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Observation and Analysis of Sulfur Sensitization Centers Formed on Octahedral Silver Bromide Grains.

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Abstract

We observed and analyzed all the sulfur sensitization centers formed on octahedral silver bromide grains in emulsions by means of an amplification treatment with a special physical developer. By this treatment, silver clusters were deposited on the centers in the absence of the concentration principle. The sensitivity of the sulfur-sensitized silver bromide emulsions and the number of the observed centers increased and reached their maxima with increasing the amount of a sulfur sensitizer. The number of the centers on the grains with the maximum sensitivity was as many as 3200/μm^2, didn't increase with further increasing the amount of the sensitizer, and was the same as that of the fog centers formed with excessive amount of the sensitizer. By comparing the number of the observed centers with the amount of silver sulfide formed by the sulfur sensitization, it was concluded that each sulfur sensitization center contained two sulfide ions on the grains with the maximum sensitivity. This result indicated that the sulfur sensitization centers were dimers of silver sulfide, supporting the proposal by Keevert and Gokhale[1], Kanzaki and Tadakuma[2], and Tani[3].

Introduction

Sulfur sensitization is indispensable to highly sensitive photographic silver halide emulsion. Sulfur sensitization is achieved by the following steps, (a) adsorption of a sulfur sensitizer on silver halide grain surface, (b) formation of silver sulfide, and (c) its rearrangement[4]. It is considered that sulfur senzitization centers are composed of aggregates of silver sulfide. Keevert and Gokhale[1] estimated the number of sulfur sensitization centers on the basis of analysis of their rearrangement process with Smoluchowski's aggregation equation, and proposed that sulfur sensitization centers were composed of dimers of silver sulfide, which were as many as 1000/μm^2 on the surface of cubic silver chlorobromide grains. Kanzaki and Tadakuma[2] studied sulfur sensitization centers by means of luminescence-modulation spectroscopy, and proposed that they were composed of dimers of silver sulfide. Tadakuma, Yoshida and Kanzaki[5] estimated that there were 2800 centers/μm^2 on the surface of cubic silver bromide grains. Tani[3] proposed that sulfur sensitization centers were composed of dimers of silver sulfide in solid solution with silver halide grain surface, and fog centers were clusters of silver sulfide themselves.

Many investigators have ever tried to observe directly sulfur sensitization centers formed on silver halide grain surface by an electron microscope. For example, Farnell, Flint and Birch[6] observed silver sulfide centers of as small as 3nm, and Aznarez[7] observed those of 2nm. In the light of the recent results as stated above, it is considered that those centers were fog centers composed of silver sulfide clusters formed on silver halide grain surface with excessive sulfur sensitization.

We considered it very difficult to directly observe all the sulfur sensitization centers, since they are composed of dimers of silver sulfide in solid solution with silver halide grain surface. In this paper, we could successfully observe the centers by means of an amplification treatment with a special physical developer to deposit silver clusters on the centers in the absence of the concentration principle.

Experimental

An emulsion containing octahedral silver bromide grains with equivalent circular diameter of 0.2μm was used in this study. The emulsion contained silver bromide of 63g and gelatin of 70g /Kg. Sulfur sensitization was carried out by digesting the above-stated emulsion in the presence of sodium thiosulfate as a sensitizer for 60 min at 60℃. The primitive and sulfur-sensitized silver bromide emulsions were coated on a TAC film base to prepare film samples with silver bromide of 2.1g and gelatin of 6g /m^2. Each film sample was exposed for 10 sec to a tungsten lamp through a continuous wedge, and developed for 10 min at 20℃ by use of a MAA-1 surface developer to get its sensitivity.

Photoconductivity of silver bromide grains in each film sample was measured at -100℃ by means of a 9GHz microwave photoconductivity apparatus[8] with third harmonic generation 355nm of a pulsed Nd:YAG laser model DCR-11 made by Spectra Physics Corp. as a light source, and given by its maximum signal intensity.

The following Solutions A and B were prepared for an amplification treatment of the sulfur sensitization centers .

Solution A	sodium sulfite	180g
	silver nitrate	10g
	water	1000*ml*
Solution B	sodium sulfite	20g
	compound-1	20g
	water	1000*ml*

Compound-1 was 4-Amino-N-ethyl-N-(β -hydroxyethyl) aniline sulfate. Before use, Solutions A and B were diluted to 10000-fold with water. Diluted Solution A of 25*ml* and diluted Solution B of 5*ml* were added to melted emulsion of 0.1g. The mixed solution was stirred for 6 hrs at room temperature in the dark. The solution of 5 μl was set on a Ni mesh covered with collodion and carbon membranes, and dried. Silver bromide grains on the mesh were fixed by the following Solution C for 10sec at room temperature.

Solution C	0.25*M* lithium thiosulfate(aq.)	125*ml*
	sodium sulfite	0.3g
	glacial acetic acid	0.5*ml*
	potassium alum	0.6g

Gelatin shells of silver bromide grains were observed in a transmission electron microscope model JEM-1200 made by JEOL.

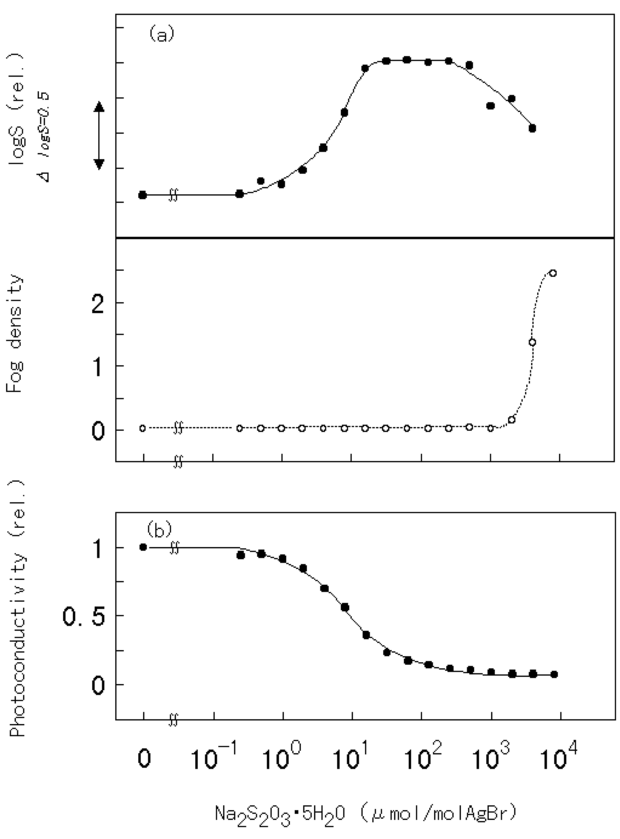

Fig.1. Photographic sensitivity S and fog density (a),and photoconductivity (b) of octahedral silver bromide grains in emulsion as a function of the amount of sodium thiosulfate used for sulfur sensitization.

Results

Fig.1(a) shows photographic sensitivity (S) and fog density of octahedral silver bromide grains as a function of the amount of sodium thiosulfate used as a sulfur sensitizer. The sensitivity increased with increasing the amount of the sensitizer and reached its maximum with the sensitizer of about 16 μ mol/mol AgBr. Fog appeared with the sensitizer beyond 2mmol/mol AgBr.

Fig.1(b) shows the microwave photoconductivity of the sulfur-sensitized silver bromide grains. The decrease in the photoconductivity and the increase in the sensitivity took place in concert with increasing the amount of the sensitizer, indicating the formation of sulfur sensitization centers, which trap photoelectrons to enhance the latent image formation.

Fig.2(a) shows an electron micrograph of gelatin shells of sulfur-sensitized silver bromide grains with sodium thiosulfate of 16 μ mol/mol AgBr without our amplification treatment. No center was observed in the shells.

Fig.2(b) shows an electron micrograh of the same grains as those in Fig.2(a), except the application of the amplification treatment to the grains. About 400 fine centers per grain were clearly observed, and the number of the centers were estimated to be as many as 3200 per μm^2 of the grain surface.

Fig.3 summarizes the number of the centers observed with and without our amplification treatment as a function of the amount of the sulfur sensitizer. The number of the centers observed by means of the amplification treatment increased as increasing the amount of the sulfur sensitizer, and was saturated at 3200/ μm^2 with the amount of the sensitizer to give the maximum sensitivity. The saturated number was the same as that of the fog centers formed with excessive amount of the sensitizer. These results are also shown in Table 1. By varying the solution concentration and the processing time of the amplification treatment, we obtained the same results as those shown in Fig.3 and Table 1.

It was found that 80% of sodium thiosulfate labeled with radio-active ^{35}S was decomposed to form silver sulfide on the silver bromide emulsion grains when digested for 60min at 60℃. Under the assumption that all the silver sulfide centers formed on the silver bromide grains surface could be observed according to the above-stated method, the number of sulfur ions contained in each observed center was estimated and shown in Table 1. It was concluded that each sulfur sensitization center on the grains with the maximum sensitivity had two sulfide ions.

Fig.4 shows an electron micrograph of gelatin shells of sulfur-sensitized silver bromide grains with 16 μ mol/mol AgBr of sodium thiosulfate, which were exposed for 30 sec and treated by the same method as shown in Fig.2(b). The one large center observed on each grain was ascribed to a latent image center. Many small centers observed were ascribed to sulfur sensitization centers, and their number was equivalent to that on the unexposed grains as shown in Fig.2 (b).

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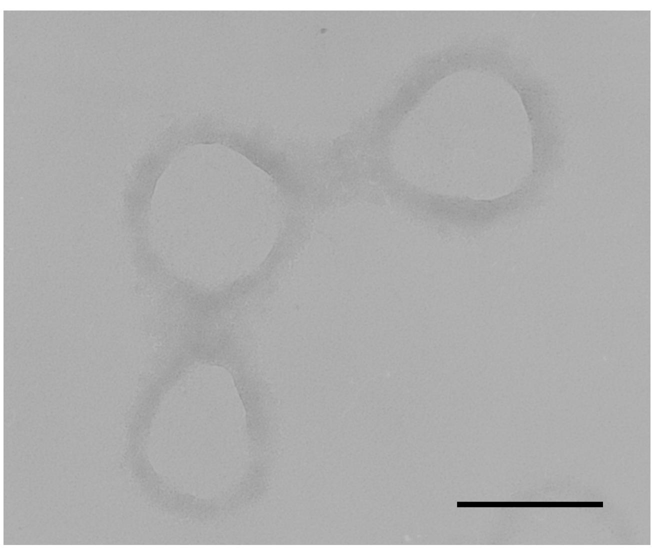
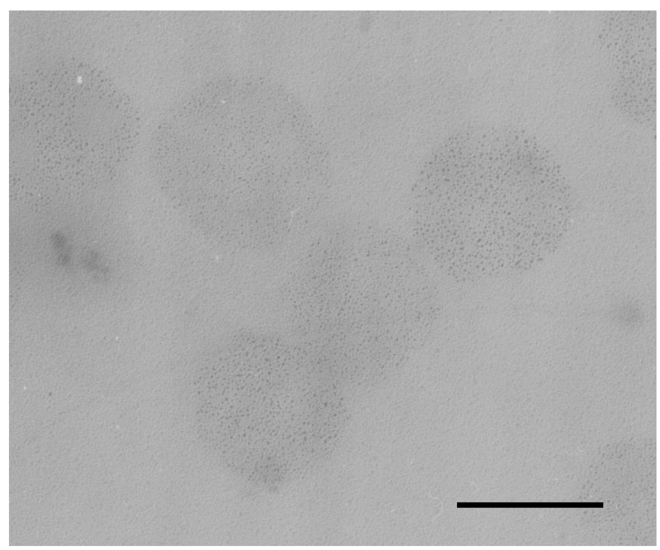
Table 1. The numbers of sulfur sensitization centers and sulfide ions /center in the presence (left) and the absence of (right) of our amplification treatment. .

	In the presence of the amplification treatment		In the absence of the amplification treatment	
$Na_2S_2O_3 \cdot 5H_2O$ (μ mol/molAgBr)	Observed Centers (/ μm^2)	Sulfide Ions per Center	Observed Centers (/ μm^2)	Sulfide Ions per Center
0	0	0	0	0
0.25	0	0		
1	420± 120	1.4		
2	910± 160	1.3		
4	1300± 300	1.7		
8	1700± 500	2.6		
16	3300± 700	2.7	0	0
32	3200± 400	5.6		
64	3000± 600	12		
130	3200± 400	23	0	0
260			0	0
510	3000± 300	95		
2000	3100± 500	370	3400± 700	340
4100			3100± 300	740
8200	3000± 300	1500	3200± 400	1400



(a)



(b)

Fig.2 Electron micrographs of gelatin shells of octahedral silver bromide grains in an emulsion, which was sulfur-sensitized with sodium thiosulfate of 16 μmol/mol AgBr, being prepared in the absence (a) and the presence (b) of our amplification treatment. The length of the bars in this figure refer to 0.2 μm.

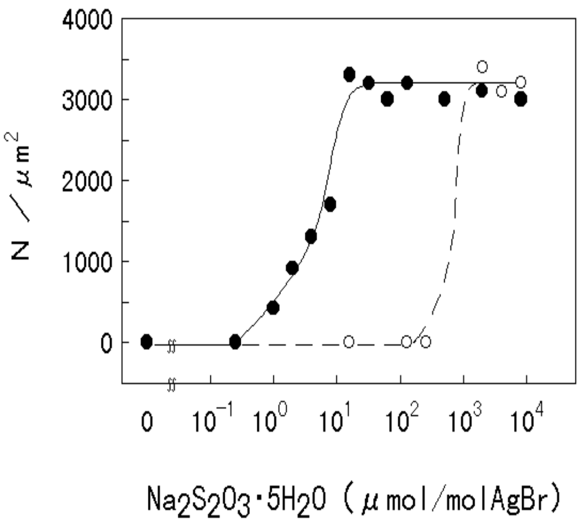


Fig.3 The number (N) of the centers observed with (●) and without (○) the amplification treatment as a function of the amount of sodium thiosulfate.

Discussion

Owing to the concentration principle, photoelectrons and interstitial silver ions take part in the formation of only one latent image center on each grain regardless of the presence of many sulfur sensitization centers as shown in Fig.4. However, it was found that silver clusters were formed and grown in the absence of the concentration principle at all the sulfur sensitization centers with our amplification treatment as shown in Fig.4. Sulfur sensitization centers enhanced the formation of silver nuclei[9]. Silver cluster formation in the absence of the concentration principle was observed and analyzed for the proposal of its mechanism elsewhere[10].

The changes in sensitivity, photoconductivity, and the number of the sensitization centers of the sulfur-sensitized grains with variation of the amount of the sensitizer were correlated well with each other as shown in Fig.1, Fig.3 and Table 1, indicating that electron-trapping sensitization centers of as many as 3200/μm^2 were formed by sulfur sensitization. By comparing the amount of silver sulfide formed with the number of the observed centers, it was concluded that each sulfur sensitization center contained two sulfide ions. This conclusion experimentally supported the hypothesis that the sulfur sensitiaztion centers were composed of dimers of silver sulfide as proposed by Keevert and Gokhale[1], Kanzaki and Tadakuma[2] , and Tani[3].

The number of sulfide ions in each sulfur sensitization center strikingly increased with further increasing the amount of the sensitizer as shown in Table 1, and became to be clusters of silver sulfide acting as fog centers.

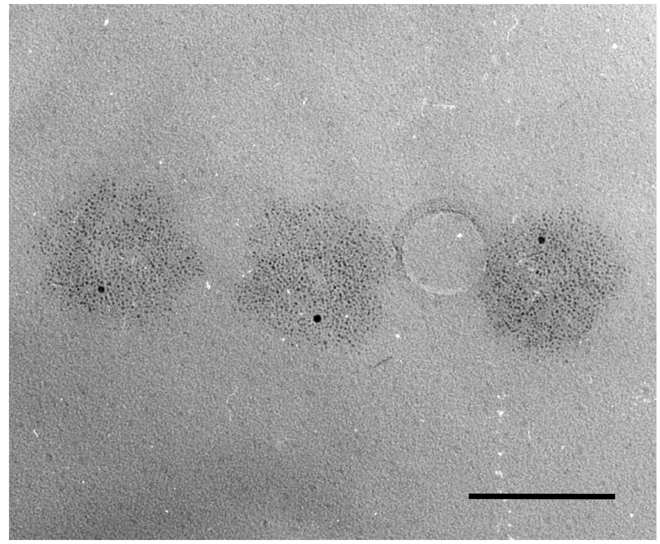


Fig.4 An electron micrograph of gelatin shells of octahedral silver bromide grains in an emulsion, which was sulfur-sensitized with sodium thiosulfate of 16 μ mol/mol AgBr, being exposed for 30sec and processed with the same amplification treatment as shown in Fig.2 (b). The length of the bar in this figure refers to 0.2 μ m.

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Biography

Hiroyuki Mifune received his M. S. degree in Chemistry from Kyoto University in 1974. Since 1974 he has been a member of Ashigara research laboratories, Fuji Photo Film Co. Ltd.