

Sensitization of Formate Ions Doped at Different Depths of Silver Bromide Microcrystals

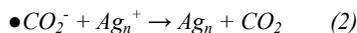
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Abstract

In the emulsifying process of AgBr microcrystals in the double-jet apparatus controlled by a microcomputer, a certain amount of formate salt was added at a specific time and pAg to a reactor to prepare a series of cubic AgBr emulsions in which formate ions were doped at different depths of AgBr microcrystals. The sensitometric results from these emulsions showed: 1) that the sensitivities of formate-doped emulsions, relative to that of the undoped emulsion as the controlled one, were remarkably increased; 2) that the closer to the surface of grains the doped formate was, the greater the sensitivity was; 3) that a cooperative sensitization by formate dopant, S+Au and dye was observed without any significant increase in fog level; 4) that the maximal sensitivity gain (S_{\max}/S_0) of undye-sensitized emulsions was greater than those of dye-sensitized ones.

Introduction

In 1998-99 Belloni et al.^[1-3] first and subsequently reported that formate ions doped in AgBr grains could remarkably sensitize the emulsion and they also proposed a mechanism for the sensitization by formate, that was:



After then, Guo et al.^[4], using ESR technique, gave indirect evidence to support for the existence of the Reaction(1), i.e. an intensified ESR signal of $\bullet CO_2^-$ was clearly detected from a dispersion of AgBr grains in solution of formate under illumination. Nevertheless, Hailstone^[5] expressed his questions, particularly about effectiveness of the sensitization of the formate-doped emulsion sensitized by green- or red-sensitive dye. It is a justified question. In the present paper, an attempt was made to observe sensitization of the emulsions doped by formate ions at different depths or positions in the interior of cubic AgBr grains.

Experimental

1. Preparations of AgBr emulsions in which the grains were doped with formate ions at different depths

A computerized double-jet apparatus was used to control all parameters of emulsifying process. AgNO₃ and KBr solutions were continuously added at a constant rate to an agitated gelatin solution at 50• and pAg was kept at 7.4. At a given time of the precipitation, pAg was adjusted to a certain value and a specific amount of sodium formate (1×10^{-4} mol/ mol Ag) in solution was injected to the emulsifying vessel. After several minutes pAg was adjusted back to 7.4 that was maintained till the ending of the precipitation. After the emulsion was treated by coagulation, washing and re-dispersed etc., pH and pAg of the emulsion were adjusted respectively to 5.5 and 7.2 for storage.

2. Sulfur-Plus-Gold Sensitization

Certain volumes of a solution of Na₂S₂O₃ (0.1%) and a mixture of AuCl₃ and NH₄SCN solutions were added in turn to a specific amount of emulsions. Then the emulsions were ripened at 50• for 60 min. and then TAI was added

3. Spectral Sensitization by dye

A green-sensitive dye, as shown in Fig.1, was used for the spectral sensitization for the emulsions. 2.5 ml of a solution of the dye in methanol (0.1%) was added to 50g of the emulsions and agitated for 5 min. at 40•.

4. Sensitometry

CGG sensitometer; Macbeth 903 densitometer; MAA-1 developer. The reciprocal exposure at density of 0.1 above the fog was taken for calculation of the relative sensitivities.

5. Measurement of grain size

JEM-100CX TEM was used for the measurement of the cubic grain sizes. The average edge length of cubic grains in the emulsions was $0.18 \pm 0.02 \mu\text{m}$.

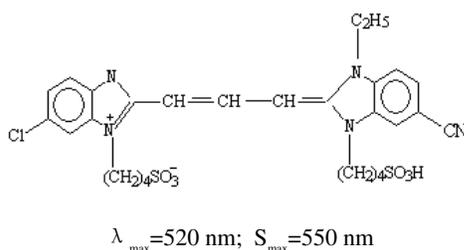


Fig.1 Structure of the green-sensitive dye

Results and Discussion

1. Relative depth or position of the formate ions doped in the cubic grains

The depth or position of the doped formate ions in the cubic grains is based on the following assumptions: 1) during the precipitation of AgBr, all additions of dopant (formate) are at the stage of grain growth when no new nuclei is formed, thus the number of grains is nearly a constant; 2) that the dopant is rapidly adsorbed on the surface of growing grains in a couple of minutes and at a specific pAg; 3) the distribution of grain sizes is quite uniform. So the relative positions of the dopant in a cubic grain can be easily calculated by $L_r(t) = [M(t)/M]^{1/3}$, where $L_r(t)$ denotes a relative length from the center to the doped layer, ranging from 0-1 relative to the half of edge length of a cubic grain, and was a function of time t when the dopant was injected to the emulsifying reactor, $M(t)$ the additional accumulative amount of Ag at the time t , M the total additional amount of Ag at the ending of precipitation. The relative depth is given by $D_r(t) = 1 - L_r(t)$. A schematic diagram for the positions of dopant in a cubic grain is shown in Fig. 2.

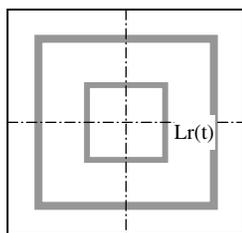


Fig.2 Schematic for positions of dopant located at a grey zone.

2. Sensitization of the emulsions in respect to different doped positions

Comparing with the sensitivity of the primitive undoped emulsion as a controlled one, the relative sensitivities for all other emulsions, including undoped and doped by formate ions at different positions of grains as well as primitive and sensitized by S+Au or S+Au+dye, were

shown in Table 1 and Fig.3. From them you can clearly find some interesting results as follows:

1) Changes in the sensitivity with the doped positions may be separated into 3 regions. In the first region, where the dopant is located at or in the relative length about 0.6 from the center of grain ($L_r(t)=0-0.6$), no sensitivity gain is significantly observed, on the contrary a little desensitization; in the second region, $L_r(t)$ are between 0.6 and 0.95, the sensitivities are, generally, gradually increased with the doped positions toward the surface though the data have some slight fluctuation; then in the third region, where $L_r(t)$ was above 0.95 and closer to the surface, sensitivities of the doped emulsions abruptly rise up. It is shown an important effect of the doped positions on the sensitization of doped emulsions. The closer to surface of grains the formate ions are, the more effective for them to trap holes than in the interior of grains, thus to exhibit higher sensitivities. These results are essentially consistent with what Belloni et al. reported although the sensitivity increment, which is about 2.5 times as high as of the controlled undoped emulsion by the same sensitization of S+Au+dye, was not so great as what they reported, i.e.10 times higher. One more different from Belloni's is that we did not find any effect of the delayed formation of latent image in our experiments, therefore it was difficult to reconfirm the existence of Reaction(2) proposed by Belloni et al.

Table1 Relative sensitivities* of the emulsions doped by formate ions at different positions of grains

No. of Emulsions	Sites of dopant $L_r(t)$	Sr for primitive	Sr for S+Au	Sr for dye
0	no dopant	100	177	1076
1	0.59	62	129	577
2	0.74	212	231	865
3	0.84	192	339	1154
4	0.93	173	346	1385
5	0.95	169	339	1462
6	0.97	423	673	2692

* : the sensitivity of the primitive emulsion without formate doped was taken as 100.

2) The regular sensitizations, such as S+Au and dye, were still applied to the formate-doped emulsions without any unwanted effect. It means that the sensitization caused by doped formate is compatible with the traditional ones and makes a cooperative sensitization possible. Obviously it should be attributed to their independent sensitizing mechanism in the process of LIF.

3) As long as all the formate-doped emulsions were concerned, the fog level was always very low (< 0.05) no matter whether or not they were chemically and spectrally sensitized. It makes them superior to the silver dimer (Ag_2) produced by reduction sensitization even though Ag_2 possesses the same function of hole scavenger also.

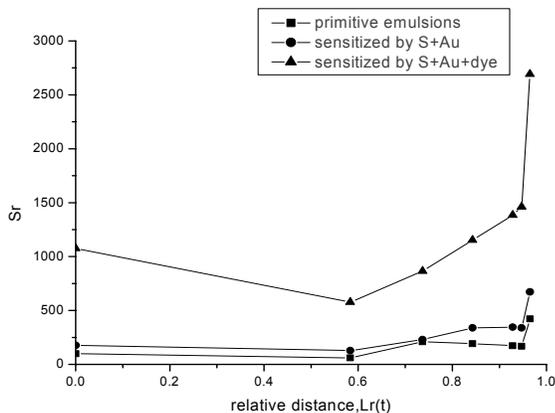


Fig.3 Relative sensitivities of emulsions doped by formate at different sites of grain.

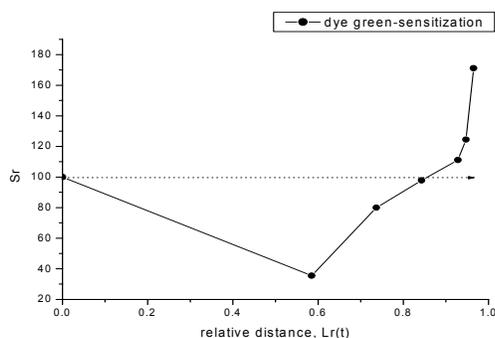


Fig.4 Sensitivity of doped emulsions sensitized by green absorbing dye, exposed to green light.

3. Interaction between internal formate ions and photo-generated holes on the surface of grains

It is well known that the photo-generated holes will be produced and situated on an interface between the adsorbed dye and the surface of grains if the dye-sensitized emulsion is exposed to a mono-light sensitive region extended by the dye. Besides, If these interfacial holes could not be captured by the internal formate ions (or no interaction of each other), then the doped formate ions would fail to exert any sensitization to the doped emulsions. For this reason, an experiment to expose the doped emulsions sensitized by green-sensitive dye to green light was carried out and the results were shown in Fig.4. Some interesting points have been noticed. Firstly, similar to the case of the samples exposed to white light, the sensitivities relative to the controlled one increased with the doped positions approaching to the surface and reached the maximum at $L_r(t)=0.97$, the closest to the surface. The maximal sensitivity gain is about 1.7 times greater than that of the controlled one at $L_r(t)=0$ (undoped). It means that the internal formate ions is still able to capture the surface holes fairly effectively. If the

doped formate ions were fixed at some position and could not be moved, then the movable species must be the surface holes, maybe via diffusion or a transfer from HOMO of the dye aggregate. Secondly, the optimal depth away from the surface, where the formate ions were doped and gave a maximal sensitivity gain (S_{max}), could be approximately estimated from the curve in Fig.4, i.e. at $L_r(t)=0.97$, $D_r(t)=0.03$, the average half length of grains $h_s = 90$ nm, so the doped depth $D_d = h_s \times D_r(t) = 2.7$ nm \approx 5 cell layers of AgBr. This datum shows the optimal doped depth just at the subsurface. A diffusing length (or depth, L_d) of the surface holes could be also roughly estimated by a similar method and data given by the curve in Fig.4. That is $L_d \approx 18$ nm \approx 30 cell layers.

In addition, it may be justified for S_{max}/S_0 to be regard as a measure of the maximal sensitivity gain for a kind of status of emulsions, where S_0 is sensitivity of the controlled undoped one at $L_r(t)=0$ and S_{max} as defined above. Value of S_{max}/S_0 implies the maximal contribution to sensitivity gain made entirely by the doped formate ions. The values of S_{max}/S_0 for different status of emulsion were listed in Table 2. It could be interestingly found that the value of S_{max}/S_0 (4.0) for the primitive and S+Au emulsions are greater than those (2.5 and 1.7) for the dye sensitized emulsions. Actually the values of S_{max}/S_0 are correlated with the space sites where hole were photo-generated and further with light absorbed by emulsions. Essentially, it is a result from a geographic relationship between the internal formate ions and the space sites at which holes were photo-generated. The data on S_{max}/S_0 obtained from our experiments may quantitatively give part of evidence to Hailstone's suspect^[5], i.e. the sensitizing efficiency of dye-sensitized emulsion is lower, but not much lower than those of undyed emulsions.

Table 2 Maximal sensitivity gain of emulsions caused by formate dopant.

Status of emulsions	Light absorbed	Site of holes generated	S_{max}/S_0
Primitive	blue (white)	inside grain	4.0
S+Au	blue (white)	inside grain	4.0
S+Au+dye	blue+green (white)	Inside grain and on surface	2.5
S+Au+dye	green (blue is cut off from white)	on surface only	1.7

Conclusion

1. The formate dopant does bring an remarkable sensitization to AgBr emulsions.
2. The closer to surface the formate dopant is, the greater the sensitivity increment is.
3. A cooperative sensitization by formate dopant, S+Au and dye could be carried out without any significant increase in fog level.

4. The maximal sensitivity gain (S_{\max}/S_0) of undye sensitized emulsions is greater than those of dye-sensitized ones.

Acknowledgement

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Biography

Wang-jing Ma received his B.S. degree in Chemistry from the University of Shanxi at Taiyuan in 1999 and worked as an assistant for the Agricultural University of Shanxi for 3 years. Since 2002, he, as a post graduated student, has been studying in the Chinese Academy of Sciences at Beijing and engaging in a research on the new sensitization of silver halide imaging system.