

Desensitization due to enhancement of dispersion of image centers by dyes (3) Effect of crystal defects

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Abstract

In the previous paper, we have proposed a new mechanism of desensitization due to enhancement of dispersion of image centers by dyes on the basis of the experiments with a sulfur-sensitized cubic silver bromide emulsion spectrally sensitized by 9-methyl-thiacarbocyanine dye. In the light of the fact that the introduction of crystal defects into emulsion grains depressed the dispersion of image centers, we introduced crystal defects, which were detected by the decrease in crystallite size, into the above-stated grains without causing any change in grain size, shape and halogen composition by adding a solution of the above-stated dye during the precipitation of the grains, and observed that the crystal defects depressed the dye desensitization. The above-stated result strongly supports the mechanism of desensitization proposed in the previous paper.

Introduction

The sensitivity of spectrally sensitized silver halide emulsions is dependent upon the light absorbance of the emulsion layers, quantum yield of spectral sensitization, and degree of desensitization caused by sensitizing dyes. The recent advances in tabular silver halide grain technology made it possible to increase the light absorbance, since tabular grains could adsorb larger amount of the dyes than other grains owing to their large specific surface area. However, the degree of desensitization was usually increased by use of tabular grains, since the amount of dyes adsorbed by each grain was increased by use of tabular grains.

The mechanisms of dye desensitization have been widely investigated and proposed by many groups

of workers. We have proposed a new mechanism of desensitization due to enhancement of dispersion of image centers by dyes in the previous papers, on the basis of the experiments with a sulfur-sensitized cubic silver bromide emulsion spectrally sensitized by 9-methyl-thiacarbocyanine.^{1,2}

On the other hand, Farnell et al reported that perfect grains were liable to disperse image centers, and that the incorporation of crystal defects restricted the latent image forming sites, thus depressing the dispersion of image centers.³ In the present paper, we investigated the effect of crystal defects upon desensitization by dyes in order to further clarify the mechanism of the dye desensitization due to enhancement of dispersion of image centers by dyes.

Experiments

The emulsion mainly employed in this study was composed of cubic silver bromide grains with average edge length of 0.58 micrometer and coefficient of variation of 7.3% and prepared by controlled double-jet addition of aqueous solutions of silver nitrate and potassium bromide into an aqueous solution of inert gelatin containing ammonia and ammonium nitrate at 50 °C with constant stirring. The pAg value of the reacting solution was maintained to be 7.8 during the precipitation. After removal of water-soluble salts, inert gelatin was added, and pH and pAg values of the emulsion were adjusted to be 6.8 and 8.6 at 50°C, respectively.

For the introduction of crystal defects, the addition of a methanol solution of 3,3'-bis(4-sulfobutyl)-9-methyl-thiacarbocyanine dye was continuously made, starting after nucleation step until the end of the addition of silver nitrate solution. The emulsion grains were cubic in shape with the average edge length of 0.58 micrometer, and some increase in coefficient of variation was observed for the grains

precipitated in the presence of the dye. The evaluation of the crystal defects introduced by the above-stated method was made by the measurement of crystallite size, for which it was necessary to use emulsion grains smaller than the above-stated grains. By eliminating ammonia and ammonium nitrate from the above-mentioned precipitation process, cubic grains with the average edge length of $0.13 \mu\text{m}$ were obtained. X-ray diffraction method and Scherrer's equation were applied to these emulsion grains to get information of their crystallite size and crystal defects.⁴ X-ray diffraction was measured by means of a diffractometer with a rotating anode X-ray tube and a monochromator to get X-ray beam of $\text{Cu-K}\alpha$. The emulsions were coated on cellulose triacetate film base and were swelled by aqueous solution of 50% glycerin for x-ray diffraction measurements. X-ray diffraction profile ascribed to $\text{K}\alpha 1$ was separated from that of $\text{K}\alpha 2$ by Rachinger's method. The crystallite size D is associated with diffraction half-width β by Scherrer's equation, $D=0.9\lambda/\beta\cos\theta$, where λ is the wavelength of X-ray beam and θ is Bragg's angle. The diffraction half-width β was determined from the measured half-width with the correction of Jones's method,⁵ in which half-width ascribed to the diffractometer used was measured by the use of a Si wafer.

Sulfur-sensitization was performed by digesting the above-stated emulsion at 50°C for 60 min in the presence of sodium thiosulfate of $0.3.0 \times 10^{-4}$ mole/mole AgBr . When any cyanine dye was not added during the precipitation process, the aqueous solution of cyanine dye was added before sulfur sensitization. Emulsion was coated at $350 \mu\text{g AgBr/cm}^2$ and $360 \mu\text{g gel/cm}^2$ on cellulose triacetate film base. The amount of the dye for the saturation coverage of the emulsion grains was determined to be 6.7×10^{-4} mole dye/mole AgBr according to the spectroscopic method.⁶ The coated films were exposed for $10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}$ and 10^{-2} sec to a Xenon flash lamp in an EG&G sensitometer and $10^{-2}, 10^{-1}, 1, 10, 100$ and 1000 sec to a tungsten lamp (color temperature: 2854K) through a filter and a continuous wedge. Fuji filters SC52 and BPB55 were used for the minus-blue exposure to excite the dye, and Fuji filter BPN42 for the blue exposure to excite the silver bromide grains. Relative radiation level was measured by EG&G radiometer (model 550-1) through the above filters and used to describe reciprocity law curves. The exposed films were subjected to the surface development by use of a Metol-ascorbic acid developer⁷ (MAA-1) at 20°C for 10 min. Gold-latensification was carried out by using an aqueous aurous solution described by James et al⁸ at 20°C for 1, 3 and 6 min, and followed by washing for 30 min. The optical density of the developed film was measured by use of a Fuji Recording Densitometer. Photographic sensitivity was represented by the reciprocal of the exposure E required to give 0.1 optical density above fog.

The photoelectron lifetime in the emulsion grains was obtained from the microwave photoconductivity

measurement.⁹ The light source was a N_2 pulsed laser (Moletron Corp., UV-24) which gave light pulses with wavelength of 337 nm and width of 20 nsec . The microwave source was a 9.5 GHz klystron whose maximum power was 200 mW , and microwave cavity was cylindrical (TE011). The signal was stored by a digital oscilloscope (Iwatsu Electric Co., TS-8123) and analyzed by a desk-top computer (Hewlett Packard, 85F). The apparatus time constant was $0.3 \mu\text{sec}$. The measurement was carried out over the temperature range between 300 and 113 K .

Results and Discussions

The X-ray diffraction patterns were measured for $0.13 \mu\text{m}$ cubic AgBr emulsion grains, which grew in the absence and presence of a thiocarbocyanine dye. Figure 1 shows the (420) diffraction profiles whose peak heights are normalized. The diffraction half-width increased with increasing amount of the dye used. Figure 2 shows the relation between grain size and crystallite size which was determined by use of Scherrer's equation. Crystallite size decreased with increasing amount of the dye used. Crystallite size was not dependent upon diffraction angle, indicating the absence of nonuniform distortion. Crystallite size was not changed by repeated measurements, reflecting negligible sample damage by the X-ray exposure. These results showed that the presence of the dye during the growth process of the grains decreased the crystallite size of the emulsion grains. The decrease in crystallite size indicated that the presence of the dye during the growth process introduced crystal defects in the grains, although it could not clarify the kind of defects. This method of introducing crystal defects was thought to be suitable for the investigation of the photographic effect of crystal defects, since it did not change the shape and composition of the grains.

Figure 3 shows characteristic curves of sulfur-sensitized cubic AgBr emulsion grains with the average edge length of $0.58 \mu\text{m}$. Sulfur-sensitization was optimized to achieve the highest sensitivity with exposure for 1 sec, and the dye was added at the amount for 100% coverage of the grain surface. The addition of the dye to the emulsion before digestion for sulfur-sensitization decreased its blue sensitivity. On the contrary, the blue sensitivity of the emulsion, to which the dye was added during its precipitation process, was nearly the same as that of the emulsion without dye. The minus-blue sensitivity was higher for the emulsion, to which the dye was added during its precipitation process, than for the emulsion, to which the dye was added before digestion for sulfur-sensitization.

Figure 4 shows the effect of the gold latensification upon the sensitivity of the dyed emulsion. In the case of the dye addition before digestion for sulfur-sensitization, the degree of the increase in sensitivity by gold latensification increased with increasing the amount of the dye added. As discussed in the previous paper, this result indicated that main cause for the desensitization by the cyanine dye in the sulfur-sensitized emulsion was the enhancement of dispersion of latent image centers by the dye. The degree of the increase in sensitivity by gold latensification did not change with increasing amount of the dye in the emulsion, to which the dye was added during its precipitation process. This means that the incorporation of crystal defects into silver bromide grains depressed the dispersion of image centers by the dye and decreased the degree of desensitization by the dye in the sulfur-sensitized emulsion. G.C.Farnell et al reported the suppression of the dispersion of image centers by the incorporation of crystal disorders into emulsion grains. Our results are consistent with their result. The degree of the high-intensity reciprocity law failure (HIRF) increased with increasing the amount of the dye added. The degree of HIRF was larger for the emulsion, to which the dye was added before digestion for sulfur-sensitization, than for the emulsion, to which the dye was added during its precipitation process. Since the dispersion of image centers is one of the causes for the high intensity reciprocity law failure,¹⁰ this result further supported the proposed mechanism. The internal sensitivity of the emulsion, to which the dye was added during precipitation process was higher than that of the emulsion, to which the dye was added before digestion for sulfur-sensitization.

Figure 5 shows the Arrhenius plot of electron-capturing rate (i.e., the reciprocal of the electron lifetime) in chemically unsensitized emulsion grains. Although the region in which electron signal decayed with the first-order kinetics became narrower with decreasing temperature, the electron lifetime of each sample was determined in the initial first-order decay region. At the same amount of dye added, the electron lifetime for the emulsion to which the dye was added during its precipitation was shorter than that for the emulsion to which the dye was added after its precipitation was finished. The degree of this phenomenon increased with increasing the amount of the dye used. It was reported that the electron lifetime was determined by the neutralization of trapped electrons by interstitial silver ions.¹¹ In the present case, the ionic conductivity of the emulsion to which the dye was added during its precipitation was lower than that of the emulsion to which the dye was added after its precipitation was finished. The increase in internal sensitivity and decrease in electron lifetime indicated

that the crystal defects introduced by the dye addition acted as electron traps. These crystal defects would intersect at the surface to give the preferential sites for the formation of chemical sensitization centers, and depress the dispersion of image centers by the dye.

Conclusion

The addition of a cyanine dye to AgBr emulsions during their precipitation process introduced to the emulsion grains crystal defects, which did not cause any change in the shape and composition of the grains and was revealed by X-ray diffraction method and Sherrer's equation. These crystal defects depressed the dispersion of image centers and the desensitization by the dye. These observation provided further evidence for the mechanism of desensitization due to enhancement of dispersion of image centers by dyes as proposed in the previous paper.

References

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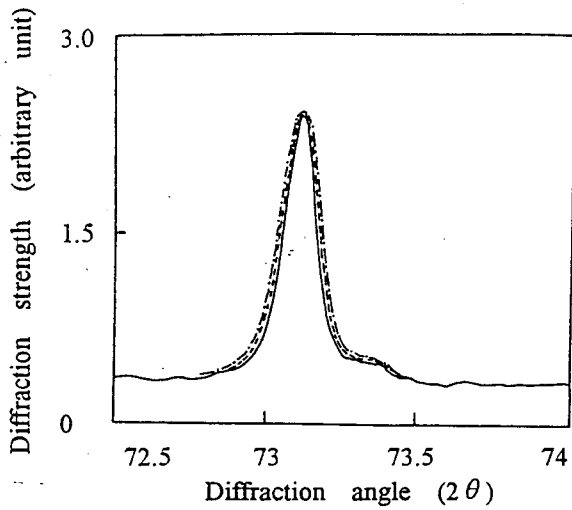


Figure 1. X-ray ($K\alpha 1$) diffraction profiles for (420) face of $0.13 \mu\text{m}$ cubic AgBr grains in emulsions, to which 9-methyl-thiacarbocyanine dye with varied amount was added during their precipitation process. The amounts of dye used were 0, 2 and 2.67 mmol/mol AgBr, and each corresponded to solid line, broken line and dot broken line.

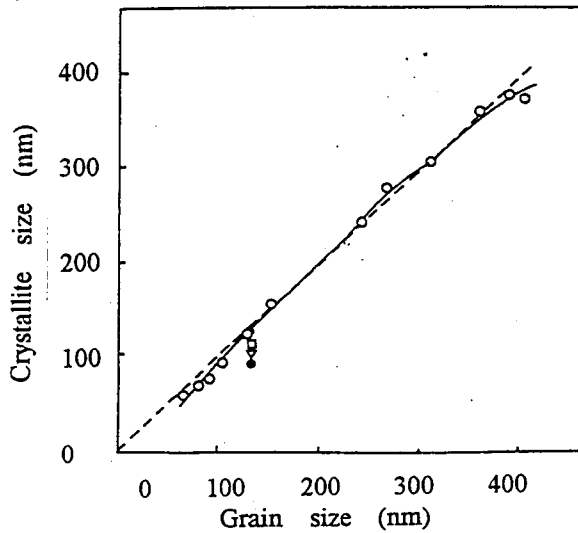


Figure 2. Relation between grain size and crystallite size for cubic AgBr grains in emulsions, to which the dye was added during their precipitation process at the amounts of 0 (open circle), 1.33 (square), 2.0 (triangle) and 2.67 (closed circle) mmol/mol AgBr.

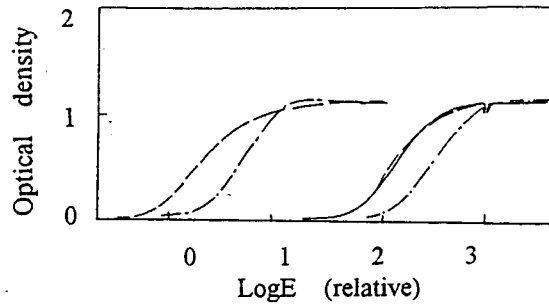


Figure 3. Characteristic curves of sulfur-sensitized cubic AgBr emulsion grains (0.58μ) to which the dye was not added (solid line), added during its precipitation process (broken line) or added before digestion for sulfur-sensitization (dot broken line). The emulsion was exposed for 1 sec through SC52 filter (minus blue exposure/left hand side) and BPN42 filter (blue exposure/right hand side), and developed by MAA-1 for 10 min at 20°C . The dye was added at the amount for 100% coverage of the grain surface.

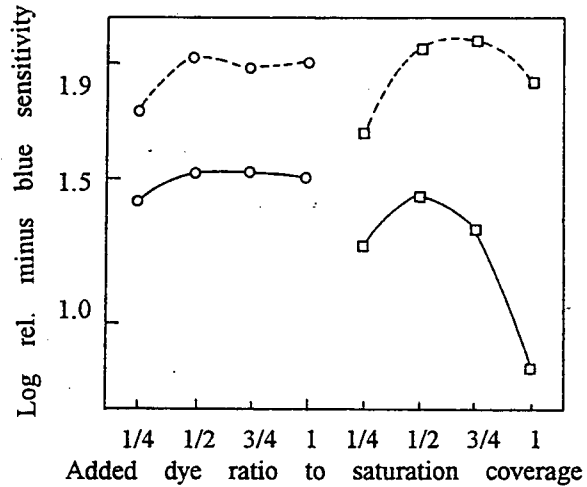


Figure 4. Effect of gold latensification upon sensitivity of sulfur sensitized emulsions to which the dye was added during its precipitation process (left hand side) and added before digestion for sulfur-sensitization (right hand side). Emulsions were exposed for 10^{-3} sec through BPB55 filter (minus blue exposure) and developed by MAA-1 for 10 min at 20°C without gold latensification (solid line), and with gold latensification (broken line).

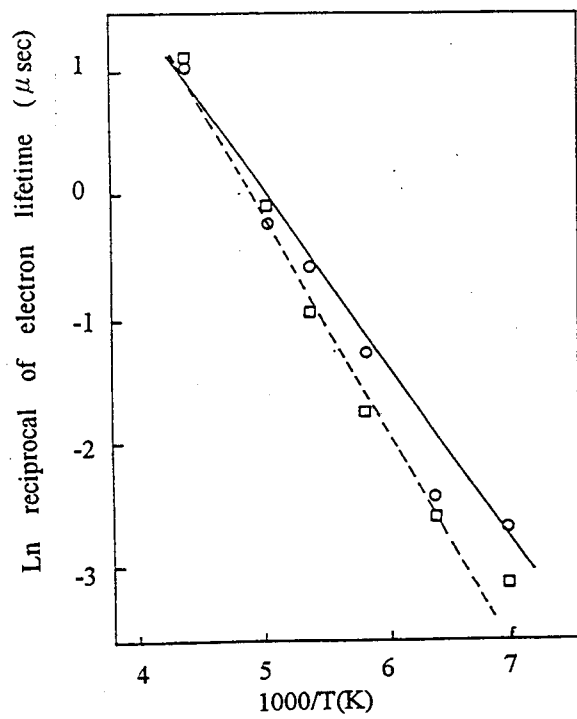


Figure 5. Arrhenius plot of reciprocal of electron lifetime of chemically unsensitized grains in emulsions, to which the dye was added during its precipitation process (circle), and added after their precipitation were finished (square). The amount of dye added was 0.67 mmol/molAgBr.