

Influence of Subsurface Lattice Defects Created by Splash Iodide Introduction on Photographic Properties of AgBrI Isometric Microcrystals

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Abstract

The cubic grains with the dislocation exit points in the centre of crystal faces were created by means of splash iodide solution addition during the synthesis process. The conditions of chemical and spectral sensitization of these grains contributing to the photographic film preparation with improved sensitivity were found out.

Introduction

The photographic speed of photographic layers with AgHal grains depends on the effective use of photoelectrons. For the photographic process in each grain, photolytic silver could be concentrated on a minimum number of latent image centers (LIC). For this purpose it is necessary to create photographic sensitivity centers (PSC) whose amount should be sufficient enough to trap all the photoelectrons. Besides, areas with higher concentration of interstitial silver ions, for a fast localization of the photoelectron in the center must be close to PSC.

One of the parameters determining the amount of PSC on grains is their habit. It is well-known that the amount of LIC on cubic {100} grains is much less than that on octahedron {111} grains; therefore, photographic layers prepared on their basis are more sensitive. Chemical sensitization (CS) on cubic surfaces proceeds selectively - mainly at corners and edges of cubes resulting in a limited number of PSC and LIC. The further reduction of the number of LIC on cubic {100} grains can lead to the further increase in sensitivity. Increase in the efficiency of the photographic process can be due to the reduction in the number of LIC and/or to the increase of Ag^+ local concentration (close to PSC). According to the patent literature [1,2], a potential possibility to increase the Ag^+ concentration is the creation of extended defects of a crystal lattice in the subsurface areas of AgBr grains by means of adding the KI solution before the total amount of AgBr is introduced.

To increase the efficiency of a photographic process on isometric grains, cubic {100} grains with the dislocation of exit points in the centre of a crystal face were prepared. The technique for creating the dislocations was chosen on the ground that silver bromide and silver iodide as to their

syngony belong to different structures and besides, the difference in their solubility amounts to 4 orders of magnitude. Therefore, their co-crystallization results in structural defects on the boundary of phases, the area of structural defects is known to have a higher concentration of interstitial silver ions. CS centers are also formed on defective sites with increased surface energy. Thus, the structure with subsurface defects provides for fast localization of a photoelectron on a small number of PSC.

Experiment

AgBr octahedron {111} grains with an average equivalent diameter $d = 0,6 \pm 0,05 \mu m$ were synthesized by two-jet crystallization. Core grains before the crystallization of AgBr shell were attacked by the KI solution (the concentration 3 mol. % at $T = 60^\circ C$ and $pBr = 1,8$). A grain shell was built up under the conditions providing for the formation of cubic {100} or octahedron {111} grains, at $pBr = 3,0$ or $1,6$ accordingly.

The built - up of the AgBr shell on AgBr/AgI grains at $pBr = 1,6$ led to the formation of octahedron {111} grains. Photolytic silver on unsensitized grains, as seen from Fig. 1a, concentrates at the corners and edges of AgBr(I) grains.

The incorporation of I⁻ ions on AgBr cubic {100} grains before crystallizing the AgBr shell at $pBr = 3$, results in the change of the grain habit (octahedron {111}) and the change of the place of concentrating photolytic silver on AgBr(I) grains as well. As seen from Fig. 1b, photolytic silver concentrates mainly in the center of AgBr(I) cubic {100} grains, which is not typical for these grains.

The study of photographic properties of resulting grains showed that photographic layers with unsensitized grains have high optical density of the fog ($D_0 = 1,5$) which can be lowered up to 0,03 by increasing the thickness of the AgBr shell. The D_0 decrease proceeds uniformly with the growth of the shell thickness. When the mass of the core / shell ratio is 1:2, $D_0 = 0,03$ (see Fig. 2).

The analysis of the electron micro photos of the shell growth showed that the thickening of the shell results in the decrease of the number of the centers concentrating photolytic silver on the grains.

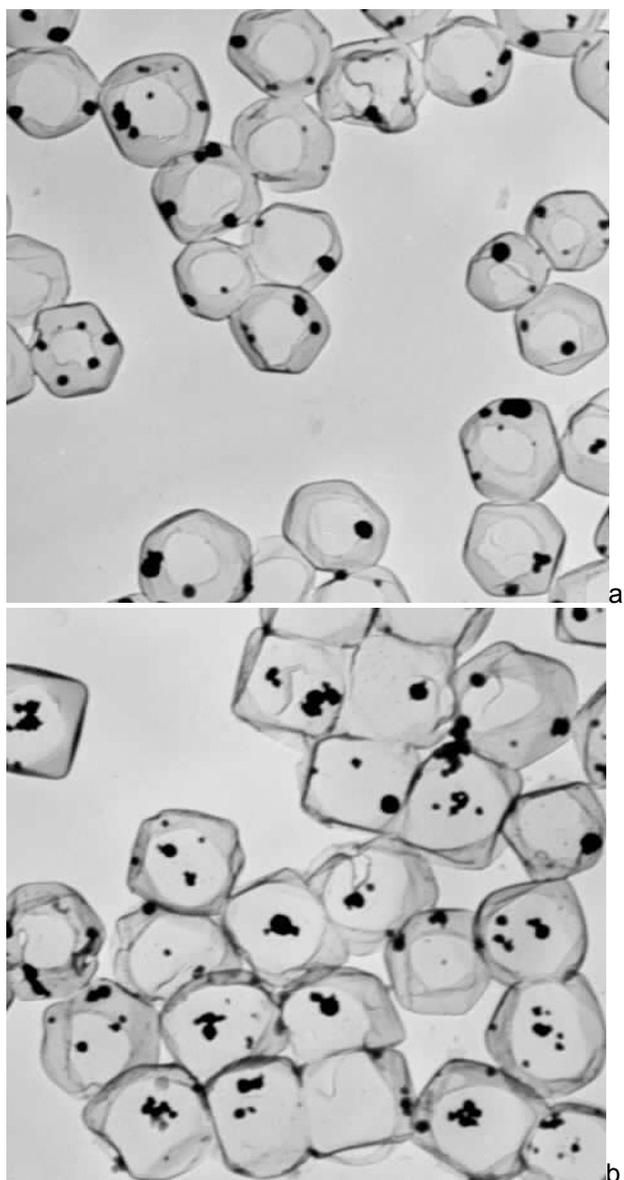


Fig. 1. The electron micro photo of AgBr(I) grains with the localization of photolytic silver on the corners and edges (a) and in the center of the cubic {100} face (b) x6000.

Then, the processes of chemical and spectral sensitization of resulting grains were investigated and optimized. Chemical sensitization of photographic emulsion is also accompanied by the appearance of the fog on the samples. However, it was experimentally found out that the adsorption of some dyes – spectral sensitizers - promotes the decrease of D_0 up to 0,07 (see Table). Thus, photographic layers with the grains obtained by the present authors possess improved photographic characteristics, viz. a higher photographic speed and a lower level of the fog.

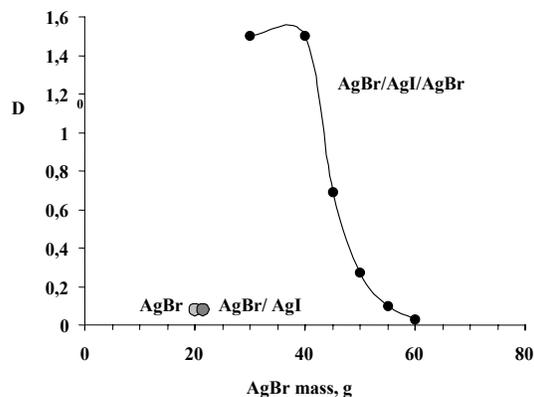
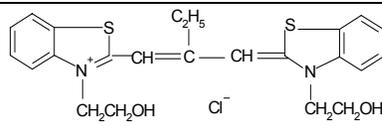
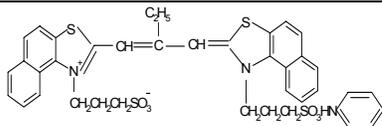
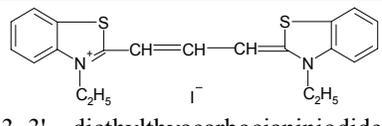
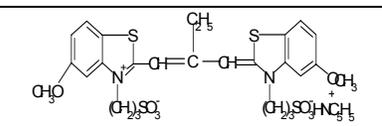
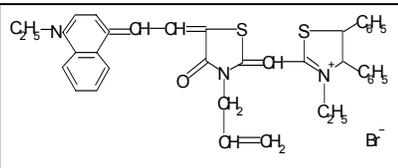


Figure. 2. Change of optical density of the fog (D_0) of photolayers in the course of building up the AgBr shell on AgBr/AgI grains.

Spectral sensitizers (dyes) and sensitometric characteristics of photolayers.

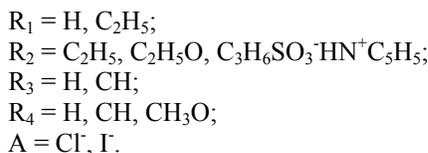
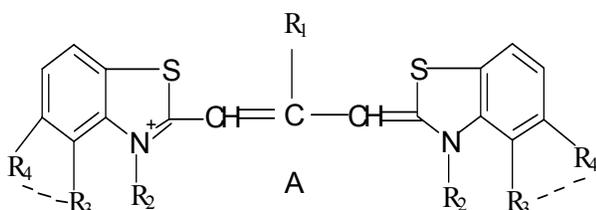
The formula of dye	S	D_{max}	D_0
-	100	1,7	0,45
 3, 3' - (β - oxiethyl) - 9 - methyl - thyacyaninchloride	250	1,1	0,07
 3, 3' - di (γ - sulphopropyl) - 9 - ethyl - 4, 5 ,4' ,5' - dibenzothya - carbo-cyaninbetaine, pyridine	220	1,4	0,07
 3, 3' - diethylthyacyaniniiodide	250	1,6	0,16
 3, 3, - di (γ - sulphopropyl) - 9 - ethyl -5, 5' - dimethoxythyacarbo - cyaninbetaine, pyridine	150	1,1	0,06

	-	0,7	0,43
3 - allyl - 3' ethyl - 4', 5' - difenil - 4 - keto - 5 (1'' - ethyldigidro - chinolililiden - 4'' - ethiliden) thya - zolinthyazocianinbromide			

Photographic layers with spectral sensitized grains do not undergo fogging, and possess better stability.

Results and discussion

The experimental data on spectral sensitization show the connection between the structure of a dye and its antifogging effect. All the dyes with antifogging effect belong to the same organic compounds with a similar formula:



The adsorption on CS centers was investigated for the given class of the dyes. According to [4, 5] the structure of a dye is responsible for its selective adsorption on Ag_2S centers. The electron micro photos show that the grains with subsurface incorporation of iodide ions create large PSC closely located to each other, easily changing into the fog centers. Selective adsorption of a dye on Ag_2S centers prevents the aggregation of PSC and fogging.

Based on the data [3], it was possible to explain the photolysis of AgBr(I) isometric grains. Large surfaces of tabular grains have crystallographic indices $\{111\}$, like the surface of octahedron grains. Assuming the fact that silver iodide crystallizes in the same way on similar surfaces, it is possible to suggest a scheme for the crystallization of AgI on octahedron grains (see Fig. 3). The crystallization of the shell under the conditions of the growth of the AgI hills by AgBr mass, changing the octahedron $\{111\}$ habit into cubic octahedron. The tops of an octahedron are located in the center of newly formed cubic surfaces (see Fig. 4). Thus, the largest structural defects located in the tops of an

octahedron, now, are in the center of cubic surfaces, where the largest amount of photolytic silver concentrates (see Fig. 1b, 5). While other concentration sites of photolytic silver located near the center of a cubic surface are likely to be due to the dislocations extending from the edges of an octahedron.

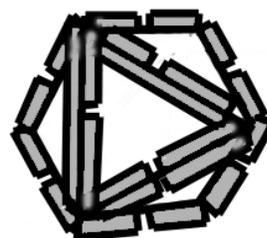


Figure. 3. The scheme for the crystallization of AgI on AgBr octahedron grains.

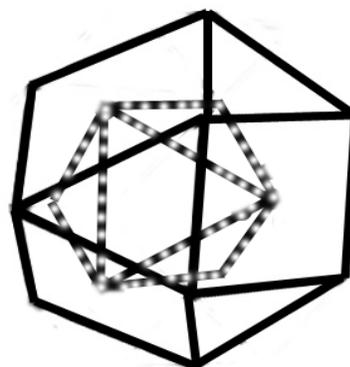


Figure. 4. The scheme for the formation of an octahedron inside a cubic octahedron.

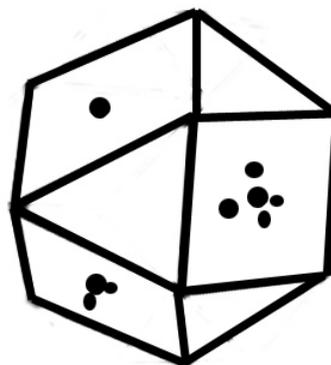


Figure. 5. The scheme of concentrating photolytic silver.

Based on the above mentioned data, the dislocations formed during the AgBr shell build-up without changing a grain habit ($p\text{Br} = 1,6$) are expected to appear on the surface

of octahedron {111} grains in the area of edges and corners of AgBr(I) grains (see Fig. 1a).

Conclusion

Grains with subsurface structural defects created by the incorporation of silver iodide before crystallizing the AgBr shell, independent from the habit, possess a number of common properties: they easily fog attacked by KSCN and/or increased concentrations of sensitizers ($\text{Na}_2\text{S}_2\text{O}_3$), but they possess a higher photographic speed.

The dislocations created by the introduction of iodide silver before the crystallization of the AgBr shell, appear on the surface of grains in the places corresponding to the location of AgI hills as powerful structural defects. If their number is great, grains are developed without of an exposure. CS products are formed on defective grain sites, and in the presence of a silver halide solvent they are also formed on additionally bleached surface areas near dislocation exits, it resulting in the overgrowing of CS centers into the fog centers.

The present authors assume that the systems obtained have a small amount of large CS centers which during the process of ageing easily become the fog centers. Also, CS in the presence of a KSCN solvent promotes concentrating the sensitization products on a few large centers and increasing the fog level.

Adsorption of some dyes - spectral sensitizers possessing selective adsorption on PSC, decreases the fog

level obtained during CS of photo emulsions, and increases the stability of photo layers because a dye, being adsorbed on the grain surface, prevents CS centers from being additionally aggregated.

From the analysis of the obtained data it follows that the investigated systems are highly promising for the preparation of highly sensitive photographic materials by means of selecting proper stabilizers.

References

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Biography

Larisa V. Sotnikova was born in Kemerovo (Russia) on October 26, 1966. In 1989 graduated from the State University of Kemerovo, Chemical Department. Since 1989 she works on Kemerovo State University's Inorganic Chemistry Chair as a Scientific Researcher. Doctor of Science since 1998. Field of research is the silver halide photographic emulsion crystallization and chemical sensitization processes, author of more than 50 scientific publications.