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Preparation of Gold Nanoparticles in a Gelatin Layer Film Using Photographic Materials (5): Characteristics of Gold Nanoparticles Prepared on an Ultrafine Grain Photographic Emulsion

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Abstract. *The authors report a process for the preparation of gold nanoparticles in a gelatin layer. This process is similar to the photographic process of gold development or gold latensification, where gold atoms are deposited on the exposed area of photographic material when it is immersed in a gold(I) thiocyanate complex solution. Gold particles have gained prominence for their nonlinear optical effect, the intensity of which depends on the density of the particles in the layer. The authors attempted to condense the particles using a photographic plate for hologram recording; this plate was made of an ultrafine grain emulsion because this emulsion was believed to be conducive to condensation. The characteristics of the particles were analyzed using photographic characteristic curves, absorption spectra, and size distributions. The characteristic curves rose gradually with the immersion period and finally showed a very high contrast curve. A sharp and strong plasmon absorption was observed at around* 550 nm *at high exposure values, while the peak exhibited a redshift and broadening at lower exposure values. The diameter of the particle increased proportionally with the square root of the immersion period. The growth rate decreased with the exposure value and was larger with high intensity exposure. The dependence on the exposure value was explained by the competition for the gold ion due to the high density of latent image specks. The larger growth rate with high intensity exposure was also explained by the low density of the latent image specks due to high intensity reciprocity failure.*

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INTRODUCTION

Gold particles have gained prominence for their nonlinear optical effects[1–4] and other useful characteristics. This optical effect will be useful for constructing nonlinear optical devices such as light switches or optical modulators. However, it is indispensable to prepare a film or solid state construction with dispersed gold particles in order to utilize gold particles in optical devices. We propose a new method to prepare gold particles dispersed in a gelatin layer by using photographic films,[5–10] wherein gold particles are prepared by immersing the exposed film in a gold(I) thiocyanate complex solution. Gold atoms are deposited on a latent image speck. By fixation, silver bromide grains are removed, and gold particles are left behind in the gelatin layer. This process is an application of the gold development process,[11–13] which produces an image of metallic gold, or gold latensification,[14] wherein gold atoms are deposited on a latent image speck to achieve developability in silver halide photography.

The preparation process of gold particles has attracted great interest and has been studied widely; however, knowledge regarding this process is still limited. Previously, we proposed that the deposition of gold atoms proceeded by the disproportionation reaction of three gold(I) ions to one gold(III) ion and two gold atoms catalyzed by latent image specks.[7] This process is similar to that of gold latensification proposed by Spencer et al.[15] Further, we reported on the reaction process, namely that the growth rate of gold atoms increased with the concentration of gold ions and that the diameter of gold particles increased proportionally with the square root of the immersion period.[8]

Meanwhile, Goertz et al. measured the Hyper-Rayleigh scattering (HRS) of AgBr nanosol decorated with sensitization centers.[16] The addition of $KAuCl_4$ enhanced the HRS of the nanosol with small silver clusters. They believed that this was due to the formation of Au atoms by the disproportionation reaction catalyzed by silver clusters followed by the incorporation of Au atoms into catalytic silver clusters. They found that the enhancement of HRS by the addition of $KAuCl_4$ reached saturation at higher densities of $KAuCl_4$ and suggested that this process was self-limiting.

The intensity of the nonlinear optical effect of gold particles depends on the density of the particles in a layer;[2,4] the higher the density, the stronger is the intensity. Therefore, condensation of the particles is necessary to enhance the nonlinear optical effect. Condensation is also important for utilizing gold particles in other applications.[17,18]

As one gold particle is formed on one latent image speck, the characteristics of the particle and the dispersing layer depend on how the latent image specks are prepared. Increasing the density of latent image specks in a layer is effective in increasing the density of gold particles. Previously, we proposed two possible methods to increase this density.[10] The first involves increasing the number of specks on a silver halide grain; this can be achieved by enhancing the dispersion of latent image specks. The second involves increasing the number of silver halide grains in a layer; this

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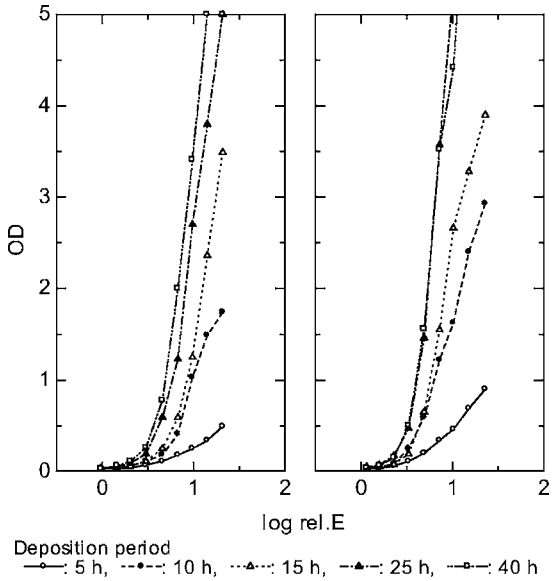

Figure 1. Photographic characteristic curves of gold particles in a gelatin layer at different immersion periods during gold deposition development. Left: high-intensity exposure for 10^{-6} s; right: low-intensity exposure for 100 s.

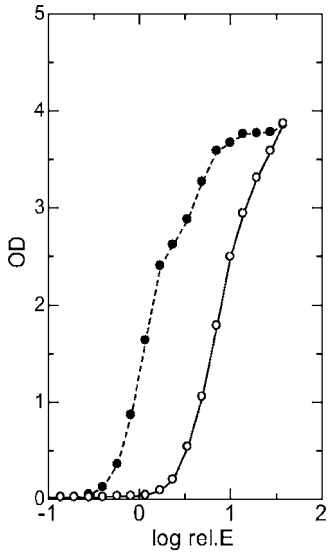

Figure 2. Photographic characteristic curves for gold deposition development and normal development. Open circles and solid line: gold deposition development, 24 h, 20 °C; closed circles and dashed line: normal development using a D72 developer diluted to 1:4, 5 min, 20 °C.

can be achieved by using an ultrafine grain emulsion. The result in our previous paper suggested that the latter technique was more effective.[10]

We then carried out observations for photographic materials that use an ultrafine grain emulsion, such as photographic plates for hologram recording, which are used for recording very fine diffraction gratings in the submicrometer range. We prepared gold particles by using a holographic plate and report the results of experiments using this plate.

EXPERIMENT

The photographic plate for hologram recording (P-5600, Konica-Minolta) was used as the sample photographic material. Ultrafine silver iodobromide grains with a diameter of ~35 nm were coated on a glass plate with high silver coverage, with the assumption that the coating was subjected to a rigorous hardening treatment in the production process.

Two types of light source were used for exposure. One was a high-intensity (HI) xenon flash lamp with an exposure period of 10^{-6} s, and the other was a low-intensity (LI) tungsten lamp with an exposure period of 100 s. The LI exposure was given using the JIS III sensitometer through a step tablet. The flash lamp for the HI exposure was set in the sensitometer, and exposure was given through the step tablet in this case as well.

The formula of the gold complex solution for gold deposition was similar to that used in earlier studies.[7–10] The concentrations of the gold ion, potassium thiocyanate, and potassium bromide were 1.0×10^{-3}, 1.2×10^{-2}, and 8.0×10^{-3} mol/l, respectively. The exposed plates were immersed in the complex solution at 20 °C for 5–40 h. We also carried out normal development using a D72 developer diluted to 1:4. The development period and temperature were 5 min and 20 °C, respectively. Fixation was carried out with a normal F-5 photographic fixer for 5 min after the completion of gold deposition or normal development.

We analyzed the characteristics of the gold particles using photographic characteristic curves, absorption spectra, and size distributions. The optical density (OD) of the plate with gold particles in the gelatin layer was measured with a densitometer through a green filter, and the characteristic curves for OD corresponding to green light were obtained. The absorption spectra of the same plate were measured with a double-beam spectrometer (Shimazu, UV-2600). The size distributions of the gold particles were obtained from observations with a transmission electron microscope (TEM) (JEOL 1200 Ex). We prepared the samples for TEM observation by applying the following suspension technique. The gelatin layer with the gold particles was scratched off from the plate and decomposed in an enzyme solution. The suspension with the gold particles was then dropped onto a grid covered with a collodion layer.

EXPERIMENTAL RESULTS

Photographic characteristic curves for gold deposition development for different immersion periods are shown in Fig. 1. The left part of the figure depicts the case of HI exposure for 10^{-6} s, while the right part depicts that of LI exposure for 100 s. Since different light sources are used for the HI and LI exposures, a comparison between the exposure values with regard to the two intensities is irrelevant. The OD increased with the immersion period, and very high contrast curves were obtained for long immersion periods.

Similar high contrast curves were also obtained in the case of normal development. The characteristic curves by gold deposition or normal development for the LI exposure are shown in Fig. 2. The sensitivity obtained by the former is

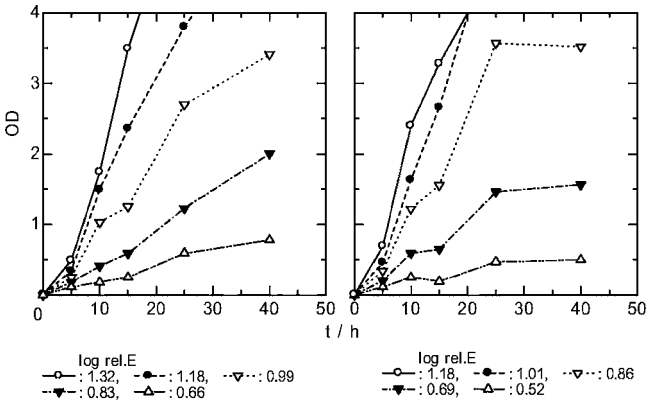

Figure 3. Increasing rates of optical density at different exposure values. Left: high-intensity exposure for 10^{-6} s; right: low-intensity exposure for 100 s.

lower—about one-fifth that obtained by the latter.

An increase in the OD of gold particles with the immersion period for the HI (left) and LI (right) exposures is shown in Fig. 3. The OD increased rapidly at higher exposure values for both intensities. Further, the OD at the HI exposure increased constantly, while the OD at the LI exposure reached saturation at longer immersion periods.

The layer with the gold particles has a red-purple color at high exposure values and a blue or blue-purple color at low exposure values. The absorption spectra clearly exhibit these characteristics. Examples of spectra of the layer with different exposure values for the HI (left) and LI (right) exposures are shown in Fig. 4. The figures at the top correspond to the high exposure values, while those at the bottom correspond to low exposure values. The spectra at high exposure values show a sharp plasmon absorption by the gold particles peaked at around 550 nm. The peak absorbance increased with the immersion period, but the spectra continued to exhibit a sharp peak at the same wavelength. On the other hand, the spectra at low exposure values became broad, and the peak shifted to a longer wavelength with the immersion period. This can be attributed to a shift from plasmon to bulk absorption with an increase in the size of gold particles. We had observed the redshift and broadening of the peak with the immersion period in the previous results as well.[7]

The tendency shown in Fig. 4 is more pronounced in Fig. 5. The relationship between the peak wavelength and peak absorbance of the layer for the HI (left) and LI (right) exposures at different exposure values are shown in Fig. 5. An increase in the peak absorbance at the high exposure value caused only a small shift in the peak wavelength. On the other hand, a large redshift of the peak occurred at the low exposure value.

The gold particles were observed with a TEM, and their diameters were measured using electron micrographs. A histogram of the diameter for each immersion period is shown in Fig. 6. The figure to the left shows the result for the HI exposure and a low exposure value, while the one to the

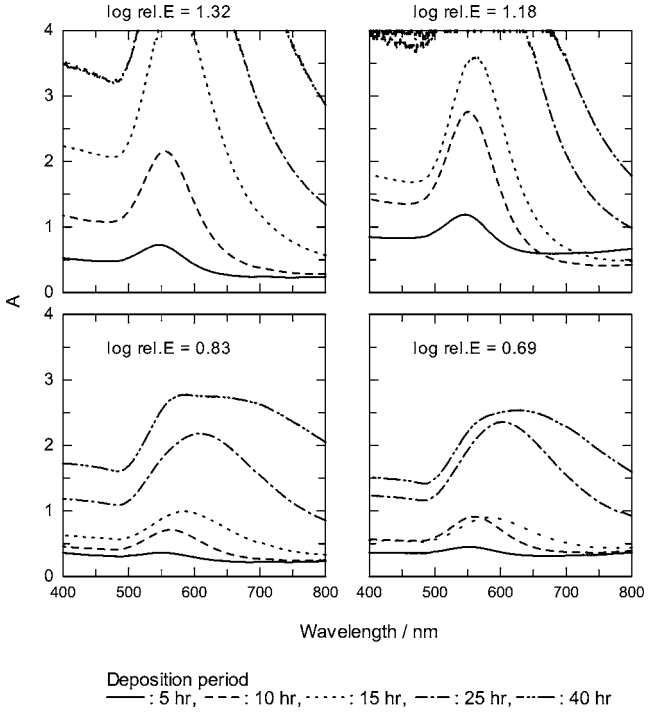

Figure 4. Absorption spectra of gold particles in a gelatin layer for different immersion periods. Figures to the left: high-intensity exposure for 10^{-6} s; top: high exposure values, bottom: low exposure values. Figures to the right: low-intensity exposure for 100 s; top: high exposure values, bottom: low exposure values. Comparison of the exposure values between the figures to the left and those to the right is irrelevant as the light sources are different.

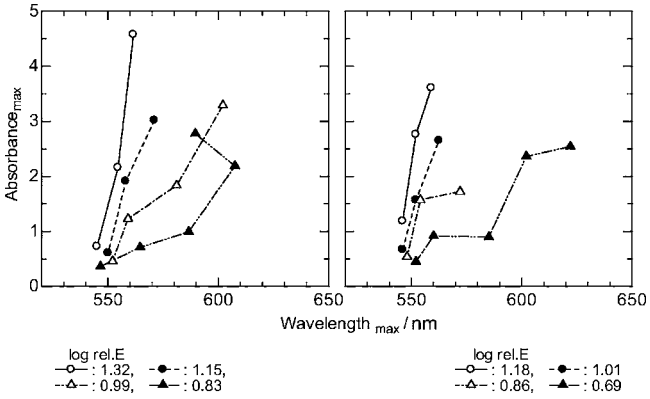

Figure 5. Relationship between peak wavelength and peak absorbance at different exposure values. Left: high-intensity exposure for 10^{-6} s; right: low-intensity exposure for 100 s.

right shows that of the LI exposure and a high exposure value. The mean diameter increased with the immersion period, thereby broadening the distribution. The histograms that take into account other conditions indicated that the growth rate of the diameter was greater in cases with the lower exposure value and HI exposure.

The growth rates at different exposure values for the HI (left) and LI (right) exposures are shown in Fig. 7. The curves were all convex to the upper site. The growth rate

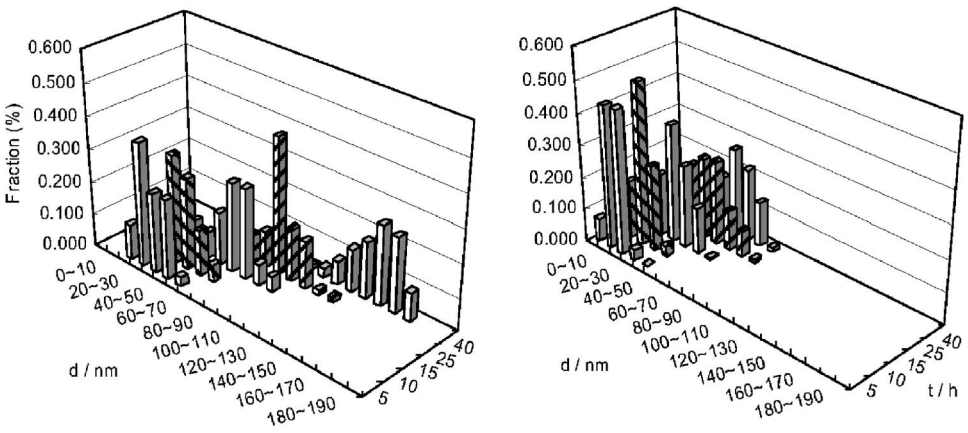

Figure 6. Size distribution of gold particles at different deposition periods. Left: high-intensity exposure for 10^{-6} s, with low exposure values of log rel.E=0.83; right: low-intensity exposure for 100 s, with high exposure values of log rel.E=1.18.

corresponding to the HI exposure was greater than that corresponding to the LI exposure, and both the rates decreased with the exposure value. These figures differ from those corresponding to an increase in the rate of OD shown in Fig. 2, where OD increased monotonously and the rate of increase of OD was greater at the higher exposure value.

Logarithmic plots of the diameter against the immersion period were straight lines, and the slopes of the lines were approximately equal to 0.5 for both the intensities and all exposure values. This suggests that the diameter d increases proportionally with the square root of the immersion period t, that is

$$d = At^{1/2}. \quad (1)$$

The curves in Fig. 7 are the best fits to Eq. (1) and the experimental results were found to fit quite well to Eq. (1). The term A in Eq. (1) represents the rate constant, and a large value of A represents a large rate of increase. The relationship between the rate constant and the exposure value is shown in Fig. 8. The value of A decreased with the exposure value at both the intensities and was greater for the HI exposure than for the LI exposure, although we could not directly compare the exposure values as the light sources were different. Moreover, the value of A might reach saturation at a higher exposure value for both the intensities.

The absorption spectra and the diameter histograms seem to suggest that the size distribution would be wider for lower exposure values. In order to verify this, the relationships between the diameter and the standard deviation are shown in Fig. 9. However, this figure reveals a result that contradicts the above expectation. The standard deviation increased with the diameter; however, it remained approximately constant regardless of the exposure value for the same diameter. The same tendency was observed at both the intensities, except that the standard deviations at the LI exposure were slightly greater than those at the HI exposure. Thus, for a particular mean diameter, the size distribution

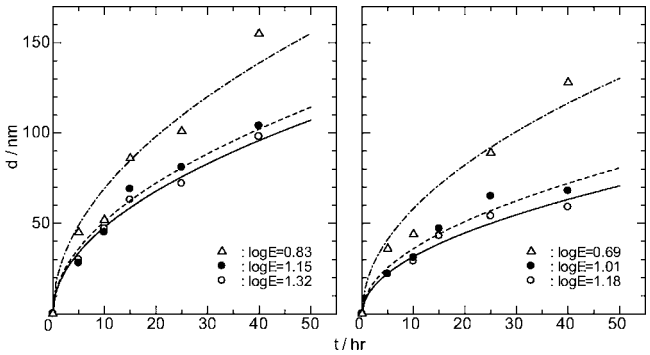

Figure 7. Growth rates of particle diameter at different exposure values. Left: high-intensity exposure for 10^{-6} s; right: low-intensity exposure for 100 s.

does not change with the exposure values; thus, the size distribution itself does not depend on the exposure value.

DISCUSSION

As expected, the ultrafine grain emulsion produced fine gold nanoparticles dispersed in a gelatin layer with high density; this resulted in a sharp and strong plasmon absorption. Since the emulsion coating has a high density of grains, a considerably larger number of latent image specks are generated in the area corresponding to a high exposure value; this results in the high density of gold particles. Therefore, an ultrafine grain emulsion is suitable to obtain a high density of gold particles.

The rapid increase in absorbance with the immersion period at high exposure values suggests an increase in the total number of gold atoms. This can be attributed to an increase in the size or number of the gold particles. However, the tendency of the gold particle to increase in size does not correlate with the increase in absorbance. The growth rate of the diameter at high exposure values was smaller than that at low exposure values, while the rate of increase of absorbance exhibited reverse characteristics. Therefore, an

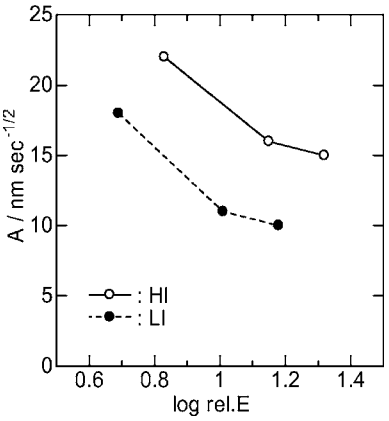

Figure 8. Relationship between exposure value and rate constant at different exposure values. Open circles and solid line: high-intensity exposure for 10^{-6} s; closed circles and dashed line: low-intensity exposure 100 s.

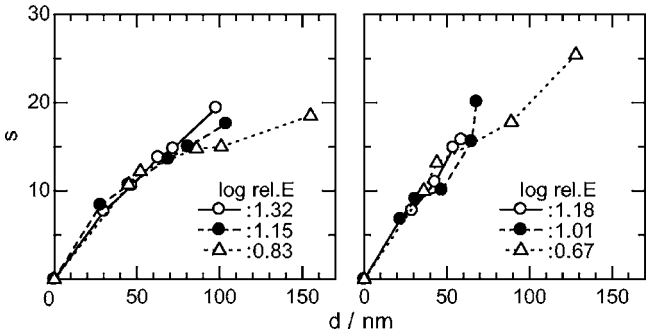

Figure 9. Relationships between particle diameter and standard deviation at different exposure values. Left: high-intensity exposure for 10^{-6} s; right: low-intensity exposure for 100 s.

increase in the number of gold particles must be the primary contributor to the increase in absorbance at high exposure values. This suggests that new particles should always be continuously formed over course of gold deposition. Unfortunately, we do not have sufficient knowledge of the rate of increase in the number of gold particles. On the other hand, the growth rate of the diameter was greater at lower exposure values. The absorption spectra simultaneously exhibited a redshift and broadening of the peak at lower exposure values; this suggested a shift from plasmon to bulk absorption of the larger gold particles. Consequently, an increase in both the number and diameter of the particles occurred at the low exposure values.

Spatial distribution of particles in a layer also affects the optical characteristics. The effect of separation distance between silver particles on this optical characteristics has been discussed.[19] Similarly, a difference in exposure value should have some influence on the optical characteristics, as the distance of latent image specks should also vary with the exposure value. However, this is a rather complicated phenomenon, and the analysis will be reported in the future.

The increase in diameter was proportional to the square root of the immersion period. A similar result had been obtained previously[7] as well and was discussed by Matejec and others[20,21] by citing an analysis of the growth rate in physical development. This analysis considered that the rate of increase in the number of silver particles m was proportional to the surface area of the particle S in the case of a reaction limited process

$$dm/dt = k_r S. \tag{2}$$

The solution of this equation suggested that the diameter d of silver particles increased proportionally with the development period.

On the other hand, the rate of increase in the number of silver particles was proportional to the diameter of the particle in the case of a diffusion limited process

$$dm/dt = k_d d. \tag{3}$$

This indicated that the diameter increased proportionally with the square root of the development period.

The analysis used for deriving Eq. (3) is based on the consideration that the chemical species pass through a thin diffusion layer around a latent image speck. This period of passage would be comparable to the normal development period of several minutes. On the other hand, gold deposition development required a longer period of several hours. It seems nearly impossible to regard the period of passage of the gold ions through the layer as several hours and thus simply apply the same analyses to the system of gold deposition. However, if the rate of increase in the number of the gold particles is proportionate to the diameter under certain conditions, a rate equation similar to Eq. (3) could be derived, which would lead to the growth rate given by Eq. (1).

The exposure value significantly affects the formation process of gold particles since the growth rate was found to decrease with the exposure value. When distributions with the same immersion periods were compared, the particle size was found to be larger and the spread of the size distribution wider at lower exposure values. However, when we compared distributions with the same diameter, the standard deviation was approximately the same regardless of the exposure value, as shown in Fig. 9. This suggests that the size distribution remains the same at constant diameter and that the exposure value affects only the growth rate. The sharp and strong plasmon absorption at high exposure values is due to the large number of small gold particles growing slowly, while the redshift and broadening at low exposure values is due to the increase in the number of larger gold particles growing rapidly.

The dependence on the exposure value is well explained insofar as the growth rate is affected by the supply of gold ions. The diffusion limited process is a case that meets this condition. At high exposure values, almost all grains have one or more latent image specks; therefore, the density of specks on the ultrafine grain emulsion is very high. As the absorbance increases continuously at high exposure values, new gold particles should be generated in succession on every latent image speck. In this case, many gold particles

compete to capture the gold ions; thus, the supply rate of gold ions should decrease, which might result in a low growth rate of gold particles. On the other hand, at low exposure values, the density is low. Therefore, sufficient number of gold ions can be supplied which would result in a larger growth rate.

The result in Fig. 2, in which the sensitivities achieved by gold deposition and normal development are compared, indicated that a higher exposure value was necessary to trigger gold deposition. Some latent image specks did not trigger gold deposition; however, they triggered normal development. Therefore, the catalytic activity of latent image specks for gold deposition depends on their size, which is similar to the case of developability in normal development. The size of the gold particles for catalytic activity in gold deposition must be larger than that in normal development.

The treatment for gold latensification is similar to that for gold deposition, except for the treatment period. In gold latensification, gold atoms are deposited even on the smaller silver specks of a latent subimage speck, thereby providing developability to these specks. However, they do not grow to gold particles by prolonged immersion. Only larger latent image specks can trigger continuous gold deposition. One possible explanation for this is that the catalytic activity of the silver atom is greater than that of the gold atom and that the incorporation of gold atoms into a silver atom cluster decreases the catalytic activity, although the mixture possesses normal developability. Based on HRS spectroscopy,[16] Goertz et al. suggested that the incorporation process of gold atoms into a silver cluster by the same disproportionation reaction may be self-limiting. Therefore, a much larger size would be necessary for the gold and gold-silver clusters to exhibit catalytic activity on continuous immersion.

Exposure intensity also seemed to affect the formation process of gold particles. The growth rate corresponding to the HI exposure was greater than that corresponding to the LI exposure. The explanation for this observation may be more complicated. One speculation is that high intensity reciprocity failure is significant, and latent image specks are not formed on every emulsion grain during the HI exposure. Some grains do not have latent image specks and this causes a decrease in the density of latent image specks, which in turn results in an increase in the growth rate.

CONCLUSION

We prepared gold particles using an ultrafine grain emulsion and successfully condensed them in a gelatin layer. We also analyzed the preparation process of gold particles. A sharp and strong plasmon absorption was observed at around 550 nm at a high exposure value, while a redshift and broadening of the absorption due to a shift to bulk absorption of metallic gold appeared at a low exposure value. In addition, the growth rate of the particle diameter decreased with the exposure value. Therefore, new gold particles were generated in succession at high exposure values; this retarded the growth of the other gold particles. The high density of latent image specks at high exposure values resulted in a competition for gold ions, which brought about a decrease in the growth rate. The particle diameter increased proportionally with the square root of the immersion period. According to a previously reported analysis on physical development, this corresponds to the case wherein the rate-determining step was diffusion limited. It is speculated that the larger growth rate corresponding to the HI exposure is due to high intensity reciprocity failure, which caused a decrease in the density of latent image specks.

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