kuge, M. Arisawa, N. Aoki, A. Hasegawa, *Jpn. J. Appl. Phys.* **2000**, *39*, 6550.
5 K. Kuge, K. Kimijima, M. Arisawa, N. Aoki, A. Hasegawa, *J. Soc. Photogr. Sci. Technol. Jpn.* **2001**, *64*, 242.
6 K. Kuge, I. Suzuki, N. Aoki, A. Hasegawa, *J. Soc. Photogr. Sci. Technol. Jpn.* **2002**, *65*, 536.
7 K. Kuge, M. Arisawa, N. Aoki, A. Hasegawa, *Imaging Sci. J.* **2004**, *52*, 176.
8 K. Kuge, T. Nakao, Y. Goto, T. Omatsu, A. Hasegawa, *J. Appl. Phys.* **2006**, *100*, 013102.
9 K. Kuge, T. Nakao, S. Saito, O. Hikosaka, A. Hasegawa, *J. Imaging Sci. Technol.* **2007**, *51*, 96.
10 K. Kuge, S. Iwakiri, Y. Endo, N. Yasuda, C. Fukushima, M. Kimura, H. Shibuya, H. Kumagai, A. Hasegawa, *Radiat. Meas.* **2007**, *42*, 1335.
11 K. Kuge, A. Hasegawa, X. Chen, T. Sakai, *J. Imaging Sci. Technol.* **2010**, *54*, 010507.
12 T. H. James, in *The Theory of the Photographic Process*, ed. by T. H. James, MacMillan, New York, **1975**, Chap. 14, I-E, p. 428.
13 H. E. Spencer, C. A. DeCann, R. T. McClearly, *J. Imaging Sci.* **1987**, *31*, 8.
14 T. Tasaka, M. Murofushi, T. Tani, *J. Imaging Sci. Technol.* **2003**, *47*, 463.
15 T. Tani, *Photographic Sensitivity*, Oxford University Press, New York, **1995**, Chap. 4.3.1, pp. 91–92.
16 A. C. Reeder, H. E. Spencer, *J. Imaging Sci.* **1987**, *31*, 126.
17 G. I. P. Levenson, in *The Theory of the Photographic Process*, ed. by T. H. James, MacMillan, New York, **1975**, Chap. 16, I-F, pp. 501–502.
18 J. F. Hamilton, in *The Theory of the Photographic Process*, ed. by T. H. James, MacMillan, New York, **1975**, Chap. 4, I-C, pp. 108–109.
19 T. Tani, *Photographic Sensitivity*, Oxford University Press, New York, **1995**, Chap. 4.2, pp. 87–91.
20 T. H. James, in *The Theory of the Photographic Process*, ed. by T. H. James, MacMillan, New York, **1975**, Chap. 14, I-A, p. 406.
21 T. Tani, *Photographic Sensitivity*, Oxford University Press, New York, **1995**, Chap. 7.3, pp. 214–215.
22 H. E. Spencer, R. E. Atwell, *J. Opt. Soc. Am.* **1964**, *54*, 498.