JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY® • Volume 45, Number 3, May/June 2001

A Study of Structure and Properties of Hollow Silver Halide Microcrystal Emulsion

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The preparation methods of hollow silver halide microcrystals have recently been reported in the literature, however the study of their properties and application has not yet appeared. In this article the preparation of hollow cubic Ag[Cl,Br], Ag[I,Cl,Br] and tabular Ag[I,Br] microcrystal emulsions is reported. The relation between structure and property of the hollow cubic and tabular silver halide microcrystal emulsions compared with the solid cubic and tabular silver halide microcrystal emulsions comprising almost the same halide composition was studied by means of EDX, SEM, TEM, development with a diluted developer, chemical and spectral sensitization. The results show that the latent image centers are always formed preferentially around the holes of the hollow cubic and tabular silver halide microcrystals. The hollow microcrystal emulsion has a higher efficiency of latent image formation, higher surface reaction activity, and therefore higher chemical and spectral sensitivities. The advantages of hollow silver halide microcrystals can be ascribed to their unique hole structure.

Journal of Imaging Science and Technology 45: 224–229 (2001)

Introduction

The silver halide photographic materials have been significantly advanced within the past two decades. A series of new kinds of silver halide microcrystals and new organic compounds useful for photography have been provided. Based on these, properties including sensitivity, sharpness, granularity, resolution, and color reproducibility of photographic materials are greatly improved and enhanced. The essential techniques involve increasing the light absorption of silver halide, reducing the recombination of electron and hole, enhancing the surface area of microcrystal to absorb more spectral sensitizing dyes, and creating the new couplers and chemical compounds with various functions. Design and technique of preparing new silver halide microcrystals have played the most important roles in improving the quality of photographic materials. New kinds of silver halide microcrystals developed in the last 20 years include tabular grains, double and multiple structures, epitaxial grains, etc.

In recent years, another novel kind of silver halide called hollow grain has been reported in publications and patents.[1–12] The possibility of designing silver halide microcrystals with holes is based on the following considerations. The essential reaction processes of silver halide emulsion occur almost entirely on the surfaces of grains, e.g., chemical sensitization, spectral sensitization, formation of latent image by light exposure, and development of exposed grains. The silver halide in the form of hollow grains might provide several advantages, for example: (1) saving expensive silver (up to 30%); (2) a high ratio of surface area and volume of grain for absorbing more spectral sensitizing dye and more light; and (3) a rapid rate of development, because development can occur simultaneously on both the external and internal surfaces. These characteristics will result in enhancing the sensitivity of hollow silver halide grain emulsion without increasing the size of the grain, or allow reducing the grain size which would be useful for improving granularity and resolving power.

The methods of preparation of hollow silver halide microcrystals have been reported in the literature. Falxa and coworkers[1] provided a method for forming a silver shell on non-silver containing grain as core in a non-aqueous system, then the water-soluble core is removed to form the grain with hollow structure. Iguchi and coworkers[2] disclosed silver halide cubic crystals having a depression on each face of a hollow portion. This was produced by precipitating first monodisperse cubic type silver halide crystals and then precipitating a second silver halide having a lower solubility than the first one, to gradually dissolve the first silver halide crystals and have a hole in the grain. The hollow grains produced by Irving and coworkers[3] were different in that they are not made by the dissolution of a differentially soluble core. Silver iodide seeds having the geometrical configuration of four truncated hexagonal bipyramids whose four [0001] faces are joined to form a common tetrahedron were firstly prepared. Then the tabular silver iodobromide are epitaxially deposited onto the end [0001] faces of each of the four truncated hexagonal bipyramids of the AgI seed grains. The resulting crystals are a novel three-dimensional arrangement of tabular crystals with hollow cores. Chang[4] provided hollow rod-shaped silver halide grains produced by using a quantity of growth modifying agent, such as hypoxanthine. The axial cross-section of both the grain and the hollow portion is typically hexagonal. Maskasky[5] disclosed a hollow silver halide grain, where

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Original manuscript received September 11, 1999

the hollow grain internally contains at least two distinct voids. Chang and coworkers[6] disclosed a tabular silver chlorobromide or silver chloroiodobromide emulsion in which at least 50% of tabular grains have a centrally located hole. Urabe[7] described a method to prepare at least 30% of a population of tabular silver halide grains having an indentation or space in the central portion of their major faces. However, the study of their properties and applications has only appeared for Iguchi's,[2] Urabe's[7] and the present author's[8–11] articles. The purpose of this article is to study the preparation and properties of hollow cubic Ag[Cl,Br], Ag[I,Cl,Br] and tabular Ag[I,Br] microcrystal emulsions, and the relation between structure and property of the hollow silver halide microcrystal emulsions compared with the solid cubic and tabular microcrystal emulsions with the same halide composition, in order to demonstrate the role of hollow structure.

Experimental

Preparation of Hollow and Solid Cubic Silver Chlorobromide Emulsions

A cubic silver chloride emulsion previously prepared as a core was added in a predetermined amount into a reaction vessel. At 60°C and pAg = 7.0, solutions of silver nitrate and potassium bromide were fed with linearly increasing rate into the vessel. Four hollow cubic chlorobromide emulsions were accordingly prepared with different durations (30, 40, 50, and 60 min) of precipitation. Then according to the same reaction conditions a solid cubic Ag[Cl,Br] emulsion was prepared for comparison using a 50 min duration of precipitation.

Preparation of Hollow and Solid Cubic Silver Iodochlorobromide Emulsions

The cubic silver chloride emulsion previously prepared as core was added in a predetermined amount into a reaction vessel. At 60°C and pAg = 7.0, solutions of silver nitrate and potassium bromide having different levels of potassium iodide (0.5, 1.0, 1.5 and 2.0 mol %) were fed with linearly increasing rate into the vessel. Four hollow cubic iodochlorobromide emulsions were accordingly obtained with the durations of precipitation as above. Then according to the same reaction conditions a solid cubic Ag[I,Cl,Br] emulsion with 1.5 mol % iodide was prepared for comparison.

Preparation of Solid and Hollow Tabular Silver Iodobromide Emulsions

At 80°C and pAg = 9.33, solutions of silver nitrate and potassium bromide were fed with linearly increasing rate into the vessel over 10 min to produce tabular AgBr; then solutions of silver nitrate and potassium bromide with 5 mol % iodide were added with linearly increasing rate into the vessel to prepare a solid tabular Ag[I,Br] emulsion.

A portion of the tabular grain emulsion was treated with a silver halide solvent (such as KSCN at low concentration) at 40°C for several min for creating small holes on the tabular grains.

Preparation of Sample for EDX Analysis

The gelatin of the samples of unhardened hollow cubic silver halide were first removed with proteolytic enzyme or simply by hot water, then the grains were covered with a thin carbon film under vacuum. An energy dispersive X-ray (EDX) spectrometer was used to determine semi-quantitatively the composition of hollow silver halide.

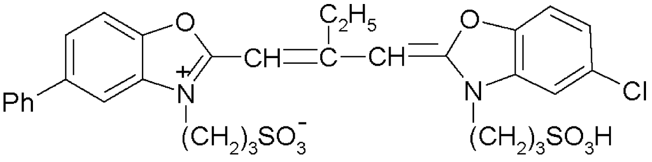
Determination of Filament Location

Samples of diluted hollow and solid unsensitized silver halide emulsions with gelatin removed were deposited onto a glass plate. After drying, the samples were exposed to a 220V–60 W incandescent light source for one sec. The exposed samples were developed with a diluted developer for 80 sec. Carbon replicas were created as above, and the samples were then fixed using 50 % KSCN solution for 3 to 5 min to remove the undeveloped silver halide. Then the samples for microscopy were shifted onto copper gauze as support for observing by TEM the location of developed silver filaments on the thin gelatin shells. The composition of developer is as following:

p-Methylaminophnol sulfate	0.2 g
Sodium sulfite	2.0 g
Hydroquinone	0.6 g
Potassium carbonate	2.5 g
Potassium bromide	0.3 g
Water	1000 ml

Chemical and Spectral Sensitization

The hollow and solid cubic, as well as tabular, silver halide microcrystal emulsions were digested at 50°C for chemical sensitization with $HAuCl_4$ plus $Na_2S_2O_3$, then green dye having a following formula was added for spectral sensitization.



Result and Discussion

Observation of Hollow Cubic Microcrystals by SEM

The four SEM micrographs of hollow cubic Ag[Cl,Br] microcrystals with different duration (30, 40, 50, and 60 min) of precipitation are shown in Fig. 1. For comparison, the SEM micrograph of solid cubic Ag[Cl,Br] microcrystals with 50 min duration of precipitation is shown in Fig. 2(a).

It can be observed from Fig. 1 that with increasing duration of precipitation of silver bromide added onto silver chloride core, the number of microcrystals with holes in center is gradually increased except for the fourth case (60 min). The reason is that when the precipitation time of silver bromide is less than about 50 min, the bromide ions act as a solvent for silver chloride in the center to form holes. However, when the precipitation duration is prolonged more than 50 min, the subsequent silver bromide may fill the holes previously produced, and the number of holes is reduced.

The four SEM micrographs of hollow cubic Ag[I,Cl,Br] microcrystals with different iodide contents (0.5, 1.0, 1.5, and 2.0 mol %) are shown in Fig. 3. For comparison, the SEM micrograph of solid cubic Ag[I,Cl,Br] microcrystals is shown in Fig. 2.

The micrographs (Fig. 2) of solid cubic Ag[Cl,Br] and Ag[I,Cl,Br] prepared by a conventional method show that under these conditions no hole structure exists in the microcrystals.

Figure 3 shows that with increasing iodide content added into silver chloride core, the number of microcrystals with holes in the center and on the surface is gradually increased. The reason is that like bromide ions, iodide has a solvent action towards silver chloride. During the precipitation of silver iodobromide on

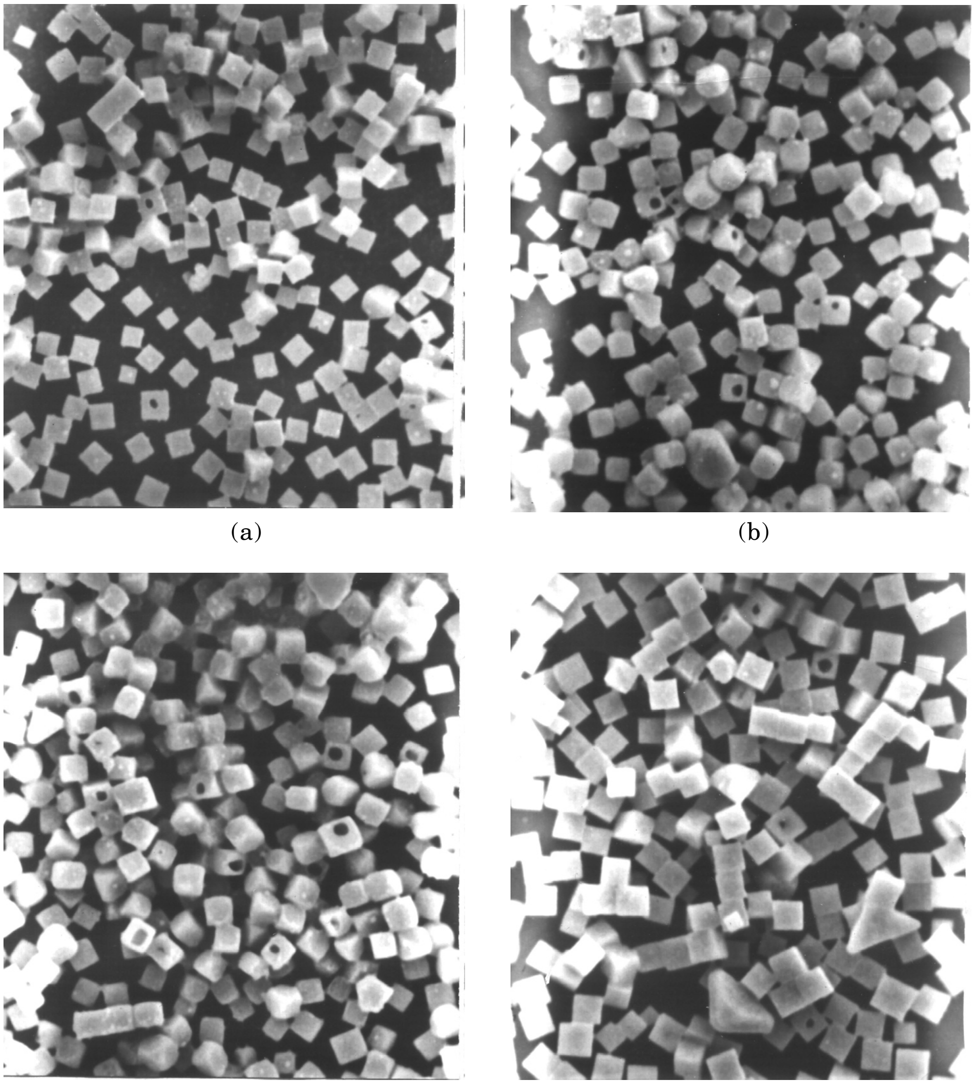

(a) (b)
(c) (d)

Figure 1. SEM micrographs (8000x) of hollow cubic Ag[Cl,Br] microcrystals with different duration of precipitation: (a) 30, (b) 40, (c) 50, and (d) 60 min.

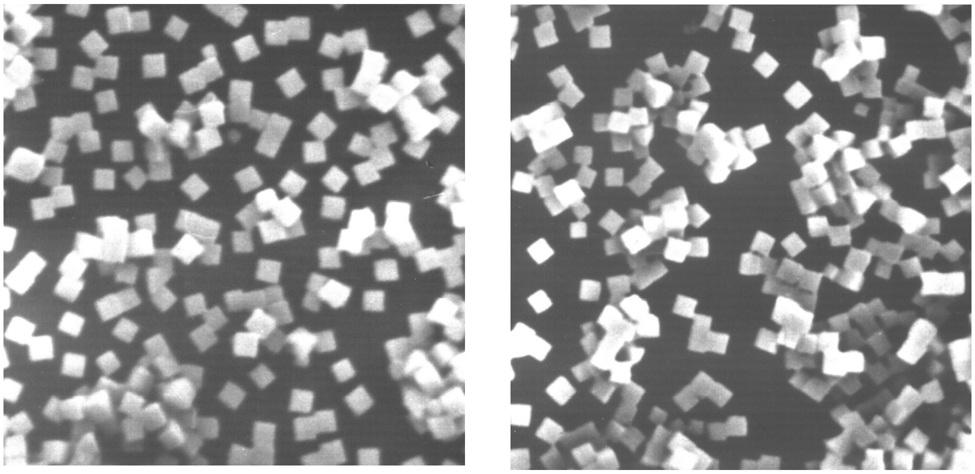
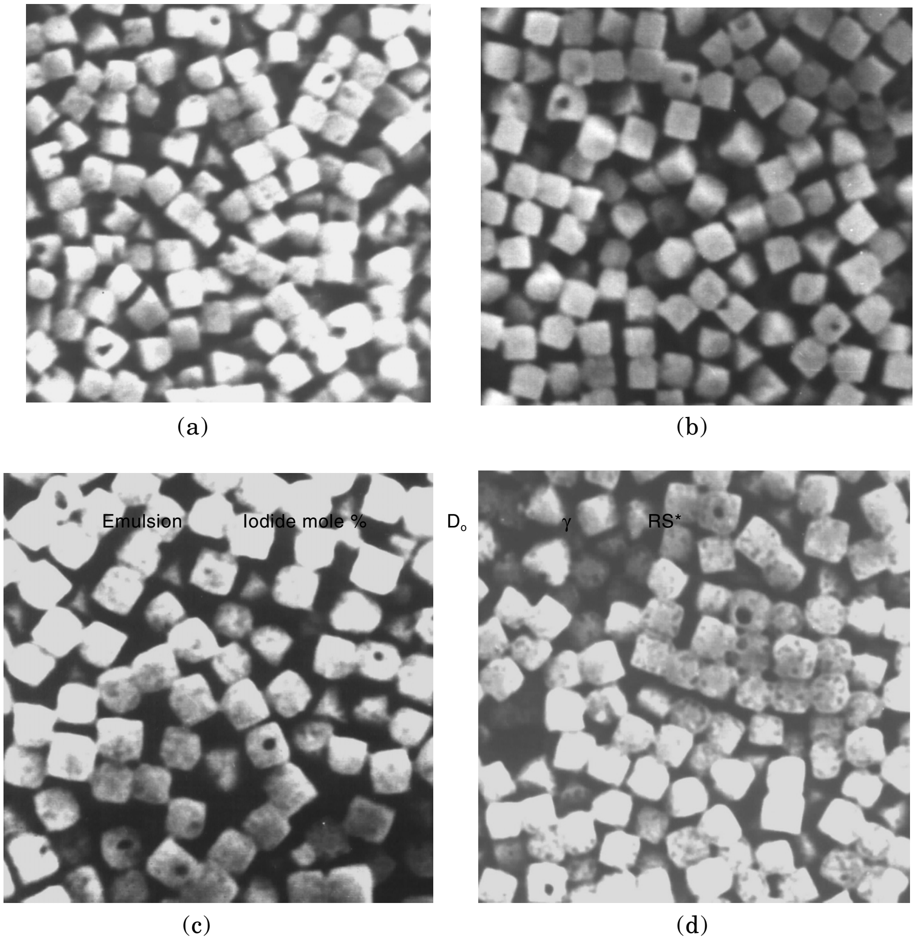

(a) (b)

Figure 2. SEM micrographs (8000x) of solid cubic Ag[Cl,Br] microcrystals of (a) 50 min durations; and (b) Ag[I,Cl,Br] microcrystals with 1.5 mol %.


(a) (b)

(c) (d)

Figure 3. SEM micrographs (x 8000) of hollow cubic Ag[I,Cl,Br] microcrystals with different iodide content (mol %): (a) 0.5, (b) 1.0, (c) 1.5, and (d) 2.0.

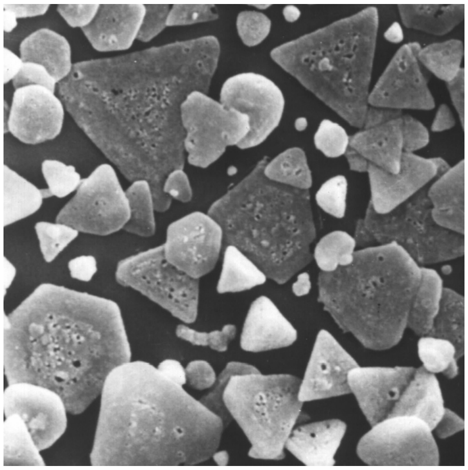


Figure 4. SEM micrograph (x 5000) of hollow tabular Ag[I,Br] microcrystals.

the surface of the silver chloride core, simultaneously the bromide and iodide ions will dissolve silver chloride to reduce the chloride composition and produce the holes or a porous structure in the center and on the surface.

The hole structure of tabular Ag[I,Br] microcrystals treated by solvent is shown in Fig. 4.

TABLE I. EDX Analysis Results of Hollow Cubic Ag[Cl,Br]

Ratio	Hollow cubic Ag[Cl,Br] a	Hollow cubic Ag[Cl,Br] b	Hollow cubic Ag[Cl,Br] c	Hollow cubic Ag[Cl,Br] d
Br/Cl	0.56/0.44	0.65/0.35	0.74/0.26	0.82/0.18
			Solid cubic Ag[Cl,Br] c	
Br/Cl			0.75/0.30	

EDX Analysis of Hollow Cubic Silver Chlorobromide

EDX analysis is applied for determining the compositions of hollow cubic silver chlorobromide microcrystals to identify semiquantitatively the Br/Cl ratio in the hollow cubic and solid Ag[Cl,Br] microcrystals. The results are shown in Table I.

The data in Table I show that chloride in the core is gradually replaced by bromide on prolonging the duration of precipitation, and that the solid cubic Ag[Cl,Br] has almost the same Br/Cl ratio compared with that of the hollow one [emulsion (c)].

Determination of Filament Location

Development with a diluted developer was carried out to observe the location of initially developed silver filaments in order to infer if the latent image center preferentially form near the hole structure of the silver halide microcrystals. The TEM micrographs of hollow

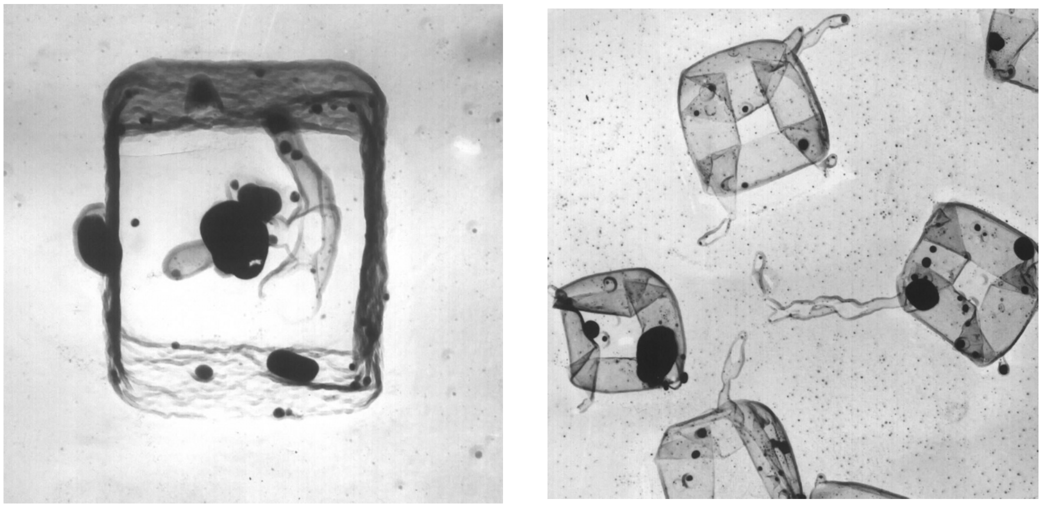

(a) (b)

Figure 5. The silver filament micrographs (25000x) of surface developed (a) hollow cubic Ag[Cl,Br]; and (b) solid cubic Ag[Cl,Br].

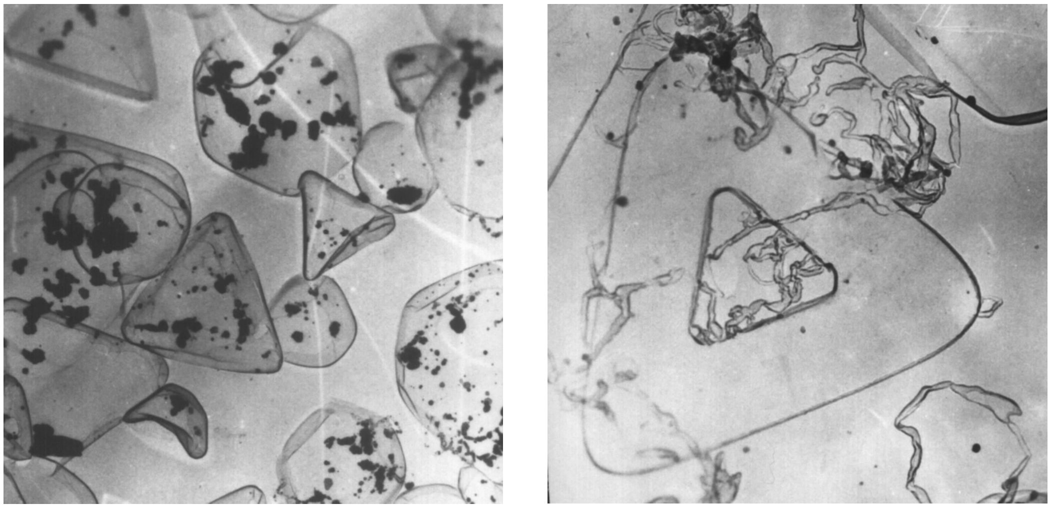

(a) (b)

Figure 6. The silver filament micrographs of surface developed (a) hollow tabular Ag[I,Br] (8000x); and (b) solid tabular Ag[I,Br] (16000x).

and solid (for comparison) cubic and tabular AgX after the development are shown in Fig. 5(a) and 5(b) and Fig. 6(a) and 6(b).

It can be seen from Fig. 5(a) and Fig. 6(a), that the silver filaments appear at the central hole. This suggests that due to the structural irregularity at sites near the holes of hollow silver halide grains, more electron traps may be provided so that latent image centers preferentially form near holes. However, for the solid cubic and tabular Ag[I,Br] microcrystals, the initial silver filaments tend to be formed at the active edge sites of grains (see Fig. 5(b) and Fig. 6(b)).

Results of Sulfur and Gold Sensitization

The results of surface development prove that the silver filaments initially spread out from the central hole of hollow grain. It appears that the hole structure of hollow AgX microcrystal may increase the efficiency of latent image formation. In order to provide more evidence of the effect of the hole structure on the photographic properties of these emulsions, sulfur and gold sensitization was carried out on both the hollow and solid AgX emulsions. The results are listed in Tables II and III.

The sensitometric results on hollow and solid cubic Ag[Cl,Br] emulsions in Table II are consistent with the above structural explanation, i.e. the sensitivity of the fourth (60 min) emulsion which has fewer holes is lower, even though the average grain size (about 0.60 μm) of the fourth emulsion is somewhat larger than that of other three (about 0.50 μm). The comparison of sensitivity of hollow Ag[Cl,Br] emulsions with the solid one having almost the same Br/Cl ratio shows that the sensitivity of all hollow Ag[Cl,Br] emulsions are higher than the solid Ag[Cl,Br] emulsion. This illustrates that the hole structure of microcrystals plays key role in the enhancing sensitivity.

According to Table III the sensitivities of hollow cubic Ag[I,Cl,Br] emulsions having almost the same average grain size (about 0.50 μm) increase with increasing of iodide content. In order to demonstrate the contribu-

TABLE II. The Comparison of Photographic Properties of Hollow and Solid Cubic Ag[Cl,Br] Emulsions Sensitized with S+Au

Emulsion	Duration of precipitation min	D_o	γ	RS*
Hollow cubic Ag[Cl,Br](a)	30	0.09	1.85	268
Hollow cubic Ag[Cl,Br](b)	40	0.08	1.80	468
Hollow cubic Ag[Cl,Br](c)	50	0.12	2.10	625
Hollow cubic Ag[Cl,Br](d)	60	0.10	1.70	237
Solid cubic Ag[Cl,Br]	50	0.13	4.10	100

*RS: Relative sensitivity, where the sensitivity of solid Ag[Cl,Br] is defined as 100

TABLE III. The Comparison of Photographic Properties of Hollow and Solid AgX Emulsions Sensitized with S+Au

Emulsion	Iodide mole %	D_o	γ	RS*
Hollow cubic Ag[I,Cl,Br](a)	0.5	0.30	2.10	110
Hollow cubic Ag[I,Cl,Br] (b)	1.0	0.30	3.60	123
Hollow cubic Ag[I,Cl,Br] (c)	1.5	0.30	4.00	188
Hollow cubic Ag[I,Cl,Br] (d)	2.0	0.29	2.80	327
Solid cubic Ag[I,Cl,Br]	1.5	0.29	2.10	100
Hollow Tabular Ag[I,Br]	5.0	0.24	1.50	185
Solid Tabular Ag[I,Br]	5.0	0.22	1.20	100

*RS: Relative sensitivity, where the sensitivity of solid AgX is defined as 100

tions of iodide content and hole structure of hollow silver halide emulsion to sensitivity, the chemical sensitization of solid AgX emulsions with the same concentration of iodide and the same average grain size (about 0.50 μm) was carried out for comparison. It was found that the sensitivity of the solid cubic emulsion is lower than that of hollow cubic emulsion (c) which has the same level of iodide (1.5 mol %). Therefore the hole structure is the main reason for enhanced sensitivity. When the reactions of precipitation and replacement are undertaken, the chloride ions are replaced by bromide and iodide ions, and the hole structures on the grains gradually appeared. Dislocations and defects near the holes should thereby be increased, which results in enhanced efficiency of latent image formation. Moreover, the more easily developable silver chloride may remain in the region of the hole; this may be another reason for increased sensitivity.

The comparison of sensitometric results in Table III also shows that the sensitivity of a hollow tabular Ag[I,Br] emulsion is also definitely higher than that of a solid one with the same iodide content.

Results of Green Spectral Sensitization

The green spectrally sensitized emulsion layers were exposed to a light source through a minus blue filter. The results of spectral sensitivity of hollow cubic and tabular AgX emulsions compared with their solid emulsion are shown in Table IV.

TABLE IV. The Comparison of Spectral Sensitivity of Hollow and Solid AgX Emulsions Sensitized by Green Dye

Emulsion	I^- (mol%)	green dye (mol/mol AgX x 10^{-6})	D	γ	RS* minus-blue
Hollow cubic Ag[I,Cl,Br](a)	0.5	2	0.30	1.90	122
Hollow cubic Ag[I,Cl,Br](b)	1.0	2	0.31	3.10	133
Hollow cubic Ag[I,Cl,Br](c)	1.5	2	0.31	3.90	213
Hollow cubic Ag[I,Cl,Br](d)	2.0	2	0.29	1.70	392
solid cubic Ag[I,Cl,Br]	1.5	2	0.29	1.90	100
Hollow tabular Ag[I,Br]	5.0	6	0.30	2.60	170
Solid tabular Ag[I,Br]	5.0	6	0.25	1.90	100

*RS: Relative sensitivity, where the minus blue sensitivity of solid AgX is defined as 100

The results in Table IV show again that the hole structure on the hollow cubic Ag[I,Cl,Br] microcrystals plays a more important role in sensitivity than iodide content, because there are holes and porous in the center and on the surface to adsorb more dyes. Moreover, a more interesting result is shown in the case of tabular AgX emulsions. The purpose of preparing tabular grains is to enhance the surface area for adsorbing more spectral sensitizer to increase sensitivity. However in the present case, the surface area of hollow tabular grains due to the holes is decreased, but their sensitivity is still higher than that of solid one with the same iodide content. The reason for this might be that the surface area of hollow tabular microcrystals is already sufficient for dye adsorption, and the hole structure enhances efficiency of latent image formation.

All these facts illustrate that due to a unique hole structure in the silver halide, the photographic properties of hollow emulsions are improved.

Acknowledgment. This work was supported by the Chinese National Fund Committee of Natural Sciences and Eastman Kodak Company.

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