

Preparation of Gold Nanoparticles Using Photographic Materials (6): Effect of Thiocyanate Ions

Ken'ichi Kuge[▲] and Akira Hasegawa[▲]

Graduate School of Advanced Integration Science, Chiba University, 1-33 Yayoi-cho, Inage-ku,
Chiba 263-8522, Japan
E-mail: kuge@faculty.chiba-u.jp

Xiang Chen

Graduate School of Science and Technology, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522,
Japan

Tomoko Sakai

Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Abstract. The authors have previously reported a method for preparing gold nanoparticles using silver halide photographic materials and gold deposition development. This process was investigated from the viewpoint of the effect of thiocyanate ion concentration. Gold particles are formed on latent image specks on the exposed silver halide grains by the disproportionation reaction of gold(I) thiocyanate complex ions. The ratio A of gold ions to thiocyanate ions in preparing the gold(I) thiocyanate complex affects gold deposition; that is, the rate of gold deposition increases when the abovementioned ratio A increases from 1:10 to 1:3. Optical measurement, atomic absorption spectroscopy, and electron microscopic observation indicate that the growth rate of gold nanoparticles does not depend on the ratio A , while the total mass of gold atoms increases with an increase in the ratio A . The mass increase is due to the increase not in size but in the number of gold particles. Excess thiocyanate ions inhibit the deposition of gold atoms on latent image specks. © 2010 Society for Imaging Science and Technology.

[DOI: 10.2352/J.ImagingSci.Technol.2010.54.1.010507]

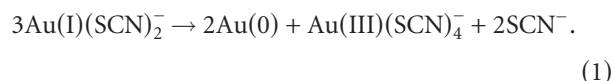
INTRODUCTION

We have previously reported a method for preparing gold particles using silver halide photographic materials and gold deposition development.^{1–5} When an exposed photographic film or plate is immersed in a gold(I) thiocyanate $[\text{Au(I)(SCN)}_2]^-$ complex solution, gold particles are deposited only on the exposed area and thus form an image. This development method has several advantages. It is well-known that gold particles have nonlinear optical effects. Further, by using this method, it is easy to fabricate image-wise patterns of gold particles for optical elements, without the coagulation of the particles. We have measured the nonlinear optical effects of gold particles in a gelatin layer.⁶ Moreover, the image formed by the deposition of gold particles has a

high resolution similar to that of an image produced by normal development.⁷ We can therefore obtain an image comprising a thin gold layer by burning the image with gold particles. We have reported the preparation of a gold-layer photograph^{8,9} and gold-layer hologram^{7,10} by using this method. Characteristics of gold particles are important to the preparation of the gold-layer image because an image with a flat gold layer is obtained from the image with monodispersed particles of a suitable size.

However, the process also has some disadvantages. One is the long period required for treatment, that is, from several hours to several tens of days.^{3,5,11} This period depends on the photographic materials, but the factors determining the period are not well understood. Therefore, an analysis of the formation of gold particles is important for the preparation of suitable gold particles in a short period.

Such gold deposition development is a photographic development process. In normal development, latent image specks work as a catalyst to form developed silver grains. Similarly, in gold deposition development, the latent image specks work as a catalyst to decompose the gold complexes and are the centers of deposition. The process is similar to gold latensification.^{12–15} The solution used in gold latensification consists of an Au(I)(SCN)_2^- complex that is formed by the reaction of gold(III) tetrachloroaurate (AuCl_4^-) and thiocyanate (SCN^-) ions.¹⁶ Previous studies have reported that gold particles form upon the immersion of exposed materials into this solution.^{17–19} It has been suggested that the deposition proceeds by the disproportionation reaction of gold(I) ions as shown in the following equation:^{2,16}



We previously investigated the preparation of a gold complex solution, particularly, the effect of the concentration of AuCl_4^- ions in producing the complex, and found an in-

[▲]IS&T Member.

Received Mar. 30, 2009; accepted for publication Jul. 28, 2009; published online Dec. 23, 2009.

1062-3701/2010/54(1)/010507/6/\$20.00.

crease in the deposition rate when the concentration was increased.⁵ However, in this case, only the concentration of AuCl_4^- ions was altered and that of SCN^- ions was not changed. We later found that the ratio of gold ions to SCN^- ions affects the deposition rate; therefore, in this study, we analyze the effect of the ratio of AuCl_4^- ions to SCN^- ions on the preparation of the complex and consider the formation process of gold particles.

EXPERIMENTAL

A commercial photographic glass plate for hologram recording (Konica Minolta, P-5600) was used as the sample photographic material. On this material, ultrafine silver iodobromide grains with a diameter of approximately 40–50 nm are coated with high silver coverage. This was the same material used in our previous study.⁵ The light source for exposure was the tungsten lamp of a JIS III sensitometer, and the exposure was provided through a step tablet for 100 s.

The method for producing the gold complex solution for gold deposition was similar to that used in earlier studies.^{1–11} The concentration of sodium tetrachloroaurate(III) (NaAu(III)Cl_4) was fixed as 5.0×10^{-4} mol/L and that of potassium thiocyanate (KSCN) was changed within the range 1.0 – 5.0×10^{-3} mol/L. Consequently, the ratio of AuCl_4^- ions to SCN^- ions changed from 1:10 to 1:2. Hereafter, we refer to the concentration ratio $\text{AuCl}_4^-:\text{SCN}^-$ as A . The concentration of potassium bromide was fixed at 8.0×10^{-3} mol/L. The exposed plates were immersed in this complex solution at 25°C for 3–24 h. Fixation was carried out with a normal F-5 photographic fixer for 5 min after gold deposition.

We investigated the characteristics of gold particles using photographic characteristic curves, absorption spectra, amount of gold atoms deposited on a plate, and size distribution of gold particles. The optical density (OD) of the plate with deposited gold particles in a gelatin layer was measured using a densitometer and green light, and photographic characteristic curves for the relationship between the OD and the exposure value were obtained. The absorption spectra for the same plate were measured with a double-beam spectrometer (Shimadzu, UV-2600). The amount of gold deposited on the plate was measured with an atomic absorption spectrometer (Varian, SpectrAA). We prepared the sample solutions by dissolving the gold particles on the plate with *aqua regia*.

The size distributions of the gold particles were determined using a transmission electron microscope (JEOL, 1200 EX). We prepared the sample grids for microscopy using the following suspension technique. The gelatin layer containing the gold particles was scraped from the plate and decomposed in an enzyme solution. The suspension containing the gold particles was then dropped onto a grid covered with collodion and dried. We observed the gold clusters on the grids and measured their size on electron micrographs in order to obtain the distribution of the cluster size.

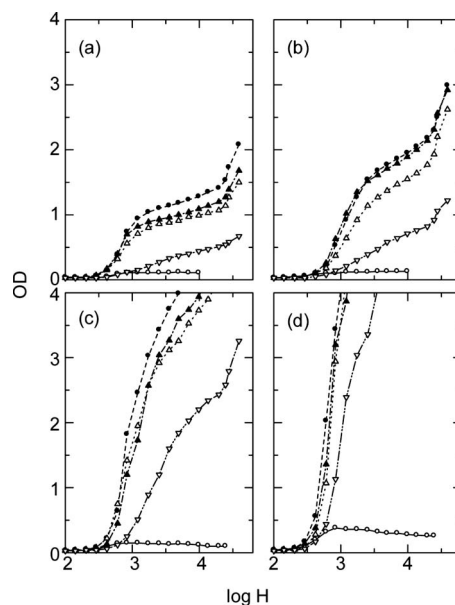


Figure 1. Photographic characteristic curves for gold deposition development in the developer with gold(III)thiocyanate complex prepared at different concentration ratios of AuCl_4^- to SCN^- . Open circles with a solid line indicate results for a ratio of 1:2, closed circles with a dashed line indicate results for a ratio of 1:3, open triangles with a dotted line indicate results for a ratio of 1:4, closed triangles with a dashed-dotted line indicate results for a ratio of 1:5, and reversed open triangles with a double-dotted-dashed line indicate results for a ratio of 1:10. Development periods are (a) 3, (b) 6, (c) 12, and (d) 24 h.

EXPERIMENTAL RESULTS

Photographic characteristic curves for gold deposition development with different development periods are shown in Figure 1. The OD because of gold particles increased with an increase in the development period; this rate of increase was affected by ratio A . The rate was maximum for $A=1:3$ and drastically low for the highest ratio $A=1:2$. The characteristic curves steepened at almost the same exposure value regardless of A . This suggests that A does not affect the photographic sensitivity of the process.

The increase in OD with an increase in the development period is shown in Figure 2 for different values of A . The rate of increase was maximum for $A=1:3$, with the rate being approximately twice that for $A=1:10$, although the rates were similar for $A=1:3$ – $1:5$. The increase in OD was almost constant for $A=1:3$ – $1:5$, while there seemed to be an induction period for the lowest ratio $A=1:10$. Gold deposition hardly proceeded when $A=1:2$.

The absorption spectra of the gold particles in the gelatin layer for different development periods are shown in Figure 3 for $A=1:3$ (top) and $1:10$ (bottom). The spectra show a sharp peak of plasmon absorption around 550–560 nm due to the presence of gold particles. The peak absorbance increased with an increase in the development period, while the spectra had similar shapes and peaked at nearly the same wavelength. The peak wavelength and the half-width (on the longer wavelength side) of the peaks compared at similar absorbance are given in Table I. Both have similar values for $A=1:3$ and $1:10$. Because both the peak wavelength and the

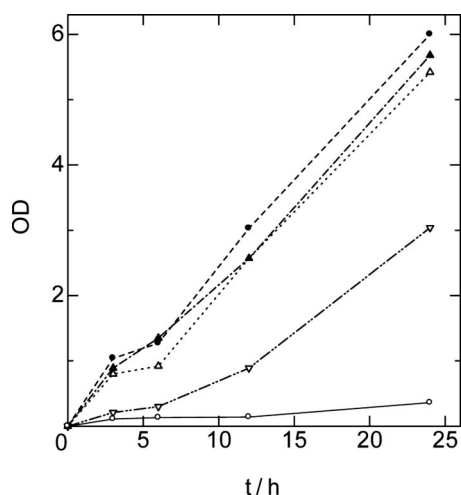


Figure 2. Increase in optical density for gold deposition development in the developer with gold(III)thiocyanate complex prepared at different concentration ratios of AuCl_4^- to SCN^- . Open circles with a solid line indicate results for a ratio of 1:2, closed circles with a dashed line indicate results for a ratio of 1:3, open triangles with a dotted line indicate results for a ratio of 1:4, closed triangles with a dashed-dotted line indicate results for a ratio of 1:5, and reversed open triangles with a double-dotted-dashed line indicate results for a ratio of 1:10.

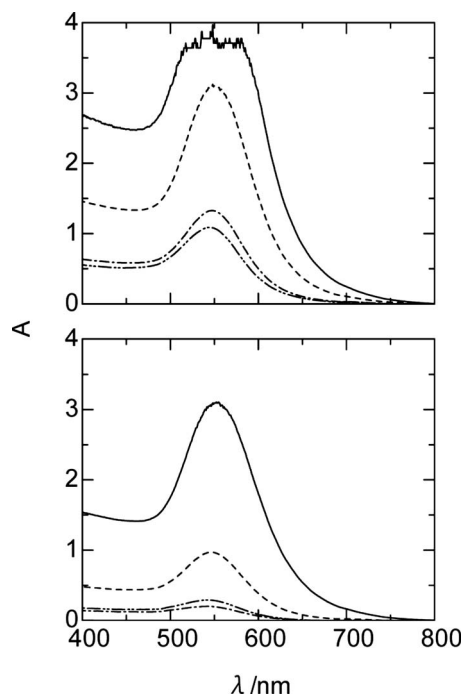


Figure 3. Absorption spectra of gold particles in a gelatin layer for gold deposition development in the developer with gold(III)thiocyanate complex prepared at concentration ratios of AuCl_4^- to SCN^- of 1:3 (top) and 1:10 (bottom). Development periods are 24 h (solid line), 12 h (dashed line), 6 h (dashed-dotted line), and 3 h (double-dotted-dashed line).

half-width are affected by the size distribution of gold particles, this result suggests that the size distributions are similar for different values of A .

The increase in the amount of gold deposited in a unit area with an increase in the development period, as measured by the atomic absorption spectroscopy, is shown in Figure 4 for $A=1:3$ and 1:10. The amount of gold deposited

Table 1. Analysis of absorption spectra.

$\text{AuCl}_4^-:\text{SCN}^-$	1:3	1:10
Development period (h)	12	24
Absorbance of the peak	3.12	3.11
Peak wavelength (nm)	548	552
Half width of the peak (nm)	51	52

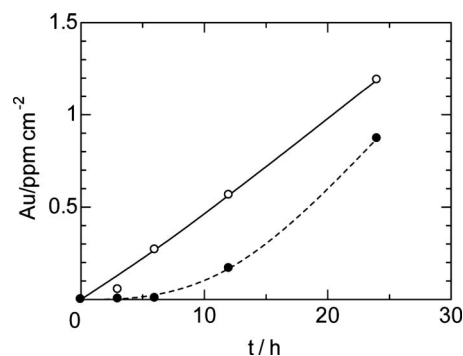


Figure 4. Increase in amount of gold deposited in a unit area measured by atomic absorption spectroscopy for gold deposition development in the developer with gold(III)thiocyanate complex prepared at concentration ratios of AuCl_4^- to SCN^- of 1:3 (open circles with a solid line) and 1:10 (closed circles with a dashed line).

for $A=1:3$ was more than that for $A=1:10$. This result suggests that the deposition rate increased with an increase in A . The rate for $A=1:10$ seems to have an induction period. Both results correspond to the increase in OD shown in Fig. 2.

Electron micrographs of gold particles developed for 24 h are shown in Figure 5 for $A=1:3$ and 1:10. The size of gold particles for $A=1:3$ seemed to be similar to or only slightly larger than that for $A=1:10$. Diameters of gold particles were determined from the electron micrographs. An increase in the mean diameter with an increase in the development period is shown in Figure 6 for $A=1:3$ and 1:10. The bars on the plotted points indicate standard deviations of the diameters. In contrast to the results presented in Figs.

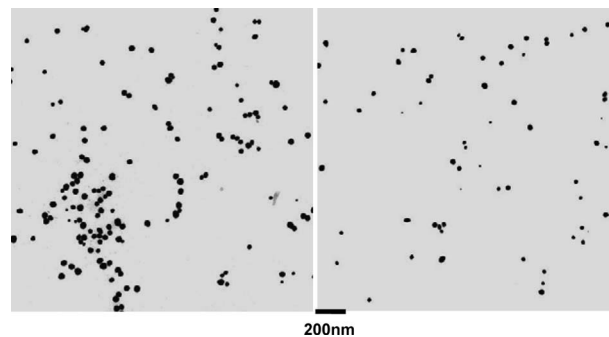


Figure 5. Electron micrographs of gold particles for gold deposition development in the developer with gold(III)thiocyanate complex prepared at concentration ratios of AuCl_4^- to SCN^- of 1:3 (left) and 1:10 (right). The development period is 24 h.

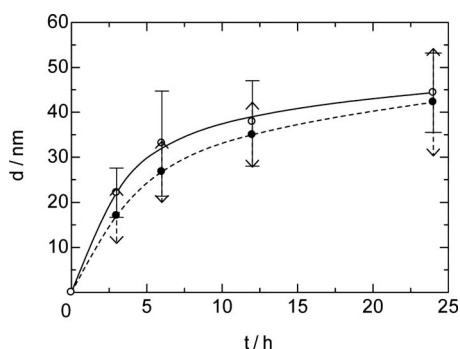


Figure 6. Growth rates of the average diameter of gold particles for gold deposition development in the developer with gold(I)thiocyanate complex prepared at concentration ratios of AuCl_4^- to SCN^- of 1:3 (open circles with a solid line) and 1:10 (closed circles with a dashed line). Bars on the circles represent standard deviations of the diameter.

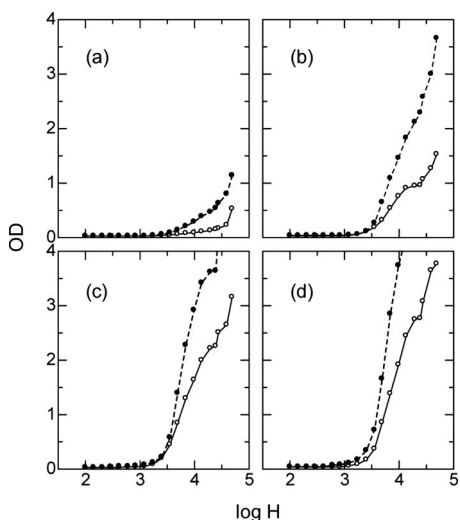


Figure 7. Photographic characteristic curves for gold deposition development after pretreatment by immersion in solution for approximately 16 h. Open circles with a solid line are results for pretreatment in KSCN solution of 5.0×10^{-3} mol/L, and closed circles with a dashed line are results for pretreatment in water (control). The developer is gold(I)thiocyanate complex solution prepared at a concentration ratio of AuCl_4^- to SCN^- of 1:4. Development periods are (a) 3, (b) 6, (c) 12, and (d) 24 h.

2 and 4, the rates of increase did not differ greatly. Fig. 6 indicates only a slightly lower growth rate for $A=1:10$ than for $A=1:3$ in the initial stage of growth. The standard deviations were also similar; this suggests that the size distributions were similar, which corresponds to the results for the absorption spectra presented in Fig. 3 and in Table I.

We pretreated exposed samples prior to the gold deposition development by immersion in a 5×10^{-3} mol/L KSCN solution for approximately 16 h or by immersion in water. Characteristic curves for the samples for different development periods are shown in Figure 7. The curves for the sample pretreated in the KSCN solution are consistently beneath the curves for the sample pretreated in water, while all curves rise at the same exposure value. The latter result suggests that sensitivity did not change with pretreatment. The rates of increase in the OD for the samples in Fig. 7 are shown in Figure 8; these also indicate a decrease in the rate

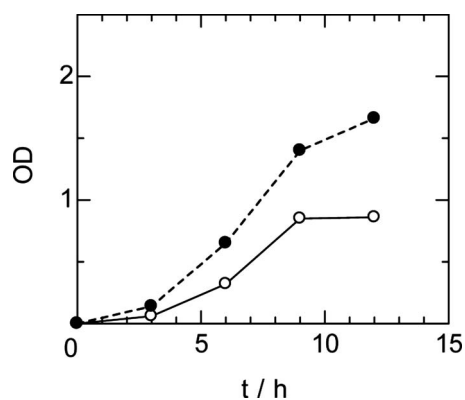


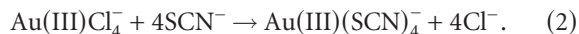
Figure 8. Increasing in optical density for gold deposition development after pretreatment by immersion in solution for approximately 16 h. Open circles with a solid line are results for pretreatment in KSCN solution of 5.0×10^{-3} mol/L, and closed circles with a dashed line are results for pretreatment in water (control). The developer is gold(I)thiocyanate complex solution prepared at a concentration ratio of AuCl_4^- to SCN^- of 1:4.

of gold deposition due to pretreatment with the KSCN solution. SCN^- ions seem to interact with latent image specks, thereby, decreasing the deposition rate. This is not a desensitization effect, in which the effect of exposure decreases, because the pretreatment does not change the steepening points in the characteristic curves.

DISCUSSION

Preparation of Au(I)(SCN)_2^- Complex

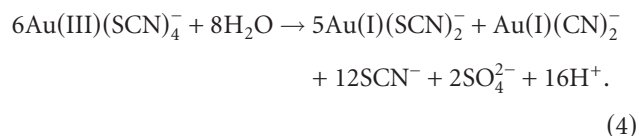
The Au(I)(SCN)_2^- complex is the main component of the gold deposition solution. Its preparation from Au(III)Cl_4^- and SCN^- ions comprises two steps. The addition of AuCl_4^- ions to the solution of SCN^- ions results in the following reaction:



The solution becomes reddish brown owing to the formation of Au(III)(SCN)_4^- just after AuCl_4^- is added. The color disappears upon mixing immediately for a warm solution and slowly for a cold solution. In this process, the Au(I)(SCN)_2^- complex ions form through the reduction of Au(III) to Au(I) by SCN^- as shown in Eq. (3),

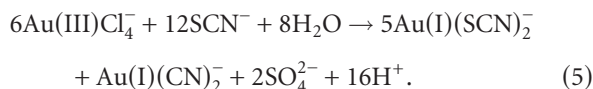


According to Eqs. (2) and (3), four SCN^- ions are required for forming one Au(I)(SCN)_2^- ion. However, Reeder and Spencer pointed out that the compound $(\text{SCN})_2$ in Eq. (3) is not stable.¹⁶ It decomposes easily and forms CN^- ions and SO_4^{2-} ions by the oxidation of sulfur. Hence, Eq. (3) can be rewritten as follows:



Reformed SCN^- ions are reused in Eq. (2). Ultimately, 6/5

AuCl_4^- ions and $12/5 \text{ SCN}^-$ ions are necessary to form one Au(I)(SCN)_2^- ion,



Therefore, the total ratio of AuCl_4^- ions to SCN^- ions to form Au(I)(SCN)_2^- is 1:2. The ratio of AuCl_4^- to SCN^- was approximately 1:10 in the formula proposed by James et al.¹² and Spencer et al.¹⁵ for gold latensification; thus, this formula had an excess of SCN^- ions. It was perhaps thought that the Au(I)(SCN)_2^- complex ions would be stabilized by the excess of SCN^- ions.

Although the minimum ratio A for forming the Au(SCN)_2^- complex is 1:2 as discussed above, gold deposition did not proceed at this ratio. Therefore, if there is no excess SCN^- ion, the Au(SCN)_2^- complex becomes unstable and gold deposition does not proceed.

Deposition of Gold Atoms

The mechanism for the deposition of gold atoms was analyzed by Reeder and Spencer¹⁶ and the present authors,² and the process seems to proceed by the disproportionation reaction of gold(I) ions as in Eq. (1). Silver clusters formed by the exposure on silver halide grains work as the catalyst, and gold atoms deposit on the exposed area to form an image. According to Eq. (1), excess thiocyanate ions interfere with this reaction. This indicates that the higher ratio A is favorable for the deposition of gold atoms as the concentration of excess SCN^- ions becomes low.

In contrast, Kawasaki and Oku found that sensitivity increased when the film was treated by gold latensification, which involves immersion in the Au(I)(SCN)_2^- solution and successive washing in potassium bromide solution or water.²⁰ As Kawasaki's Au(I)(SCN)_2^- solution contained excess SCN^- ions ($A=1:5-5000$), this increase in sensitivity may be due to the removal of the excess ions. However, this is not the removal of interference by SCN^- ions in the latensification process, which is the same process as Eq. (1). Excess ions are occluded in the emulsion layer, and it is possible that these inhibit the development.

Formation of Gold Particles

The formation of gold particles depends on A . The concentration of free SCN^- ions increases with A decreasing to 1:10. These excess ions should affect the process. The effects of A or the concentration of SCN^- ions on the process are as follows:

1. The deposition rates determined from the OD and the amount of gold atoms increased with an increase in A from 1:10 to 1:3, as shown in Figs. 2 and 4.
2. The growth rates of the average diameter of gold particles were almost the same for different values of A , as shown in Fig. 6.
3. There was no difference in the size distributions of gold particles with similar average diameters for different values of A , as shown in Table I and in Fig. 6.

4. The photographic sensitivity was not affected by A or the concentration of SCN^- ions, as shown in Figs. 1 and 7.

The size characteristics of gold particles were almost the same for different values of A , while the amount of deposited gold increased with an increase in A . This suggests that the increase in the amount of gold deposited is due to the increase not in the size but in the number of gold particles. Therefore, the ratio A affects the nucleation rate of gold particles rather than the growth rate. The relative rates of nucleation and growth on many processes can be affected by many parameters, and some processes forming nanometal particles exhibit the same characteristics.^{21,22}

The sensitivity does not change for different values of A , and this suggests that the catalytic activity of latent image specks in gold deposition is not affected by A . Some latent image specks lose their developability with excess SCN^- ions. The number of specks beginning the gold deposition is small for a small value of A ; gold deposition begins with the remaining latent image specks. The gold particles grow in the same manner and show the same size characteristics.

When the exposed film was immersed in the KSCN solution before gold deposition, the deposition rate decreased, while the sensitivity was not affected, as shown in Fig. 7. The behavior was similar to the phenomenon observed by Kawasaki and Oku as described above.²⁰

Therefore, excess SCN^- ions occluded in the emulsion layer decreases the probability of development, both normal development and gold deposition development. This decrease is more severe with a greater concentration of the excess ions.

One possible explanation for this is the adsorption of SCN^- ions. The latent image specks, on which a certain number of SCN^- ions adsorb, lose their developability as the ions cover the latent image specks and inhibit the approach of developing reagents or gold complex. There is a threshold for the number of adsorbed ions to cover latent image specks compactly. Decreasing A increases the amount of adsorbed SCN^- ions by increasing the number of excess free ions. The ratio of latent image specks that lose developability increases with decreasing A .

In contrast, excess SCN^- ions dissolve silver halide slowly to form silver thiocyanate complexes. The removal of SCN^- ions in the dissolving process decreases the number of excess ions, and so SCN^- ions desorb from the latent image specks. Then gold deposition begins, and an induction period is observed, after which the gold particles grow with similar rates.

CONCLUSION

A process for preparing gold nanoparticles on exposed silver halide photographic materials with Au(I)(SCN)_2^- complex was investigated from the viewpoint of the effect of the SCN^- ion concentration. Ratio A of AuCl_4^- ions to SCN^- ions in the preparation of the complex affected the deposition of gold atoms:

1. The deposition rates determined from the OD and the amount of gold atoms increased with an increase in A from 1:10 to 1:3.
2. The growth rates of the average diameter of gold particles were almost the same for different values of A .
3. There was no difference in the size distributions of gold particles with similar average diameters for different values of A .
4. There was no difference in the photographic sensitivity for different values of A .

These results indicate that the growth rates of individual gold nanoparticles did not depend on A , while the total mass of gold atoms increased. The mass increase was due to an increase not in the size but in the number of gold particles. Excess SCN^- ions should decrease the probability of deposition of gold atoms on a latent image speck, although the deposition begins with the remaining latent image specks in the same growth rate.

ACKNOWLEDGMENT

This work was supported by the industry's doctor science foundation (BK2009582) of Jiangsu, China.

REFERENCES

- ¹ K. Kuge, M. Arisawa, N. Aoki, and A. Hasegawa, *Jpn. J. Appl. Phys.* **39**, 6550 (2000).
- ² K. Kuge, K. Kimijima, M. Arisawa, N. Aoki, and A. Hasegawa, *J. Soc. Photogr. Sci. Technol. Jpn.* **64**, 242 (2001).
- ³ K. Kuge, I. Suzuki, N. Aoki, and A. Hasegawa, *J. Soc. Photogr. Sci. Technol. Jpn.* **65**, 536 (2002).
- ⁴ K. Kuge, M. Arisawa, N. Aoki, and A. Hasegawa, *Imaging Sci. J.* **52**, 176 (2004).
- ⁵ K. Kuge, N. Aoki, S. Saito, O. Hikosaka, and A. Hasegawa, *J. Imaging Sci. Technol.* **51**, 96 (2007).
- ⁶ K. Kuge, S. Saito, O. Hikosaka, T. Hirose, T. Omatsu, and A. Hasegawa, *Particles 2003* (particles.org, Toronto, ON, 2003), p. 103.
- ⁷ K. Kuge, N. Aoki, Y. Goto, T. Omatsu, and A. Hasegawa, *J. Appl. Phys.* **100**, 013102 (2006).
- ⁸ K. Kuge, Y. Goto, T. Nakao, Y. Hikosaka, T. Sakai, and A. Hasegawa, *J. Soc. Photogr. Sci. Technol. Jpn.* **67**, 490 (2004).
- ⁹ K. Kuge, Y. Nakanishi, and T. Sakai, *J. Soc. Photogr. Sci. Technol. Jpn.* **71**, 86 (2008).
- ¹⁰ K. Kuge, M. Ooki, T. Kobayashi, T. Sakai, T. Nakao, and A. Hasegawa, *J. Soc. Photogr. Sci. Technol. Jpn.* **69**, 276 (2006).
- ¹¹ K. Kuge, S. Iwakiri, Y. Endo, N. Yasuda, C. Fukushima, M. Kimura, H. Shibuya, H. Kumagai, and A. Hasegawa, *Radiat. Meas.* **42**, 1335 (2007).
- ¹² T. H. James, W. Vanselow, and F. R. Quirk, *Photogr. Soc. Am.* **14**, 349 (1948).
- ¹³ T. H. James, *The Theory Of The Photographic Process*, 4th edition (Macmillan, New York, 1977), Chap. 14–IE, p. 428.
- ¹⁴ T. Tani, *Photographic Sensitivity* (Oxford University Press, Oxford, UK, 1995), Chap. 6–3, p. 176.
- ¹⁵ H. E. Spencer, C. A. DeCann, and R. T. McCleary, *J. Imaging Sci.* **31**, 8 (1987).
- ¹⁶ A. C. Reeder and H. E. Spencer, *J. Imaging Sci.* **31**, 126 (1987).
- ¹⁷ T. H. James, *J. Colloid Sci.* **3**, 447 (1948).
- ¹⁸ D. C. Birch, G. C. Farnell, and R. B. Flint, *J. Photogr. Sci.* **23**, 249 (1975).
- ¹⁹ S. Jablonka, C. Mora, P. M. Nowak, and A. Zaleski, *J. Inf. Rec. Mater.* **23**, 249 (1996).
- ²⁰ M. Kawasaki and Y. Oku, *J. Imaging Sci. Technol.* **42**, 409 (1998).
- ²¹ Z.-Y. Huang, G. Mills, and B. Hajek, *J. Phys. Chem.* **97**, 11542 (1993).
- ²² X. Zhai and S. Efrima, *J. Phys. Chem.* **100**, 1779 (1996).