Silver Clusters of Photographic Interest: Observation and Analysis of Latent Image and Fog Centers

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Abstract

Latent image centers formed at shoulders and plateaus of characteristic curves and fog centers formed by excessive reduction sensitization of cubic silver bromide grains with average circular diameter of 0.2μm were directly observed in their gelatinate shells by an electron microscope. The number and size distribution of those centers provided useful knowledge for the study of the growth mechanism of silver clusters formed on silver halide grains.

The presence of a concentration center acting as a strong electron trap and many reduction sensitization centers enabled the growth of latent image centers with efficiency of unity. The concentration principle strongly worked for silver cluster formation by light, which gave only one latent image center per grain, whereas it did not work for silver cluster formation by reduction of silver halides, which gave many fog centers per grain. The nucleation and growth of silver clusters by reduction of silver halides was explained by the proposed mechanism, according to which dimers of silver atoms were formed at a time with contribution of neither a free electron nor a single silver atom, and then coagulated to give large clusters.

The application of Smoluchouski's equation to the size distribution of fog centers indicated that the growth of silver clusters by reduction was not brought about by successive coagulation, but by rather abrupt coagulation of dimers of silver atoms after the saturation of surface kink sites by dimers of silver atoms.

Introduction

Silver clusters play important roles in photographic processes.[1] It has been demonstrated that there are two kinds of silver clusters on silver halide grains. One of them acts as a trap for a photoelectron, growing under illumination, and is called a P center. The other acts as a trap for a positive hole, disappearing under illumination, and is called an R center. In this series of papers,[2-6] the present authors characterized those centers on fine silver halide grains in emulsions formed during digestion for their reduction sensitization by means of various experiments to get their sensitivity, fog density, and diffuse reflectance spectra, photoconductivity of the grains, and oxidation potential of the centers.

Much attention has ever been paid on the smallest latent image centers, and R centers and P centers of reduction sensitization.[1] It is considered that the smallest latent image center is composed of three atoms in gold-sensitized emulsions and four to five atoms in sulfur-sensitized emulsions, and that both R centers and P centers of reduction sensitization are dimers of silver atoms. It is obvious that they are too small to be observed by an electron microscope. It seems that an attempt to directly observe latent image centers has been hardly made because of the above-stated situation.

It was demonstrated in the former paper[7] that latent image centers actually formed in tonal regions of characteristic curves were much larger than the smallest latent image centers. On the basis of the above-stated result, an attempt to directly observe latent image centers and fog centers formed during excessive reduction sensitization by electron microscopy was made in this paper in order to get new knowledge for the study of growth of silver clusters on silver halide grains.

Experiments

The emulsion used was composed of cubic silver bromide grains with average circular diameter of 0.2 μm, and prepared by means of a controlled double jet method.[8,9] The pH value of the reaction solution was kept to be 2 in order to minimize the formation of reduction sensitization centers during precipitation. Reduction sensitization was carried out by digesting at 60°C for 60 min the above-stated emulsion, to which an aqueous solution of dimethylamineborane (DMAB) was added. The above-stated emulsions were coated on TAC film base, dried, and used for various experiments.

The sensitometric experiments were carried out according to the methods employed in this series of papers[2-7]. Coated emulsion layers were exposed to a Xenon lamp or a halogen lamp through an interference filter transmitting light of 419.4 nm. Quantum sensitivity of the above-stated emulsions was measured according to the method described in the literature.[10] In order to directly observe latent image centers and fog centers formed on silver bromide grains, an electron microscope Model JEM-2000FX-II (JEOL, Tokyo, Japan) was applied to gelatinate shells, which were prepared by the method described in the former papers.[6,11,12] Latent image centers and fog centers, which were larger than 15 A in diameter, could be observed in the shells by an electron microscope.

Results and Discussions

Observation and Analysis of Latent Image Centers Formed on Fine Silver Bromide Grains

Latent image centers were observed with exposure to give shoulders and plateaus of characteristic curves, and only one latent image center was observed on each grain regardless of exposure. Size in number of silver atoms of latent image centers thus observed was measured and compared with number of absorbed photons per grain and quantum sensitivity for the study of their growth process.

The quantum yield of the growth of latent image centers (η_G) was estimated by comparing between average number of silver atoms per latent image center and that of absorbed photons per grain. The quantum yield of the formation of the smallest latent image center (η_N) was estimated on the basis of quantum sensitivity and size of the smallest latent image center, which was assumed to be four atoms.

The values of η_N were 0.001 for an unsensitized emulsion, and 0.03 for a reduction-sensitized one. It was found that η_G was larger than η_N for both unsensitized and reduction-sensitized emulsions. This result indicated that concentration centers acting as strong electron traps (i.e., latent image centers) was effective for achieving high value of η_G.

The value of η_G for a reduction-sensitized emulsion was nearly unity in the presence of reduction sensitization centers, and became to be less than unity when reduction sensitization centers were photobleached during exposure. It was found that the necessary condition for η_G of unity was the combination of a concentration center with reduction sensitization centers on a grain.

Observation and Analysis of Fog Centers Formed by Excessive Reduction Sensitization.

Fog centers were observed by electron microscopy on excessively reduction-sensitized emulsion grains, all of which bore fog centers. The number and size distribution of fog centers were measured to give the number of silver atoms formed and the quantum yield of reduction of silver bromide grains by DMAB under the assumption that a DMAB molecule has the ability to reduce six silver ions.[13,14] The results are shown in **Table**.

The quantum yield was thus estimated to be roughly unity on the basis of the observation that the number of silver atoms formed was roughly equal to that of silver atoms to be given by DMAB added.

Table. Number and size of fog centers formed by excessive reduction sensitization of cubic silver bromide grains (circular diameter; 0.2μm) with DMAB, which was assumed to reduce six silver ions per molecule.[13,14]

Amount of DMAB Sites for fog centers Number of fog centers Number of Ag atoms	to form 7,100 Ag/grain corners 1. 4/grain 1,200/center 11,000/grain
Amount of DMAB Sites for fog centers Number of fog centers Number of Ag atoms	to form 29,000 Ag/grain corners + edges 31/grain 600/center 19,000/grain
Amount of DMAB Sites for fog centers Number of fog centers Number of Ag atoms	to form 120,000Ag/grain corners + edges 80/grain 1,300/center 100,000/grain
Amount of DMAB Sites for fog centers Number of fog centers Number of Ag atoms	to form 460,000 Ag/grain corners + edges 165/grain 3,300/center 550,000/grain

It was also found that the amounts of DMAB to give 7000, 29000, 120000, and 460000 silver atoms per grain formed 9, 31, 80, and 165 fog centers per grain, respectively. Namely, more than one fog centers were formed on each grain, and the number of fog centers increased with increasing the amount of DMAB. Fog centers appeared at corners of a grain, and then on edges of a grain with increasing the amount of DMAB. It is noted that only one latent image center was formed on each grain regardless of exposure.

The formation of only one latent image center per grain regardless of exposure was brought about by the concentration principle,[1] which took place for the formation of a silver cluster (i.e., a latent image center) on a silver halide grain under illumination. It is therefore considered that the formation of many fog centers per grain in excessively reduction-sensitized emulsion resulted from the absence of the concentration principle in the case of the formation of silver clusters by reduction of silver halide grains.

Movement of free electrons and interstitial silver ions in a silver halide grain made it possible for the concentration principle to take place for the formation of a latent image center. It is noted that a single silver atom is unstable and dissociates to give a free electron and an interstitial silver ion within several seconds.[1] It is therefore considered that neither a free electron nor a single silver atom took part in the formation of silver clusters by reduction of silver halide grains.

It has been proposed that dimers of silver atoms were formed at a time as a result of reduction of a silver halide grain, migrate on the grain surface, and coagulate to give larger aggregates of silver atoms.[4,6]

The growth process of fog centers was analyzed by applying the Smoluchowski's equation for successive coagulation to their size distribution. It was found that no fog center was observed by an electron microscope on the grains in emulsions, which were digested in the presence of the amount of DMAB, with which considerable number of fog centers should be observed by an electron microscope according to the successive coagulation. The result thus supported the growth mechanism of silver clusters, according to which dimers of silver atoms were especially stable and preferentially formed in abundance at surface kink sites to act as reduction sensitization centers, and large silver clusters such as fog centers were formed after the saturation of the sites by dimers of silver atoms.

Conclusion

It was found that silver clusters such as latent image centers formed with exposure to give shoulders and plateaus of characteristic curves and fog centers formed by excessive reduction sensitization of fine silver halide grains could be directly observed by electron microscopy. The number and size distribution of those clusters provided useful knowledge for the study of the growth mechanism of silver clusters and an evidence to support the proposed mechanisms for the formation and growth of silver cluster by reduction of silver halide grains in contrast to the mechanism of latent image formation.

References

1. Tadaaki Tani, Photographic Sensitivity: Theory and Mechanisms, Oxford University Press, New York, 1995, Chapter 4.
2. T. Tani, M. Murofushi, *J. Imaging Sci. Technol*., **38**, 1(1994).
3. T. Tani, *J. Imaging Sci. Technol.*, **41,** 577(1997).
4. T. Tani, N. Muro, A. Matsunaga, *J. Imaging Sci. Technol.*, **42,** 349(1998).
5. T. Tani, *J. Imaging Sci. Technol.*, **42,** 402(1998).
6. T. Tani, T. Tomoki, M. Murofushi, K. Hosoi, A. Hirano, *The Imaging Sci. J.*, in print.
7. T. Tani, M. Murofushi, "Silver Microclusters on Silver Halide Grains as Latent Image and Reduction Sensitization Centers II. Size, Absorption Spectra and Developability", in the preprint book of *ICPS'94 and IS&T's 47th Annual Conference* (May, 1994, Rochester, NY), Vol. 1, pp.342-343.
8. C. R. Berry, D. C. Skillman, *Photogr. Sci. Eng*., **6**, 159(1962).
9. E. Klein, E. Moisar, *Photogr. Wiss*., **11,** 3(1962).
10. R. K. Hailstone, N. B. Liebert, M. Levy, R. T. McCleary, S. R. Gilolmo, D. L. Jeanmaire, C. R. Boda, *J. Imaging Sci.*, **32,** 113(1988).
11. T. Tani, *J. Imaging Sci. Technol.*, **39,** 386(1995).
12. T. Tani, *J. Imaging Sci. Technol.*, **42,** 135(1998).
13. I. Ohno, O. Wakabayashi, S. Haruyama, *Denki Kagaku*, **53,** 196(1986).
14. J. E. A. M. Van Den Meerakker, *J. Appl. Electrochem.*, **11,** 395(1981).