

Original Paper

Analysis of gold and silver content in particles formed by gold deposition development

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Abstract: The content of gold and silver atoms in the particles formed by gold deposition development on silver halide grains was investigated. An increase in the amounts of gold and silver with development time was observed using atomic absorption spectroscopy, transmission electron microscopy, and energy-dispersive X-ray spectroscopy. While silver atoms formed by photolysis already existed before development, only the amount of gold increased and that of silver did not. The gold deposition development was intensified by the addition of ascorbic acid (AA) to the developer, and in this case, the amount of silver increased slightly with development time. The amount of gold increased more, but the size of the particles was smaller than the case without AA. It was suggested that the reduction of silver halide by AA proceeded, but it was still unclear that this reduction affected the acceleration of development rates or not.

Key words: Silver-salt photographic materials, Gold particles, Gold-deposition development, Photolysis of silver halide, Reduction by ascorbic acid

1. Introduction

We have reported the formation of gold particles on exposed silver-salt photographic materials by gold-deposition development¹⁻⁷. This method is a modification of the gold development process, which forms gold atoms on latent image specks composed of photolytic silver atoms⁸⁻¹⁰. In this process, gold atoms are deposited by the decomposition of the Au (I) thiocyanate complex $[\text{Au (I) (SCN)}_2^-]$, and the latent image specks act as a catalyst for this reaction. As the photolytic silver atoms remain in the gold particles, the particles should include some silver atoms. However, the amount of silver contained in the gold particles has not yet been investigated.

Because the minimum number of silver atoms in a developable latent image speck is estimated as four atoms for a normal development process¹¹, the amount of silver will be very little in this case. On the other hand, Tasaka observed latent image specks directly using an electron microscope and reported that they were several nm in size¹². In this case, percent level of silver atoms is included in a minute particle with a size of about 10 nm. Hereafter, we call the latent image specks as photolytic silver particles, because we also observed them with an electron microscope as described later and they have enough size to be called particles.

This gold deposition development is greatly accelerated when ascorbic acid (AA) is added to the developer⁷. It is considered that this is because of the reduction of gold (I) ions by AA. However, as AA is a reductant used as a devel-

oping agent^{13, 14}, it may be possible that it reduces a part of the silver halide to silver atoms directly by the catalytic action of the photolytic silver particles, similar to the normal development process. Usually, such a reduction reaction depends on the pH and proceeds faster under alkaline conditions. Photographic developers using AA is also at a high pH¹⁴. However, as developers for the gold deposition development do not contain alkaline reagents and are strongly acidic, the reduction ability of AA may be weak.

When the reduction of silver ions proceeds on a photolytic silver particle and silver atoms are deposited on it, the number of silver atoms in the particle will increase. Previously, we reported that the rate of gold deposition without AA increased with the exposure value and this could be explained as follows; photolytic silver particles formed at a larger exposure value had a larger particle size, and larger ones had a higher catalytic activity of the disproportionation reaction to deposit gold⁵. In this case, AA reacts to intensify this reaction. However, it has not yet been confirmed whether or not the reduction from silver halide to silver actually proceeds during the gold-deposition process with AA.

This solution can be obtained by analyzing the content of gold and silver in the particles. However, as the content of silver in the particles will change with the size of the particles, it is necessary to measure the content considering the particle size.

We quantitatively analyzed the content of gold and silver using atomic absorption spectroscopy. At the same time, these particles were observed using transmission electron microscopy (TEM), and the content of gold and silver was

analyzed using an energy-dispersive X-ray spectroscope (EDX) attached to the electron microscope after the measurement of particle size. Then, we analyzed the relationships between the ratio of gold to silver and the size of particles, and report the results.

2. Experimental

A silver iodobromide ultra-fine grain emulsion (diameter 40–50 nm), the same as used in our previous reports¹⁵⁾, was used for the preparation of photographic materials. It was coated on a glass plate. The plates were exposed uniformly for several microseconds to a high-intensity white light from a xenon flash lamp. The exposure was enough to ensure that almost all silver halide grains could be developed even though the emulsion was not sensitized.

The formula of the developer for gold-deposition development is shown in Table 1. In the case of the developer with AA, the AA solution was added to the developer just before development. The final concentration of AA was 2×10^{-3} mol/L and the concentration of other reagents was the same as shown in Table 1. The development temperature was 293 K. Development times without AA were 5 min–48 h, and with AA were 5–240 min. Because the development rate increases with the addition of AA to the developer⁷⁾, the development times in the latter case were shortened to obtain similar optical density after development. Every sample was fixed with a photographic fixer F-5 after development to remove the silver halide grains, and the gold particles were dispersed in the gelatin layer. The optical density of the developed plates was measured using a photographic densitometer.

The amount of gold and silver deposited on the plate was measured using atomic absorption spectroscopy (Varian, SpectrAA). We prepared the sample solutions by dissolving the particles on the plate on a certain area with aqua regia.

The particle size was measured using TEM (HITACHI, H-7650). We observed the particles on sample grids and measured their size from the electron micrographs. The sample grids for microscopy were prepared using the following suspension technique. The gelatin layer containing the particles was scraped from the plate and decomposed in an enzyme solution. The suspension containing the particles was then dropped onto a grid covered with a collodion layer and dried.

Table 1 Formula of developer for gold deposition development

| Reagent | Concentration(mol/L) |
|---|----------------------|
| KSCN | 4×10^{-3} |
| $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ | 1×10^{-3} |
| KBr | 8×10^{-3} |
| Ascorbic acid | 2×10^{-3} |

Ascorbic acid solution was added just before development to obtain this concentration.

The gelatin gel capsule method^{12,16,17)} was also used for the observation of photolytic silver particles on each silver halide grain. The exposed emulsion layer, which contains the silver halide grains, was scraped from the plate without development and dissolved in warm water. The suspension of the grains in gelatin solution was then dropped onto grids and dried. The grid was immersed in a glutaraldehyde solution to harden the gelatin layer, and then, immersed in the fixer solution to remove the silver halide. In this method, the silver particles were kept in a gelatin gel capsule formed by dissolving the silver halide grains. Consequently, the position relationship between the silver particles and a silver halide grain is defined clearly.

We analyzed the composition of the particles using an EDX attached on the TEM at the same time as the TEM observation. Because the intensity of the X-rays emitted from one particle was insufficient, we analyzed an area with a few particles, all of which were of average diameter. Analysis of the atomic ratio between gold and silver was performed using the intensity of the L-lines in the EDX spectra. We measured different areas several times and estimated the average ratio.

3. Experimental Results

The increase in the optical density of the developed plates with the development time is shown in Fig. 1. Open circles with a solid line and closed circles with a dashed line represent the sample treated with the developers without and with AA, respectively. A rapid increase and subsequent saturation in the optical density at around 60 min was observed for the sample treated with the developer with AA, whereas the density for the sample without AA shows a slow but continuous increase. This acceleration of the increasing rate with AA was the same behavior reported previously⁷⁾.

The amounts of gold and silver in the particles measured using atomic absorption spectroscopy are shown in Fig. 2

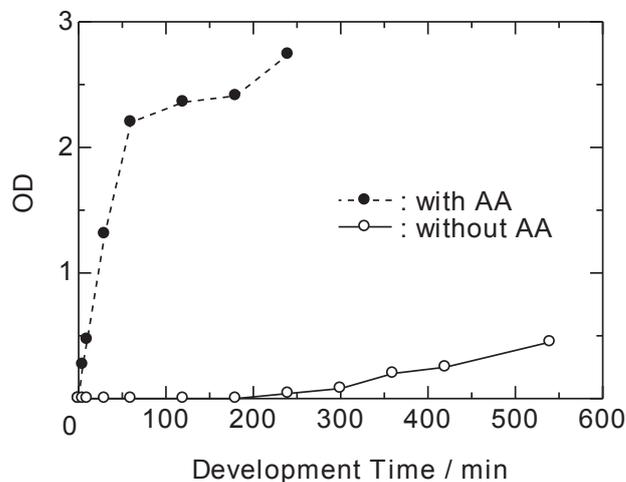


Fig. 1. The rate of increase of optical density (OD) of layers with gold particles as a function of development time.

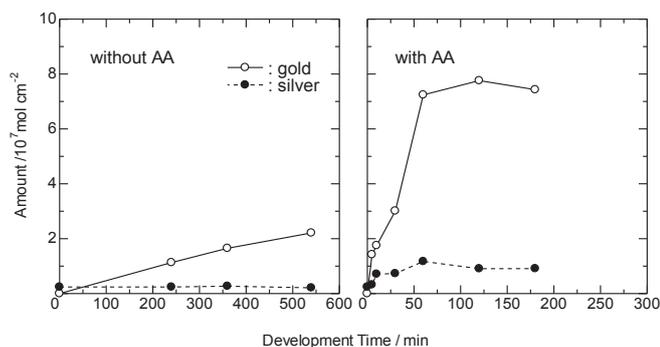


Fig. 2. The rate of increase in the amount of gold or silver in the layer as a function of development time, as measured using atomic absorption spectroscopy. Left: developer without ascorbic acid (AA), right: with AA.

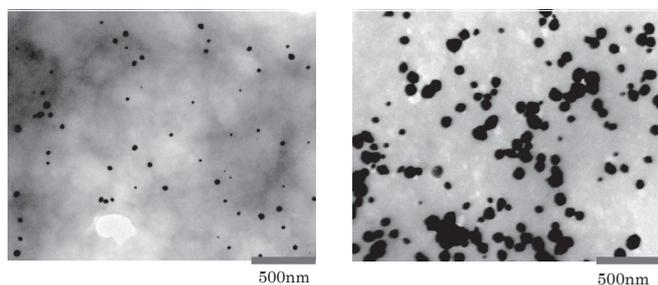


Fig. 3. Electron micrograph of gold particles formed by the developer without AA at a lower magnification. Development time: left = 4 h, right = 48 h.

for each development period. The left figure shows the result with AA and the right shows the result without AA. The amount of gold increased with the development time and this suggested the formation of gold atoms. This figure also shows an acceleration of the rate for the developers with AA, but the increase in the amount of gold saturated at around 60 min. On the other hand, this amount increased continuously for the developer without AA. A small amount of silver was observed even before the development, and this silver should be photolytic silver atoms. The amount of silver was nearly the same for all development times for the developer without AA, whereas this amount gradually increased with the development time and then saturated at around 10 min for the sample with AA.

Electron micrographs for the developed particles for several development times are shown in Fig. 3 and Fig. 4. The former shows the particles developed without AA for development times of 4 h (left) and 48 h (right) at a lower magnification. The latter shows the particles with AA for shorter development times of 10 min (left) and 180 min (right) at a higher magnification. The average size of both particles increased with the development time, although the particles had a size distribution. Particles in Fig. 3 were nearly spherical and had a smooth surface. On the other hand, the particles in Fig. 4 had an indeterminate form and a rough surface with protrusion.

Both figures show that the addition of AA accelerated the rate of size increase. This increase in size is shown in Fig. 5,

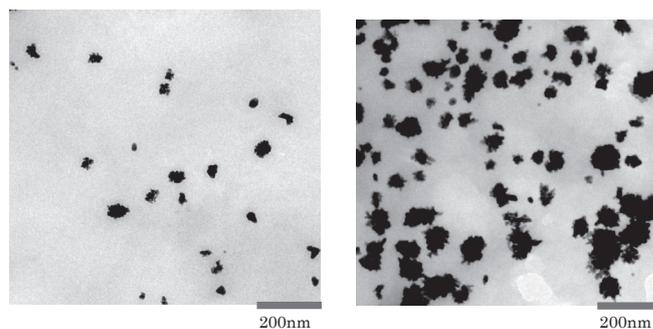


Fig. 4. Electron micrograph of gold particles formed by the developer with AA at a higher magnification. Development time: left = 10 min, right = 180 min.

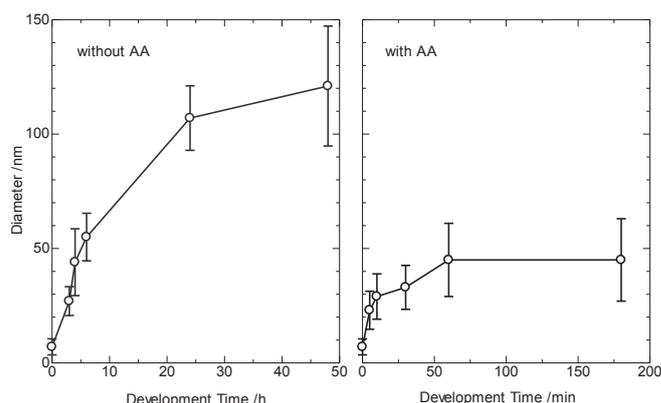


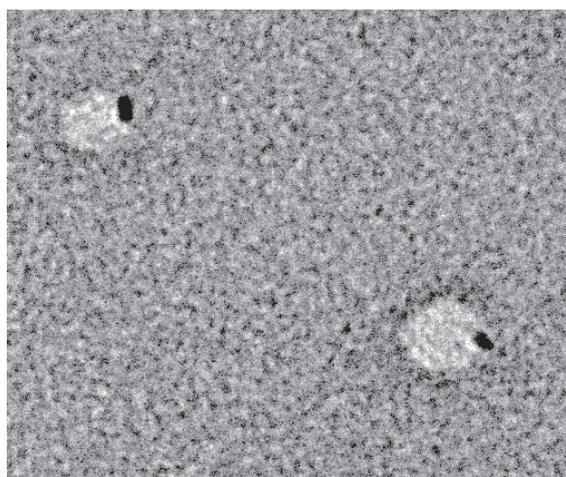
Fig. 5. Rate of increase in the diameter of gold particles as a function of development time, measured using TEM. Left: developer without ascorbic acid (AA), right: with AA. The bar on each circle shows the standard deviation of the particle size.

as shown in the scale of abscissa. The left figure for the developer without AA shows a continuous increase in size, while the right figure for the one with AA shows that the increase in size saturated at around 60 min. Therefore, the final size of the gold particles without AA is larger than that with AA, although the deposited amount of gold with AA was much larger than that without AA. This suggests that the number of deposited particles with AA was significantly more than that without AA.

Electron micrographs of the photolytic silver particles observed using the gelatin gel capsule method are shown in Fig. 6. This method can be used to observe the particles on each silver halide grain. The white circles indicate the envelope of the silver halide grains and the black points on the circle are the photolytic silver particles. The average size of the silver particle was 7 ± 3.5 nm.

EDX spectra are shown in Fig. 7. The silver L lines at 3.3 keV and gold at 9.7 keV were used for the analysis. Other peaks for carbon, oxygen, copper, and aluminum were also present, but they originated from the grid or holders supporting the sample. This analysis did not give the absolute amounts of gold and silver, but we could obtain the atomic ratio of gold and silver in each particle, which were compared with these L lines.

We also calculated the ratio of gold and silver from the



100 nm

Fig. 6. Electron micrograph of photolytic silver particles before gold-deposition development measured using the gelatin-gel capsule method. The white circles are the gelatin-gel capsules of silver halide grains and the black points are the silver particles.

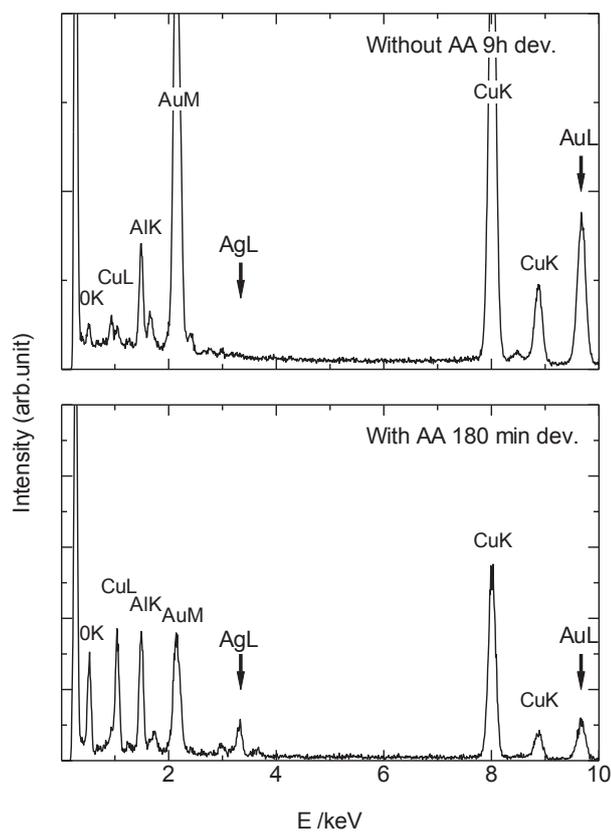


Fig. 7. EDX spectra of gold particles. Arrows indicate the peak positions of the Au L-line and Ag L-line used for analyzing the atomic ratio. Top: developer without AA, 9 h development, bottom : developer with AA, 180 min development.

atomic absorption spectroscopy results in Fig. 2. Both ratios are shown in Table 2. At a shorter development time, the ratio of silver is high, but this ratio decreases and the ratio of gold increases with the development time. At longer development time the ratio of silver with AA is higher than that without AA.

Table 2 Atomic ratio of gold and silver in the particles

| | Development time | Atomic Absorption | EDX on TEM | |
|----------------------|------------------|-------------------|------------|---------------------------|
| | | Atomic Ratio | | Average particle size /nm |
| | | Au : Ag | Au : Ag | |
| Developer without AA | 4 h | 82 : 18 | 75 : 25 | 29 |
| | 9 h | 91 : 9 | 98 : 2 | 62 |
| Developer with AA | 5 min | 82 : 18 | 72 : 28 | 23 |
| | 180 min | 89 : 11 | 87 : 13 | 45 |

4. Discussion

Both atomic absorption and EDX revealed that the amount of silver was not zero before development, and the particles prepared by the gold-deposition method included silver atoms. This silver should be the photolytic silver atoms that catalyze the gold-deposition reaction. The average size of these silver atom particles observed with TEM was about 7 nm. This value is fairly larger than the value reported by Tasaka¹²⁾. This was considered that the exposure value used here was much larger than that used by Tasaka and this caused the formation of larger silver particles.

This amount of silver for the developers without AA was kept the same along with the development time, and so these silver atoms were covered with the depositing gold atoms. On the other hand, the amount of silver increased gradually for the developer with AA. This suggests that the reduction of silver halide by AA proceeded simultaneously with gold deposition. As the formation rate of silver atoms was not so large because of the low pH and low concentration of AA in the developer, the ratio of silver atoms decreased and these silver atoms would also be covered with the gold phase. Therefore, the gold layer in the gold-layer photographs reported recently¹⁸⁻²³⁾ should be composed of an alloy with a large amount of gold and a smaller amount of silver. There is the possibility that this small amount of silver somewhat affects the property of the layer of these gold-layer photographs. Anyway, the reduction of silver halide to silver atoms occurs with AA, and the amount of silver in the gold particles increases slightly.

In many cases, the relative content of silver measured with EDX was larger than that measured using atomic absorption spectroscopy. Perhaps, the accuracy of the former was not enough and included significant noise because the EDX peak was not large enough to estimate the amount of gold and silver. These would make the values apparently larger.

The growth rate of gold particles with AA saturated with the development time. This saturation started around 60 min of development for the optical density (Fig. 1), the amount of gold (Fig. 2), and the particle diameter (Fig. 4). One possible reason is the consumption of AA or gold ions. As the amount of AA is 2 times that of gold ions, it is more

probable that the consumption of gold ions causes the saturation. On the other hand, the amount of silver with AA saturated much faster, around 10 min. As mentioned before, the silver particles were gradually covered with gold atoms, and would lose their catalytic activity for the reduction of silver halide.

Addition of AA decreased the average size of the particles, but increased their numbers. At the same time, the addition of AA increased the sensitivity, and this suggests that the photolytic silver particles of smaller size become developable⁷. Then, the number of developable specks increases and this brings about the competition of gold ions between the photolytic silver particles to form particles of smaller size.

It is not obvious that this formation of silver atoms affects the acceleration of gold deposition by AA. The formation of gold particles without AA proceeds through the disproportionation reaction of Au(I)², although the reaction rate is very slow. Addition of AA to this system accelerates the deposition of gold atoms, and there are two possibilities for this acceleration. One is the direct reduction of Au(I) by AA and the other is the intensification of the disproportionation reaction. In the former case, the photolytic silver particles or the growing gold particles catalyze the reaction between the gold ions and AA effectively.

Formation of silver atoms proceeds at the same time as gold deposition. As mention above, we reported that the rate of gold deposition increased with the exposure value, and explained that photolytic silver particles formed at a larger exposure value had a larger particle size and they had higher catalytic activity of gold deposition⁹. In the latter case, increase in the size of silver particles intensifies the disproportionation reaction.

However, it is still uncertain whether this increase in the size of silver particles intensifies the disproportionation reaction or not. This will be clarified by an analysis of the quantitative relationships between the amounts of AA and Au(I), a subject of future study.

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